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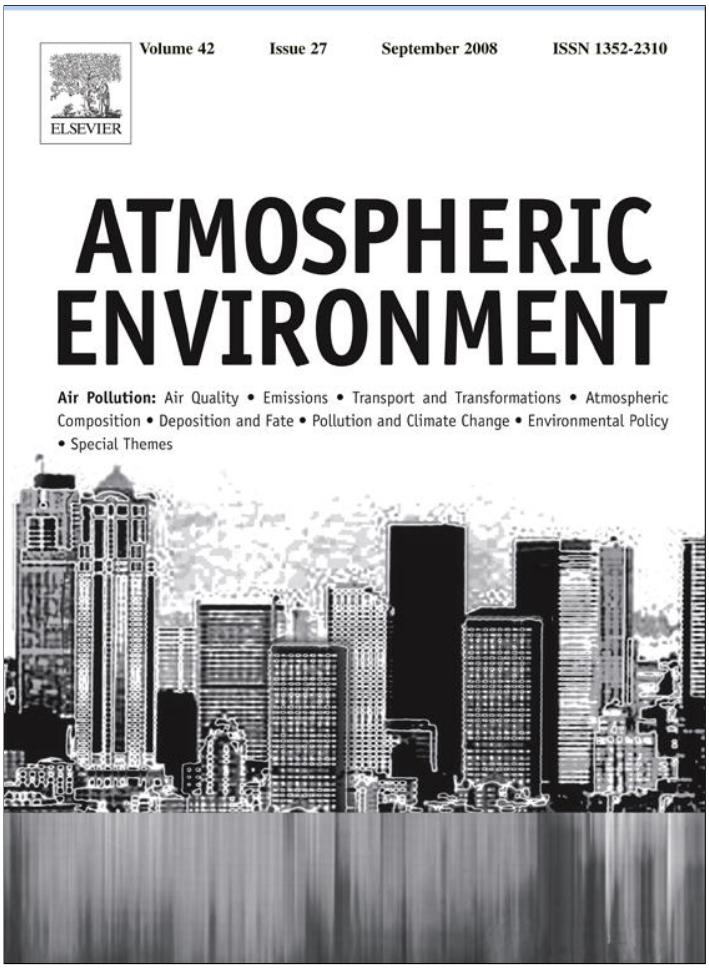

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Chemical and morphological properties of particulate matter (PM_{10}, $PM_{2.5}$) in school classrooms and outdoor air

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ABSTRACT

Studies have shown high concentrations of particulate matter (PM) in schools. Further insights into the sources and the composition of these particles are needed.

During school hours for a period of 6 weeks, outdoor air and the air in two classrooms were sampled. PM was measured gravimetrically, and PM filters were used for the determination of the elemental and organic carbon, light absorbance, and 10 water-soluble ions. Some filters were further analyzed by scanning electron microscopy (SEM) and energy dispersive microanalysis (EDX).

The median PM_{10} concentrations were 118.2 $\mu g\,m^{-3}$ indoors and 24.2 $\mu g\,m^{-3}$ outdoors; corresponding results for $PM_{2.5}$ were 37.4 $\mu g\,m^{-3}$ indoors and 17.0 $\mu g\,m^{-3}$ outdoors. Using PM_{10} and $PM_{2.5}$ data, we calculated the following indoor/outdoor ratios: 0.3 and 0.4 (sulfate), 0.1 and 0.2 (nitrate), 0.1 and 0.3 (ammonium), and 1.4 and 1.6 (calcium).

Using the measured sulfate content on PM filters as an indicator for ambient PM sources, we estimated that 43% of $PM_{2.5}$ and 24% of PM_{10}, respectively, were of ambient origin. The composition of the classrooms' PM (e.g., high calcium concentrations) and the findings from SEM/EDX suggest that the indoor PM consists mainly of earth crustal materials, detrition of the building materials and chalk.

Physical activity of the pupils leads to resuspension of mainly indoor coarse particles and greatly contributes to increased PM_{10} in classrooms. The concentration of fine particles caused by combustion processes indoors and outdoors is comparable.

We conclude that PM measured in classrooms has major sources other than outdoor particles. Assuming that combustion-related particles and crustal materials vary in toxicity, our results support the hypothesis that indoor-generated PM may be less toxic compared to PM in ambient air.

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1. Introduction

Ambient particulate matter (PM) is considered to be an important indicator of outdoor air quality, since a number of health problems have been associated with high concentrations (WHO, 2004; US-EPA, 2004). Short-term epidemiological studies have revealed respiratory and cardiopulmonary effects, increased health care utilization and increased cardiopulmonary mortality (Peters et al., 2000; Samet et al., 2000; Le Tertre et al., 2002). Increased mortality due to pulmonary and cardiovascular diseases

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has been indicated in long-term studies (Krewski et al., 2000; McDonnell et al., 2000; Lipfert et al., 2000; Hoek et al., 2002; Gehring et al., 2006; Miller et al., 2007). In a large cohort study of 552,000 subjects with a follow-up period of 16 years (American Cancer Society Study), each additional 10 μg $PM_{2.5}$ m^{-3} led to an increase of cardiovascular mortality by 8–18% (Pope et al., 2004).

Although the school environment normally lacks typical indoor PM sources such as smoking and cooking, many children are present in a limited space over a period of several hours. There is growing evidence of comparatively high concentrations of PM in classrooms (e.g., Janssen et al., 2001; Lahrz et al., 2003; Link et al., 2004; Son et al., 2005; Fromme et al., 2007; Stranger et al., 2007). These findings may be explained by: (1) insufficient ventilation in schools (especially in winter), (2) infrequently and unthoroughly cleaned indoor surfaces, and (3) a large number of pupils in relation to room area and volume, with constant resuspension of particles from room surfaces.

However, these high concentrations do not necessarily result in higher health risks to pupils, because the sources and the composition of PM in indoor air may differ from those in outdoor air (Schwarze et al., 2006). Therefore, the composition of indoor PM and its sources need to be clarified.

To the best of our knowledge, so far there are only limited data available concerning the chemical properties of PM in schools, i.e., data on water-soluble ion concentrations derived from Greek and American schools (Diapouli et al., 2008; John et al., 2007) and on elemental carbon (EC) from German, Dutch and American classrooms (Janssen et al., 2001; Lahrz et al., 2003; Fromme et al., 2005; Ward et al., 2007).

The aim of the present study was to characterize the chemical and morphological properties of PM (PM_{10} und $PM_{2.5}$) in classrooms and in corresponding outdoor air. For this purpose the following components of PM were quantified: water-soluble ions, elemental carbon (EC), organic carbon (OC) and the absorption coefficient of the filters. This information should improve understanding of the sources of the high PM in schools and how these sources contribute to overall exposure.

2. Materials and methods

2.1. Study objects and sampling time

PM was collected in the indoor air of two classrooms of one primary school and simultaneously in outdoor air in front of the windows on a balcony. At a school located in northern Munich, sampling was carried out in October and November 2005 for a time period of 6 weeks. The school is located in a densely populated residential area on a side road about 160 m away from a very busy street. No specific industrial sources for emissions are known of in this area. The school was erected in 1970. Both classrooms had a linoleum floor and relied on natural ventilation. Both classrooms were located on the first floor with floor space of 59 m^2 and a volume of 187 m^3. The classrooms were occupied by 21–23 pupils.

2.2. Sampling procedure/analysis

The sampling was conducted during teaching hours, i.e., for about 5 h day^{-1}. The measurement equipment was placed in the middle of the back wall, about 50 cm apart, opposite the blackboard. The sampling devices were located at the height of 90 cm. Outdoor air measurements followed the same time schedule as indoor sampling and made on the first floor, just outside the classrooms.

Particulate matter indoors and outdoors were sampled using a median volume sample MVS 6.1 (Firma Derenda, Teltow, Germany) with a flow-controlled pump with a constant flow of 2.3 m^3 h^{-1}. Sample volumes were calculated from elapsed time indicators and flow measurements before sampling with calibrated rotameters. The filters (47 mm – quartz fiber filter, Firma Whatman) were conditioned for at least 48 h before weighing and weighed according to DIN/EN 12341. Filters were weighed at room temperature of 20 °C and humidity of 50% using a microbalance type AX26DR/M (Mettler Toledo) with a 2 μg resolution. Filters were weighed 4 times and the mean result was used in further analyses.

Water-soluble ions were analyzed according to DIN 3497, page 4. One half of the filter was put in a PP centrifuge tube and 20 ml purified water was added. The tube was shaken overnight (12 h), and subsequently eluted in an ultrasonic bath. An aliquot was taken from the eluate, and the cations sodium, ammonium, potassium, magnesium, and calcium were analyzed by ion chromatographic methods according to DIN EN ISO 14911. Chloride, nitrite, nitrate, phosphate, and sulfate were quantified by ion chromatographic methods according to DIN EN ISO 10304-1 (D19). The limit of detection (LOD) was 0.5 μg m^{-3} for sulfate, chloride, phosphate and potassium, 0.25 μg m^{-3} for nitrate, sodium, ammonium and calcium, and 0.13 μg m^{-3} for nitrite and magnesium.

Measurements of EC and OC were conducted in accordance to VDI 2465 page 1 (VDI, 1996). A quarter of the filter was burned in oxygen at 650 °C and the generated carbon dioxide (CO_2) was determined by calorimetry. This method covers both organic and elemental carbon, but not carbonate (determination of TC, "total carbon"). Elemental carbon was analyzed using an additional filter aliquot, which was covered with toluene. The extractable organic compounds were removed by shaking overnight (12 h). The filter aliquot was dried in a drying cupboard to remove the adhering solvent. Afterwards, a thermodesorption in nitrogen and then the burning in oxygen was carried out, and generated CO_2 was detected with colorimetry (determination of EC). OC was calculated as the difference between TC and EC.

A reflectometer (EEL model 43, Diffusion System Ltd., London, U.K.) was employed to measure the absorbance of the filter of both PM fractions. Each filter was measured 4 times and the average was used in further calculations. The reflection was reset to 100% before each measurement with a blank filter. According to ISO 9835 reflectance was transformed into an absorption coefficient using the following equation.

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$$\mathrm{Abs_{coeff}} = (0.5^{*}A)^{*}\ln(R_0/R_f)/V$$

where A describes the loaded filter area (in m^2), R_0 the reflection of the blank filter (in %), R_f the reflection of the loaded filter (in %) and V the total sampled volume of air (in m^3).

To characterize the morphology, five paired indoor and outdoor filters were further examined by scanning electron microscopy (SEM) (LEO 1455 VP, Firma Zeiss, Oberkochen, Germany) in combination with energy dispersive X-ray spectrometry (EDX) (QX 200, Oxford Instruments, Wiesbaden). Small pieces of filter material were affixed to aluminium SEM stubs for further analysis. Each sample was coated with gold using a Polaron E 51000 to achieve conductivity and vacuum durability and then scanned with an electron beam. While scanning, electrons are emitted from the surface [secondary electrons (SEs) and back scattered electrons (BSEs)]. The number of emitted electrons determines the brightness of the image on the monitor. In this analysis the emitted electrons were recorded by a specific detector, a four-quadrant semiconductor detector (QBSD). Its high sensitivity enables this detector to produce an "element contrast picture". Heavy elements and compounds reflect more electrons than light elements, and thus appear lighter in the picture.

In the EDX, signals are displayed according to the mean energy. On the *X*-axis of a graph, the energy (in keV), on the *Y*-axis, the number of signals per time unit are displayed, and thus the length of each line reflects the concentration of one element.

2.3. Statistical methods

Concentrations below the limit of detection were assigned half of the detection limit. One outlier (ratio indoor/outdoor concentration >5) for sulfate PM_{10} was detected and excluded from further analyses.

Spearman rank correlations were computed and differences between groups were tested for significance using the Wilcoxon rank sum test. All statistical analyses were implemented in SPSS 13.0.

The contribution of indoor and outdoor sources to PM concentration was estimated according to Hänninen et al. (2004). The total PM concentration indoors (C_i) is the sum of indoor-generated PM (C_{ig}) and PM originating from outdoor sources. The contribution of outdoor PM to indoor PM depends on the outdoor concentration (C_a) and the infiltration factor (F_{INF}).

$$C_i = F^{*}_{INF}C_a + C_{ig} \quad (1)$$

The infiltration factor for PM can be derived from the infiltration factor for sulfate and a correction factor, which results from the division of β^{PM} (increase of indoor PM per outdoor PM, linear relationship) by β^{sulf} (increase of indoor sulfate per outdoor sulfate, linear relationship).

$$F^{PM}_{INF} = \frac{\beta^{PM}}{\beta^{sulf}} \times F^{sulf}_{INF} \quad (2)$$

Assuming that there is no indoor source of sulfate, the infiltration factor for sulfate equals the observed ratio of indoor to outdoor sulfate.

$$F^{sulf}_{INT} = \frac{C^{sulf}_i}{C^{sulf}_a} \quad (3)$$

The indoor-generated PM can thus be calculated as

$$C_{ig} = C_i - \frac{\beta^{PM}}{\beta^{sulf}} \times \frac{C^{sulf}_i}{C^{sulf}_a} \times C_a \quad (4)$$

3. Results

The mean daily indoor temperature during school time did not vary considerably (21–24 °C), while a large variability existed in outdoor temperature (−6 °C to 19 °C). Indoor relative humidity varied between 33% and 55%, and outdoor humidity between 47% and 99%.

3.1. Particulate matter/absorption coefficient

The results of the measurements are given in Table 1. The daily indoor PM concentration ranged between 57.8 μg m^{-3} and 209.9 μg m^{-3} (PM_{10}) and between 19.3 μg m^{-3} and 105.9 μg m^{-3} ($PM_{2.5}$), respectively. Results for the Abs_{coeff} were of similar magnitude in indoor and outdoor air. The concentration of EC determined in PM_{10}, was slightly higher in indoors (range: 6.4–13.6 μg m^{-3}) than outdoors (range: 1.6–12.6 μg m^{-3}).

In the outdoor air, a high correlation between the Abs_{coeff} and the EC in PM_{10} was observed ($r = 0.94$), but in the indoor air this was not the case ($r = 0.41$). In both the outdoor and the indoor air, the PM_{10} concentration was significantly correlated with EC ($r = 0.78$ and $r = 0.48$, respectively).

The strongest correlations between the outdoor and indoor concentrations can be seen for Abs_{coeff} in PM_{10} ($r = 0.95$) and Abs_{coeff} in $PM_{2.5}$ ($r = 0.92$) followed by $PM_{2.5}$ ($r = 0.86$), PM_{10} ($r = 0.68$) and EC in PM_{10} ($r = 0.51$). No correlation could be seen for OC in PM_{10}. The median ratio between indoor and outdoor concentration was 3.6 (range: 1.5–15.9) for PM_{10} and 2.1 (range: 0.7–5.5) for $PM_{2.5}$.

3.2. Ions in airborne dust

Nitrite and phosphate were below LOD in both PM fractions ($PM_{2.5}$ and PM_{10}) both indoors and outdoors (Table 1). Potassium was detectable in the indoor air only. The ion chlorides, potassium, or magnesium were found only in a few samples, indoors and outdoors, above the limit of detection.

Regarding PM_{10}, significant correlations were found between the indoor and outdoor concentrations of sulfate ($r = 0.70$), nitrate ($r = 0.96$), ammonium ($r = 0.95$), calcium ($r = 0.43$), and chloride ($r = 0.44$). Regarding $PM_{2.5}$, significant correlations were found between the indoor and outdoor concentrations of sulfate ($r = 0.78$), nitrate ($r = 0.96$), ammonium ($r = 0.95$) and calcium ($r = 0.33$).

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Table 1
Distribution of daily results regarding PM^{10} (in $\mu g\,m^{-3}$), absorption (Abs_{coeff}) and concentration of ions (in $\mu g\,m^{-3}$) (values in parentheses pertain to $PM_{2.5}$)

		%>LOQ	Min.	Median	90. P.	Max.
PM	Indoor	100 (100)	57.8 (19.3)	118.2 (37.4)	161.0 (85.7)	209.9 (105.9)
	Outdoor	100 (100)	4.7 (5.1)	24.2 (17.0)	69.4 (57.3)	127.2 (67.4)
EC	Indoor	100	6.4	10.2	12.2	13.6
	Outdoor	100	1.6	4.5	10.9	12.6
OC	Indoor	100	11.7	22.0	33.6	36.3
	Outdoor	100	4.1	6.5	12.7	15.1
$Abs_{coeff} \times 10^{-5}$	Indoor		1.04 (1.2)	2.9 (2.6)	5.6 (5.6)	6.2 (6.7)
	Outdoor		1.09 (1.1)	3.1 (3.0)	8.0 (7.9)	8.2 (8.5)
Sulfate	Indoor	100 (100)	1.0 (0.7)	2.9 (1.9)	4.9 (3.2)	6.4 (4.5)
	Outdoor	100 (100)	0.8 (0.7)	2.4 (2.1)	5.0 (4.1)	5.5 (5.3)
Nitrite	Indoor	0 (0)				
	Outdoor	0 (0)				
Nitrate	Indoor	94 (91)	0.1 (0.1)	1.2 (0.9)	2.7 (2.3)	7.5 (6.9)
	Outdoor	100 (100)	0.4 (0.1)	3.6 (3.1)	6.8 (6.3)	16.1 (13.4)
Chloride	Indoor	85 (11)	0.3 (0.3)	0.8 (0.3)	1.2 (0.4)	1.3 (0.7)
	Outdoor	13 (5)	0.3 (0.3)	0.3 (0.3)	0.6 (0.3)	0.7 (0.7)
Phosphate	Indoor	0 (0)				
	Outdoor	0 (0)				
Sodium	Indoor	100 (70)	0.5 (0.1)	1.0 (0.4)	1.3 (0.5)	1.7 (1.0)
	Outdoor	74 (68)	0.1 (0.1)	0.3 (0.3)	0.7 (0.4)	1.5 (1.3)
Ammonium	Indoor	90 (94)	0.1 (0.1)	0.7 (0.8)	1.9 (2.1)	3.1 (3.6)
	Outdoor	91 (91)	0.1 (0.1)	1.9 (1.8)	3.7 (3.8)	7.0 (6.4)
Potassium	Indoor	63 (6)	0.3 (0.3)	0.6	0.8	1.0 (0.6)
	Outdoor	0 (0)				
Magnesium	Indoor	90 (6)	0.1 (0.1)	0.2 (0.1)	0.2 (0.1)	0.3 (0.2)
	Outdoor	13 (0)	0.1 (–)	0.1 (–)	0.2 (–)	1.2 (–)
Calcium	Indoor	100 (100)	0.8 (0.3)	3.2 (0.8)	4.4 (1.3)	7.2 (4.7)
	Outdoor	78 (59)	0.1 (0.1)	0.9 (0.3)	2.0 (0.6)	2.1 (0.6)
Sum Ions	Indoor		4.0 (3.0)	11.0 (5.8)	15.4 (9.6)	21.2 (16.2)
	Outdoor		3.5 (2.2)	9.2 (7.7)	15.7 (14.4)	29.7 (26.1)

LOQ: limit of quantification; EC: elemental carbon; OC: organic carbon. Values below the LOQ are assigned half the LOQ.

3.3. Composition of particulate matter

In indoor PM the percentage of calcium to overall ions was greater than in outdoor PM. In outdoor PM, nitrate and sulfate were the dominating ions (Fig. 1). In indoor PM_{10} calcium (30%) and sulfate (28%) were the dominating ions, while in outdoor PM_{10} nitrate (36%) and sulfate (27%) both made up a high proportion. In indoor $PM_{2.5}$ the proportion of sulfate and nitrate in overall ions was increased, but the proportion of calcium was decreased.

The total of EC, OC and ions amounted to 55% of the PM_{10} in outdoor air, but only to 36% in indoor air (Fig. 2).

In Table 2, the median percentage in the corresponding PM and the resulting ratio of indoor and outdoor percentage (I/O) are given for each substance. For nearly all soluble ions, the proportion was greater in outdoor than in indoor air, with the exception of calcium, where a greater indoor proportion was found (I/O ratio of 1.4 for PM_{10} and 1.6 for $PM_{2.5}$). The corresponding ratios regarding PM_{10} are 0.7 for EC and 1.1 for OC.

3.4. Proportion of PM generated indoors to total indoor PM

In understanding the relationship between the fraction of indoor exposure resulting from indoor-generated PM or from PM of ambient origin, it is important to differentiate between them. In the absence of specific indoor sources, which can be presumed for classrooms, sulfate has proven to be a good indicator of combustion processes in outdoor air, and thus of PM of outdoor origin. This provides us with the opportunity to approximately calculate the infiltration factor of PM using the ratio of the indoor and outdoor sulfate concentrations. The application of the previously mentioned Eq. (4) using PM and sulfate monitoring data lead to the fraction of PM generated indoors.

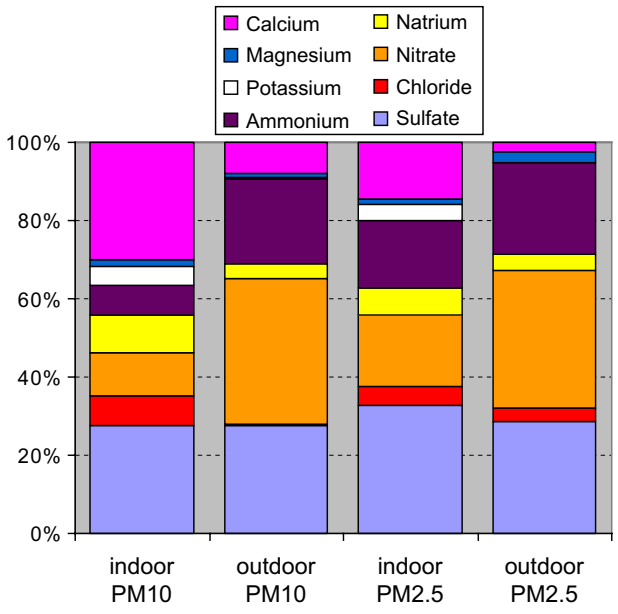

Fig. 1. Contribution of ions to total ion concentration stratified by PM fraction and indoor and outdoor air.

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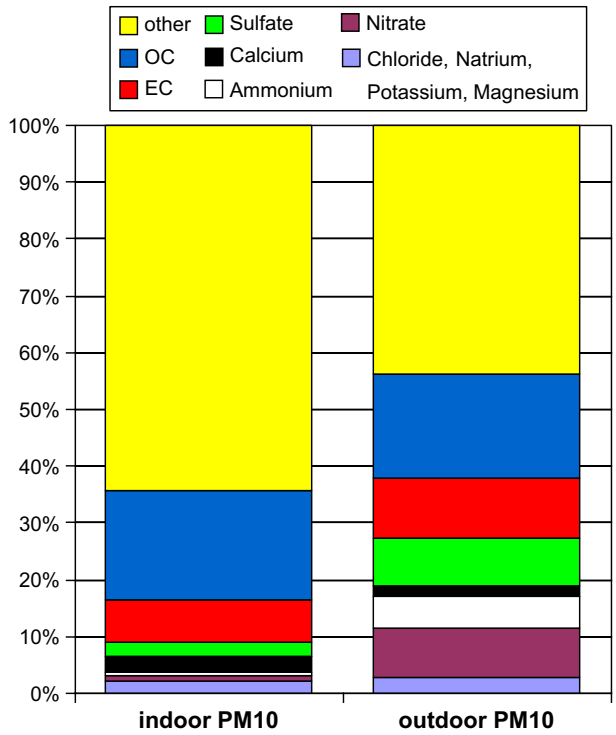

Fig. 2. Contribution of water-soluble ions and elemental and organic carbon to PM_{10} concentration indoors and outdoors.

Applying median values of the measured concentrations, we found that nearly 57% of the $PM_{2.5}$ and 76% of the PM_{10} was generated indoors, rather than being carried inside from outdoors.

3.5. Analysis with scanning electron microscopy (SEM)

Typical pictures generated with SEM/EDX render visible the discrepancy of higher PM-load indoors (166 $\mu g\,m^{-3}$ PM_{10}) compared to outdoors (49 $\mu g\,m^{-3}$ PM_{10}) (see Fig. 3a and b).

Contrary to outdoor filter surfaces, semi-transparent skin flakes were common on indoor filters. Clothing fibers were not found on the filters analyzed. Due to the volume and density of the skin flakes, it seems unlikely that skin flakes contribute significantly to total particle mass.

A multitude of other mainly irregular particles and some aggregates were prominent indoors. It is apparent from the SEM/EDX analyses that indoor particles are composed of various constituents of silicon (Si), oxygen (O), calcium (Ca) and carbon (C). While metallic particles are rare indoors, they were found outdoors, especially transition metals like iron (Fe).

Table 2
Ratio of the contribution of specific contents of PM to particle mass indoors and outdoors (median)

		PM_{10}		$PM_{2.5}$	
		% Proportion	Indoor/ outdoor	% Proportion	Indoor/ outdoor
Sulfate	Indoor	2.4	0.3	4.4	0.4
	Outdoor	8.5		9.0	
Nitrate	Indoor	1.0	0.1	2.4	0.2
	Outdoor	8.9		9.8	
Chloride	Indoor	0.6	0.6	0.7	0.5
	Outdoor	1.0		1.5	
Sodium	Indoor	0.8	0.9	0.6	0.6
	Outdoor	1.2		1.1	
Ammonium	Indoor	0.7	0.1	2.3	0.3
	Outdoor	5.5		7.9	
Potassium	Indoor	0.4		0.7	
	Outdoor	0		0	
Magnesium	Indoor	0.2	0.6	0.2	0.5
	Outdoor	0.3		0.4	
Calcium	Indoor	2.8	1.4	1.9	1.6
	Outdoor	1.8		1.1	
EC	Indoor	7.7	0.7	–	
	Outdoor	10.4		–	
OC	Indoor	19.2	1.1	–	
	Outdoor	18.3		–	

EC: elemental carbon; OC: organic carbon.

4. Discussion

Our investigation is one of the first attempts to determine and compare the composition of indoor and outdoor particulate matters in schools. The data indicate that indoor PM concentrations are substantially higher than outdoors. These increased concentrations are accompanied by a reduced proportion of EC, OC and most of the ions, leaving the greater percentage of indoor PM unexplained. It seems that particularly larger particles originate from indoor sources. Analysis with the SEM/EDX suggests that the additional PM in indoor air is partly of human origin (skin flakes) and mainly of mineral origin.

4.1. Ambient air

Our findings on concentrations of particle components concur with the results of measurements conducted at a traffic-related measurement site of the Bavarian Environment Agency in Munich (LfU, 2005). Data from a 9-day period of our project when measurements were made at 24 h intervals are available. The median concentrations were 3.5 $\mu g\,m^{-3}$ for sulfate, 3.0 $\mu g\,m^{-3}$ for nitrate, 1.7 $\mu g\,m^{-3}$ for ammonium, 0.1 $\mu g\,m^{-3}$ for magnesium, and 1.2 $\mu g\,m^{-3}$ for calcium. While OC concentrations were similar to our results (6.7 $\mu g\,m^{-3}$ vs. 6.5 $\mu g\,m^{-3}$), EC concentrations were considerably higher (10.9 $\mu g\,m^{-3}$ vs. 4.5 $\mu g\,m^{-3}$), probably due to the high traffic volume at this station.

Furthermore, similar concentrations of water-soluble ions were found at a station in Vienna (Schneider and Lorbeer, 2002), while higher concentrations of sulfate and nitrate were reported in North Rhine-Westphalia (Kappos et al., 2004).

4.2. Indoor air

The PM concentrations found in our study conform to the results of other previous studies (see Table 3). However, in one Greek study, concentrations of PM in classrooms were on average 2 times higher (Diapouli et al., 2008). These high indoor concentrations might have been caused by the corresponding high outdoor concentrations, which were 6.8 (PM_{10}) and 3.3 ($PM_{2.5}$) times higher than in our study.

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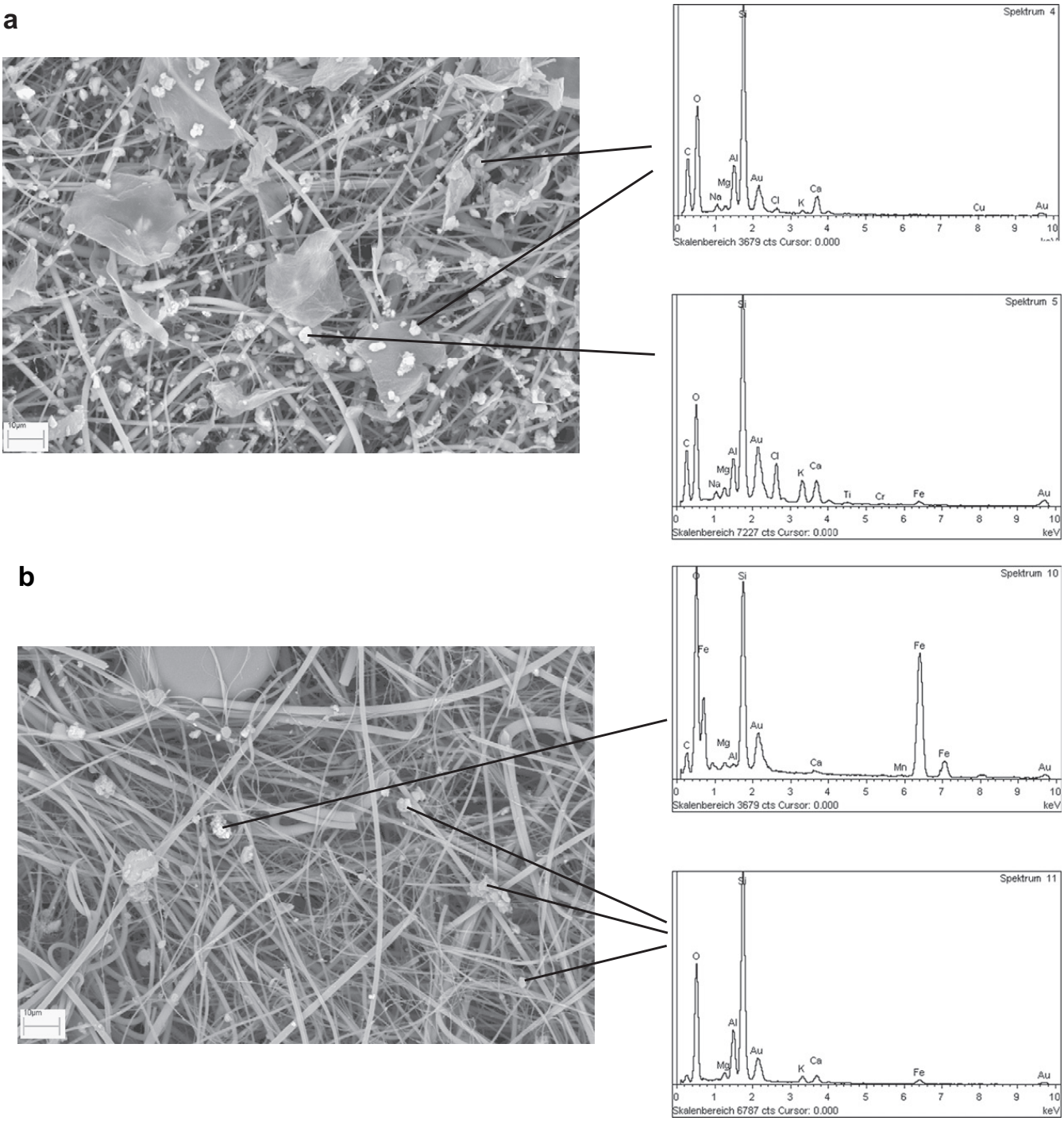

Fig. 3. SEM microphotographs and EDX profile of a PM_{10} filter from a classroom (a) and from outdoor air (b) and the corresponding EDX spectra of single particles.

In our investigation, as in other studies, the Abs_{coeff} of PM_{10} and $PM_{2.5}$ filters are very similar, since the blackness of the filter depends strongly on the fraction $<1\,\mu m$ (Fischer et al., 2000; Cyrys et al., 2003). The absorption is considered a simple and accurate indicator of the amount of carbonaceous combustion products on a filter (Gotschi et al., 2002; Cyrys et al., 2003). Our results with I/O ratios close to unity indicate that this critical fraction of aerosol is found in comparable concentrations in classrooms and outdoors.

The results of indoor-sampled particles indicate that they consisted mainly of detrited building materials such as cement and gypsum, earth crust material from tracked-in soil, and chalk. Moreover, particles with high salt content found indoors may have been formed by absorption of cleaning agents.

Only two studies have recently been published measuring ions in PM from schools (Diapouli et al., 2008; John et al., 2007). One investigation was conducted in seven schools in Athens during the winters of 2003 and 2004. In

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Table 3
Median concentrations (range) of particulate matter in public indoor places (in $\mu g\,m^{-3}$)

Source	Median (Min–Max)			Methods
	$PM_{2.5}$	PM_{10}	EC	
Janssen et al. (1997)	–	81 (57–234)	–	Netherlands; three schools; teaching hours; 1994/1995
Roorda-Knape et al. (1998)	–	73 (51–166)	–	Netherlands; 12 schools; weekly mean; 1995
Janssen et al. (2001)	23 (7.7–52.8)	–	11.8 (8.7-21.5)	Netherlands; 24 schools; teaching hours; 1997–1998
Lee and Chang (2000)	–	(21–617)	–	Hong Kong; five schools; 1997–1998
John et al. (2007)	15.6/17.3/16.2	–	–	Columbus, USA; three schools; 1 week; 1999
Keeler et al. (2002)	8.0–16.4	8.7–31.6	–	Detroit, USA; two schools at five time points; 24 h; 1999–2000
Fromme et al. (2005)	54 (13–128)+	–	2.0 (0.8–8.1)	Berlin; 73 kindergartens; time of attendance; 2000/2001
Link et al. (2004)	13 (5-40)	–	–	Baden-Wurttemberg; 54 classrooms; weekly mean; 2001/2002
Shaughnessy et al. (2002)	17# (4–17)(H) 9.9# (8–25)(C)	–	–	Arkansas, USA; five classrooms with hard surfaces (H); five classrooms with carpets (C); teaching hours
Liu et al. (2004)	44* (~10–180)	133* (~70–390)	–	Peking; seven classrooms; 2002–2003
Stranger et al. (2007)	61 (11–166)*	–	–	Antwerp, Belgium; 27 schools; urban and rural; 12 h daytime; 2002–2003
Lahrz et al. (2003)	60 (24–106)+	–	3.5 (0.9–14.8)	Berlin; 40 schools; teaching hours; 2002
Son et al. (2005)	–	46* (6.2-135.5)	–	Choongnam, Korea; 40 classrooms; 2003
Diapouli et al. (2008)	82*	229*	–	Athens, Greece; seven schools; teaching hours 2003–2004
Molnár et al. (2007)	8* (3.3–19.0)	–	–	Stockholm, Sweden; 10 classrooms at five schools; teaching hours; 2003–2004
Fromme et al. (2007)	20 (3–81) (W) 13 (5–35) (S)	92 (16–313) (W) 65 (18–178) (S)	–	Munich; winter 79 and summer 74 classrooms; teaching hours; 2004/2005
Ward et al. (2007)	(14.2–54.0) (E) (4.6–10.8) (M)	–	2.7 (E) 0.9 (M)	Libby, USA; two schools (E: elementary school; M: middle school); 24 h; 2005
This study	37 (19.3–106)	118 (57.8–210)	10.2 (6.4–13.6)	Munich; two classrooms at one school; teaching hours; 2005

W: winter; S: summer; *: mean; #: geometric mean; +: PM_4.

five of these schools classrooms were examined for 2–5 days (Diapouli et al., 2008). PM_{10} and $PM_{2.5}$ consisted, respectively, of 2.3% and 5.8% sulfate, and of 1.0% and 1.9% nitrate. These values are very similar to our findings. In ambient air, however, the proportion of ions was reduced by about 50%.

The second study took place in Ohio between September 1999 and August 2000 (John et al., 2007). The proportion of ions in $PM_{2.5}$ during teaching hours was determined in one rural and two urban schools. A distinctly high proportion of sulfate (13% vs. 4.4% in our study) and a high I/O ratio (0.8 vs. 0.4 in our study) were found indoors. The outdoor proportion of sulfate was 17% (vs. 12% in our study). Similarly, a high ratio indoors to outdoors was found for nitrate (1.3 vs. 0.2 in our study). Interestingly, this study was marked by low indoor $PM_{2.5}$ concentration, which was virtually the same as outdoors, and no information on the ventilation system was given.

The I/O ratios for nitrate and ammonium were similarly described in other studies of residential buildings (Hidy et al., 2000; Patterson and Eatough, 2000; Lunden et al., 2003a, b; Sarnat et al., 2006). In ambient air these ions are usually present as ammonium nitrate (NH_4NO_3), which as a volatile substance, is in equilibrium with its gaseous constituents ammonium and nitric acids. Ammonium nitrate becomes volatilized more quickly and adheres to room surfaces in indoor environments. Due to its temperature sensitivity, this process is hastened in indoor environments.

To our best knowledge, no data from scanning electron microscopy in classrooms of schools have been presented in the scientific literature. However, it must be noted that Teflon or nucleopore filters are typically used for microanalysis and not quartz fiber filters. Because we aimed to characterize different ions as well as elemental and organic carbon it is essential to use quartz fiber filters in our study. As seen in Fig. 3, a higher proportion of coarse particles could be observed on the top layer of the filter. The fine particles disappeared into the filter material and thus prevented further observation. For that reason, and due to the small number of filters analyzed, our results are limited. Nevertheless, a first qualitative impression of the coarse fraction of indoor particles was gained.

Although beyond the scope of this paper, further comparative assessment of the potential health impact of particles from indoor and outdoor sources is an interesting approach. Our SEM/EDX observations show some indications that particles containing transition metals such as iron were less frequently found indoors than outdoors. It is well known that particles containing these elements could be associated with respiratory and cardiopulmonary effects (Aust et al., 2002; Park et al., 2005). Thus, our results could support the notion that indoor-generated particles may have a different health impact compared to outdoor particles.

This would be in line with recent results demonstrating that $PM_{2.5}$ generated in the ambient environment increases inflammation markers in asthmatic children more strongly than $PM_{2.5}$ generated indoors (König et al., 2005). Epidemiological literature also supports the hypothesis that particles derived from earth crust material cause fewer health problems than particles generated by combustion processes (Laden et al., 2000; Mar et al., 2000; Hoek et al., 2002; Janssen et al., 2005). However, two toxicological in vitro studies have come to inconclusive results on the potential for indoor air generated particles to elicit inflammatory responses (Long et al., 2001; Monn and Becker, 1999) demonstrating the need for further toxicological and epidemiological studies to elucidate this issue.

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5. Conclusion

Our findings on morphological characteristics and chemical constituents of particulate matter in classrooms suggest that important indoor sources of especially coarse PM exist in this microenvironment. Despite the inherent limitations of our somewhat rough model estimates, we can conclude that 24% of PM_{10} and 43% of $PM_{2.5}$ were of ambient origin. Resuspension of these comparatively large particles thus appears to play a major role of PM exposure in classrooms.

The comparatively high proportion of potassium and magnesium indicates large contributions from earth crust materials and minerals; the high ratio indoors to outdoors for calcium (1.4 for PM_{10} and 1.6 for $PM_{2.5}$), a substantial contribution of calcium carbonate and gypsum chalk to total particle mass. This is in accordance with our preliminary results of SEM/EDX analyses.

Our somewhat preliminary results warrant further investigations of the chemical characterization and source apportionment in schools. In addition, it is urgent that studies be conducted to clarify the toxicological and biological relevances of PM exposure in schools in comparison to PM exposure in outdoor air.

References

Aust, A.E., Ball, J.C., Hu, A.A., Lighty, J.S., Smith, K.R., Straccia, A.M., Veranth, J.M., Young, W.C., 2002. Particle characteristics responsible for effects on human lung epithelial cells. Res. Rep. Health Eff. Inst. 110, 1–65.

Cyrys, J., Heinrich, J., Hoek, G., Meliefste, K., Lewne, M., Gehring, U., Bellander, T., Fischer, P., van Vliet, P., Brauer, M., Wichmann, H.E., Brunekreef, B., 2003. Comparison between different traffic-related particle indicators: elemental carbon (EC), $PM_{2.5}$ mass, and absorbance. J. Expo. Anal. Environ. Epidemiol. 13, 134–143.

Diapouli, E., Chaloulakou, A., Mihalopoulos, N., Spyrellis, N., 2008. Indoor and outdoor PM mass and number concentrations at schools in the Athens area. Environ. Monit. Assess. 136, 128–136.

Fischer, P.H., Hoek, G., van Reeuwijk, H., Briggs, D.J., Lebret, E., van Wijnen, J.H., Kingham, S., Elliott, P.E., 2000. Traffic-related differences in outdoor and indoor concentrations of particles and volatile organic compounds in Amsterdam. Atmos. Environ. 34, 3713–3722.

Fromme, H., Lahrz, T., Hainsch, A., Oddoy, A., Piloty, M., Rüden, H., 2005. Elemental carbon and respirable particulate matter in the indoor air of apartments and nursery schools and outdoor air in Berlin (Germany). Indoor Air 15, 335–341.

Fromme, H., Dietrich, S., Twardella, D., Heitmann, D., Schierl, R., Liebl, B., Rüden, H., 2007. Particulate matter in the indoor air of classrooms – exploratory results from Munich and surrounding. Atmos. Environ. 41, 854–866.

Gehring, U., Heinrich, J., Krämer, U., Grote, V., Hochadel, M., Sugiri, D., Kraft, M., Rauchfuss, K., Eberwein, H.G., Wichmann, H.E., 2006. Long-term exposure to ambient air pollution and cardiopulmonary mortality in women. Epidemiology 17, 545–551.

Gotschi, T., Oglesby, L., Mathys, P., Monn, C., Manalis, N., Koistinen, K., Jantunen, M., Hänninen, O., Polanska, L., Künzli, N., 2002. Comparison of black smoke and $PM_{2.5}$ levels in indoor and outdoor environments of four European cities. Environ. Sci. Technol. 36, 1191–1197.

Hänninen, O.O., Lebret, E., Ilacqua, V., Katsouyanni, K., Künzli, N., Sram, R.J. , Jantunen, M., 2004. Infiltration of ambient $PM_{2.5}$ and levels of indoor generated non-ETS $PM_{2.5}$ in residences of four European cities. Atmos. Environ. 38, 6411–6423.

Hidy, G.M., Lachenmayer, C., Chow, J., Watson, J., 2000. Urban outdoor–indoor $PM_{2.5}$ concentrations and personal exposure in the deep south. Part II: inorganic chemistry. Aerosol Sci. Technol. 33, 357–375.

Hoek, G., Brunekreef, B., Goldbohm, S., Fischer, P., van den Brandt, P.A., 2002. Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study. Lancet 360, 1203–1209.

Janssen, N.A.H., Hoek, G., Harssema, H., Brunekreef, B., 1997. Childhood exposure to PM_{10}: relation between personal, classroom, and outdoor concentrations. Occup. Environ. Med. 54, 888–894.

Janssen, N.A.H., van Vliet, P.H.N., Aaarts, F., Harssema, H., Brunekreef, B., 2001. Assessment of exposure to traffic related air pollution of children attending schools near motorways. Atmos. Environ. 35, 3875–3884.

Janssen, N.A.H., Lanki, T., Hoek, G., Vallius, M., de Hartog, J.J., Van Grieken, R., Pekkanen, J., Brunekreef, B., 2005. Associations between ambient, personal, and indoor exposure to fine particulate matter constituents in Dutch and Finnish panels of cardiovascular patients. Occup. Environ. Med. 62, 868–877.

John, K., Karnae, S., Crist, K., Kim, M., Kulkarni, A., 2007. Analysis of trace elements and ions in ambient fine particulate matter at three elementary schools in Ohio. J. Air Waste Manag. Assoc. 57, 394–406.

Kappos, A.D., Bruckmann, P., Eikmann, T., Englert, N., Heinrich, U., Höppe, P., Koch, E., Krause, G.H.M., Kreyling, W.G., Rauchfuss, K., Rombout, P., Schulz-Klemp, V., Thiel, W.R., Wichmann, H.-E., 2004. Health effects of particles in ambient air. Int. J. Hyg. Environ. Health 207, 399–407.

Keeler, G.J., Dvonch, T., Yip, F.Y., Parker, E.A., Israel, B.A., Marsik, F.J., Morishita, M., Barres, J.A., Robins, T.G., Brakefield-Caldwell, W., Sam, M., 2002. Assessment of personal and community-level exposure to particulate matter among children with asthma in Detroit, Michigan, as part of Community Action Against Asthma (CAAA). Environ. Health Perspect. 110 (Suppl. 2), 173–181.

Köenig, J.Q., Mar, T.F., Allen, R.W., Jansen, K., Lumley, T., Sullivan, J.H., Trenga, C.A., Larson, T.V., Liu, L.-J., 2005. Pulmonary effects of indoor- and outdoor-generated particles in children with asthma. Environ. Health Perspect. 113, 499–503.

Krewski, D., Burnett, R.T., Goldberg, M.S., Hoover, K., Siemiatycki, J., Jerrett, M., Abrahamowicz, M., White, W.H., 2000. Reanalysis of the Harvard Six Cities Study and the American Cancer Society Study of Particulate Air Pollution and Mortality. HEI Special Report. Health Effects Institute, Cambridge, MA, USA.

Laden, F., Neas, L.M., Dockery, D.W., Schwartz, J., 2000. Association of fine particulate matter from different sources with daily mortality in six U. S. cities. Environ. Health Perspect. 108, 941–947.

Lahrz, T., Piloty, M., Oddoy, A., Fromme, H., 2003. Gesundheitlich Bedenkliche Substanzen in Öffentlichen Einrichtungen in Berlin. Untersuchungen zur Innenraumluftqualität in Berliner Schulen. Bericht des Instituts für Lebensmittel, Arzneimittel und Tierseuchen. Fachbereich Umwelt- und Gesundheitsschutz, Berlin, Germany.

Lee, S.C., Chang, M., 2000. Indoor and outdoor air quality investigation at schools in Hong Kong. Chemosphere 41, 109–113.

Le Tertre, A., Medina, S., Samoli, E., Forsberg, B., Michelozzi, P., Boumghar, A., Vonk, J.M., Bellini, A., Atkinson, R., Ayres, J.G., Sunyer, J., Schwarz, J., Katsouyanni, K., 2002. Short-term effects of particulate air pollution on cardiovascular diseases in eight European cities. J. Epidemiol. Community Health 56, 773–779.

LfU, Bavarian Environment Ageny, Messergebnisse der Verkehrsmessstation Landshuter Allee (München) des Bayerischen Landesamtes für Umwelt in der Zeit vom 31.10.2005 bis zum 14.11.2005. Personal Communication J. Diemer.

Link, B., Gabrio, T., Zöllner, I., Schwenk, M., Siegel, D., Schultz, E., Scharring, S., Borm, P., 2004. Feinstaubbelastung und Deren Gesundheitliche Wirkungen bei Kindern. Bericht des Landesgesundheitsamtes. Baden-Württemberg, Stuttgart, Germany.

Lipfert, F.W., Perry, H.M., Miller, J.P., Baty, J.D., Wyzga, R.E., Carmody, S.E., 2000. The Washington University-EPRI Veterans' Cohort Mortality Study: preliminary results. Inhal. Toxicol. 12 (Suppl. 4), 41–73.

Liu, Y., Chen, R., Shen, X., Mao, X., 2004. Wintertime indoor air levels of PM_{10}, $PM_{2.5}$ and PM_1 at public places and their contributions to TSP. Environ. Int. 30, 189–197.

Long, C.M., Suh, H.H., Kobzik, L., Catalano, P.J., Ning, Y.Y., Koutrakis, P., 2001. A pilot investigation of the relative toxicity of indoor and outdoor fine particles: in-vitro effects of endotoxin and other particulate properties. Environ. Health Perspect. 109, 1019–1026.

Lunden, M.M., Thatcher, T.L., Hering, S.V., Brown, N.J., 2003a. Use of time- and chemically resolved particulate data to characterize the infiltration of outdoor $PM_{2.5}$ into a residence in the San Joaquin Valley. Environ. Sci. Technol. 15, 4724–4732.

Lunden, M.M., Revzan, K.L., Fischer, M.L., Thatcher, T.L., Littlejohn, D., Hering, S.V., Brown, N.J., 2003b. The transformation of outdoor ammonium nitrate aerosols in the indoor environment. Atmos. Environ. 37, 5633–5644.

Mar, T.F., Norris, G.A., Koenig, J.Q., Larson, T.V., 2000. Association between air pollution and mortality in Phoenix, 1995–1997. Environ. Health Perspect. 108, 347–353.

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McDonnell, W.F., Nishino-Ishikawa, N., Petersen, F.F., Chen, L.H., Abbey, D. E., 2000. Relationships of mortality with the fine and coarse fractions of long-term ambient PM_{10} concentrations in nonsmokers. J. Expo. Anal. Environ. Epidemiol. 10, 427–436.

Miller, K.A., Siscovick, D.S., Sheppard, L., Shepherd, K., Sullivan, J.H., Anderson, G.L., Kaufman, J.D., 2007. Long-term exposure to air pollution and incidence of cardiovascular events in women. N. Engl. J. Med. 356, 447–458.

Molnár, P., Bellander, T., Sällsten, G., Boman, J., 2007. Indoor and outdoor concentrations of PM2.5 trace elements at homes, preschools and schools in Stockholm, Sweden. J. Environ. Monit. 9, 348–357.

Monn, C., Becker, S., 1999. Cytotoxicity and induction of proinflammatory cytokines from human monocytes exposed to fine ($PM_{2.5}$) and coarse particles ($PM_{10-2.5}$) in outdoor and indoor air. Toxicol. Appl. Pharmacol. 155, 245–252.

Park, J.H., Han, K.T., Eu, K.J., Kim, J.S., Chung, K.H., Park, B., Yang, G.S., Lee, K.H., Cho, M.H., 2005. Diffusion flame-derived fine particulate matters doped with iron caused genotoxicity in B6C3F1 mice. Toxicol. Ind. Health 21, 57–65.

Patterson, E., Eatough, D.J., 2000. Indoor/outdoor relationship for ambient PM2.5 and associated pollutants: epidemiological implications in London, Utah. J. Air Waste Manag. Assoc. 50, 103–110.

Peters, A., Perz, S., Döring, A., Stieber, J., König, W., Wichmann, H.-E., 2000. Activation of the autonomic nervous system and blood coagulation in association with an air pollution episode. Inhal. Toxicol. 12, 51–61.

Pope, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., Godleski, J.J., 2004. Cardiovascular mortality and long-term exposure to particulate air pollution. Epidemiological evidence of general pathophysiological pathways of disease. Circulation 109, 71–77.

Roorda-Knape, M.C., Janssen, N.A.H., De Hartok, J.J., Van Vliet, P.H.N., Harssema, H., Brunekreef, B., 1998. Air pollution from traffic in city districts near major motorways. Atmos. Environ. 32, 1921–1930.

Samet, J.M., Dominici, F., Curriero, F.C., Coursac, I., Zeger, S.L., 2000. Fine particulate air pollution and mortality in 20 U.S. cities, 1987–1994. N. Engl. J. Med. 343, 1742–1749.

Sarnat, S.E., Coull, B.A., Ruiz, P.A., Koutrakis, P., Suh, H.H., 2006. The influences of ambient particle composition and size on particle infiltration in Los Angeles, CA, residences. J. Air Waste Manag. Assoc. 56, 186–196.

Shaughnessy, R.J., Turk, B., Evans, S., Fowler, F., Casteel, S., Louie, S., 2002. Preliminary study of flooring in school in the U.S.: airborne particulate exposure in carpeted vs. uncarpeted classrooms. Proceedings of Indoor Air, pp. 974–979.

Schneider, J., Lorbeer, G., 2002. Inhaltsstoffe von PM_{10} und $PM_{2.5}$ an Zwei Messstationen. Bericht BE-208 für das Umweltbundesamt, Wien, Österreich.

Schwarze, P.E., Øvrevik, J., Låg, M., Refsnes, M., Nafstad, P., Hetland, R.B., Dybing, E., 2006. Particulate matter properties and health effects: consistency of epidemiological and toxicological studies. Hum. Environ. Toxicol. 25, 559–579.

Son, B.S., Song, M.R., Yang, W.H., 2005. A Study on PM10 and VOCs Concentrations of Indoor Environment in School and Recognition of Indoor Air Quality. Proceedings of Indoor Air, Peking, China, pp. 827–832.

Stranger, M., Potgieter-Vermaak, S.S., Van Grieken, R., 2007. Comparative overview of indoor air quality in Antwerp, Belgium. Environ. Int. 33, 789–797.

US-Environmental Protection Agency, 2004. Air Quality Criteria for Particulate Matter. EPA/600/P-99/002aF bis bF. Washington DC, USA.

Verein Deutscher Ingenieure, 1996. Measurement of Soot (immission) – Chemical Analysis of Elemental Carbon by Extraction and Thermal Desorption of the Organic Carbon. VDI – Manual 2465, Part 1. Beuth-Verlag, Berlin, Germany.

Ward, T.J., Noonan, C.W., Hooper, K., 2007. Results of an indoor size fractionated PM school sampling program in Libby, Montana. Environ. Monit. Assess. 130, 163–171.

World Health Organization, 2004. Meta-Analysis of Time-Series Studies and Panel Studies of Particulate Matter (PM) and Ozone (O3). Report of a WHO Task Group, Available at: <http://www.euro.who.int/document/E82792.pdf>, [accessed 4 January 2008].