

Characterisation of particulate matter in different types of archives



Ludmila Mašková*, Jiří Smolík, Petr Vodička

Laboratory of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals of the CAS, Rozvojová 135, 165 02, Prague 6, Czech Republic

H I G H L I G H T S

- Chemical compositions of size-resolved particles were investigated in four archives.
- Organic matter was the dominant component of indoor aerosols.
- Chemical components explained 95% and 115% of indoor PM₁ and PM₁₀₋₁, respectively.

A R T I C L E I N F O

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To determine the composition of particulate matter (PM) in the indoor environments of four different types of archives (three naturally ventilated and one filtered), intensive size-resolved sampling was performed for four seasons of the year. For reconstituting indoor PM, nine aerosol components were considered. Organic matter was the dominant component of both fine and coarse fractions and represented approximately 50–80% of the PM. In the fine fraction, the next most abundant components were elemental carbon and sulphate, and in the coarse fraction the next most abundant were crustal matter, sulphate and nitrate. The resulting mass closure explained 95(±13)% and 115(±38)% of the gravimetric indoor PM in the fine and coarse size fractions, respectively. The results revealed that all the particles found indoors can be considered to be potentially threatening to the stored materials. The results also showed that the most important source of indoor PM in the naturally ventilated archives was penetration from the outdoor air, whereas in the filtered archive, the concentrations of particles were strongly reduced. In naturally ventilated archives the influence of domestic heating, road traffic and local sources (industrial pollution, camp fires) was observed. Furthermore, activities of the staff were identified as an indoor source of coarse particles in all archives.

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1. Introduction

Indoor air pollution in cultural heritage buildings such as museums, libraries and archives can be harmful to materials stored there. The adverse effects of most gaseous pollutants are well described (Grosjean et al., 1993; Katsanos et al., 1999; Shaver et al., 1983; Tétreault et al., 2013; Thomson, 1965; Whitmore and Cass, 1988, 1989), but less is known about airborne particles. Particles have a wide range of sizes and a variable composition. These characteristics determine their transport to the surfaces and also possible harmful effects (Nazaroff and Cass, 1989).

Particulate matter (PM) is especially harmful for artwork because it may cause degradation of materials. Particles can cause

soiling and darkening of the surface (Baer and Banks, 1994; Brimblecombe and Grossi, 2004). Coarse particles are abrasive and can damage works of art by mechanical abrasion when they are moved or handled (Nazaroff and Cass, 1991). Fine particles can penetrate into books (Smolík et al., 2013), where they may cause chemical degradation or moistening due to their hygroscopicity (Hatchfield, 2002). Particles can also serve as nutrients for microorganisms, whose biological activities can cause discolouring and decomposition (Altenburger et al., 1996; Garg et al., 1995; Pangallo et al., 2007; Sanchez-Moral et al., 2005; Sturaro et al., 2003; Urzi et al., 2001).

Detailed studies of the chemical composition of size resolved PM in the indoor environment of cultural heritage buildings are scarce. A few studies address some aspects of the composition of particles in museums, galleries and churches that are strongly influenced by visitors (Brimblecombe et al., 1999; Camuffo et al., 1999, 2001; Cao et al., 2005; De Bock et al., 1996; Godoi et al.,

* Corresponding author.

E-mail addresses: maskova@icpf.cas.cz (L. Mašková), smolik@icpf.cas.cz (J. Smolík), vodicka@icpf.cas.cz (P. Vodička).

2008; Hu et al., 2009; Injuk et al., 2002; Ligocky et al., 1993; Van Grieken et al., 2000; Worobiec et al., 2008). Less is known about the indoor environment of depositories and archives, where penetration from outdoor air is the most important source of particles. Air quality in these indoor environments is important because artefacts are stored there for a very long time period. The aim of this study was to describe in detail the chemical composition of size resolved particles in the indoor environment of four different types of archives and to determine the sources of the indoor PM.

2. Experimental

2.1. Measurement sites

The measurements were carried out in four archives in the Czech Republic, representing different outdoor environments (Fig. 1): (1) the Depository of the Research Library of South Bohemia in Zlatá Koruna (rural), (2) the State Regional Archives in Třeboň (small town), (3) the Library in the Regional Museum in Teplice (industrial area), and (4) the National Archives in Prague (large city). All of the archives are closed to the public except for the archive in Prague, which is occasionally visited by very small groups. Concerning cleaning activities, the floor in the archive in Prague is washed only with clean water about once a year, and the other archives are almost never cleaned. Other indoor activities are also very limited.

The State Regional Archives in Třeboň is situated in the centre of the town in a castle complex (49°0′11.211″N, 14°46′10.977″E, 434 m above sea level – a.s.l.). Approximately 8.5 thousand people live in Třeboň, but the number is about three times higher during tourist seasons. The library holds approximately 24,000 m of archives dating from the 13th century to recent times, which are stored in original wooden shelves. The archive is divided into small depositories. The monitored depository has an area of approximately 30 m², a volume of 120 m³, and an estimated surface/volume (S/V) ratio of approximately 3.3/m. Concerning the ventilation, the archive does not have any heating, ventilation, or air conditioning (HVAC) system and is equipped with only simple windows with gaps, i.e., the only ventilation is through cracks and small openings in the building, windows and doors. During the summer, all windows in the archive were opened to control relative humidity, except for the windows in the monitored depository.

The depository of the Research Library of South Bohemia in Zlatá Koruna is located in a former monastery in a small village Zlatá Koruna (48°51′20.599″N, 14°22′16.846″E, 473 m a.s.l.). The population of Zlatá Koruna is approximately 700 people. The library

holds approximately 32 000 books dating from the 14th to 19th centuries, which are stored in metal shelves. The monitored depository has an area of approximately 250 m², a volume of 1000 m³ and an estimated S/V ratio of approximately 3.2/m. The archive is equipped with an electrical heating system and double glassed windows. There is a camp with a capacity of approximately one thousand people located approximately 200 m from the archive with frequent campfires during the summer.

The library of the Regional Museum in Teplice is located in a castle complex in the centre of the town (50°38′14.410″N, 13°49′32.582″E, 230 m a.s.l.). Teplice has a population of approximately 50 thousands people and represents a region polluted by the chemical and glass industries, thermal power plants and mining of coal in open pit mines. In the library, approximately 18,000 books dating from the 14th century to recent times are stored in wooden or metal shelves. The monitored depository has an area of approximately 120 m², a volume of 450 m³ and an estimated S/V ratio of approximately 2.6/m. The library is also equipped with an electrical heating system and double glassed windows.

The depository of the National Archives in Prague is located in a modern building in the northern part of Prague, close to a busy road (50°5′45.602″N, 14°24′5.570″E, 210 m a.s.l.). Prague has a population of approximately 1.3 million people. In the monitored depository, approximately 2000 books dating from the 16th to 19th centuries are stored in metal shelves. The depository has an area of approximately 200 m², a volume of 550 m³ and an estimated S/V ratio of approximately 2.9/m. This indoor environment is isolated from the outdoor air and is equipped with a ventilation and filtration system with air circulation.

2.2. Particulate matter sampling and analysis

The samplings were performed during four intensive campaigns in different seasons of the year at every location in the years 2012–2014. The sampling of PM was performed on a daily basis with two parallel samplings at each location during individual campaigns (i.e., 32 sampling days in total). A list of sampling days is provided in Table 1.

A 24-h sampling was carried out from 10 am (± 1 h) to the morning of the next day using four Leckel LVS-3 instruments (Sven Leckel Ingenieurbüro, Germany) collecting fractions PM₁ and PM₁₀ from the indoor air. Particles were deposited on Teflon (Pall, pore size 2 μ m, 47 mm, flow rate 1 m³/h) and quartz filters (Pall, Tissuequartz, 47 mm, flow rate 2.3 m³/h). Backup quartz filters were used to evaluate and correct for the positive sampling artefact. The samples were taken at a height of approximately 1.2 m above the floor. In parallel with the PM₁ and PM₁₀ samplings, two Berner type Low Pressure Impactors (BLPI, 25/0.018/2, Hauke, Austria) collected particles from the indoor and outdoor air. The BLPI samples were deposited on Nuclepore foils (flow rate 1.5 m³/h). The foils were greased with Apiezon L vacuum grease to reduce particle bounce. The impactors separated PM into 10 size fractions. The cut



Fig. 1. Location of the sampling sites.

Table 1
The list of sampling days.

	Spring	Summer	Autumn	Winter
Třeboň	24.4.2012	18.7.2012	24.10.2012	31.1.2012
	25.4.2012	19.7.2012	25.10.2012	2.2.2012
Zlatá Koruna	17.4.2012	24.7.2012	30.10.2012	24.1.2012
	18.4.2012	25.7.2012	31.10.2012	26.1.2012
Teplice	6.3.2013	26.6.2013	19.11.2013	8.1.2014
	7.3.2013	27.6.2013	20.11.2013	13.1.2014
Prague	19.3.2013	17.7.2013	6.11.2013	21.1.2014
	20.3.2013	18.7.2013	7.11.2013	22.1.2014

diameters of the stages were 0.026, 0.057, 0.1, 0.16, 0.25, 0.44, 0.87, 1.8, 3.5, and 6.7 μm (Hillamo et al., 1999). The impactors were equipped with inlets with the cut-point calculated as 13.7 μm . Both impactors were situated inside the library at a distance of approximately 1 m from the window. Indoor samples were taken at a height of approximately 1.5 m above the floor, and outdoor samples were taken using a sampling train put through a wooden panel fixed into the window frame. Both impactors were equipped with the same sampling tubing. In the archive in Prague, only indoor samplings of PM₁ and PM₁₀ were performed because it was not possible to drain the BLPI pump emissions from the isolated indoor environment.

Parallel to aerosol sampling, the ventilation rate was measured using tracing gas (CO_2) with an Indoor Air Quality Monitor PS32 (Sensotron, Poland). Considering ventilation rates (Mašková et al., 2014), penetrated PM represented approximately 5–20% of the aerosol fraction collected by all instruments. Additionally, basic meteorological parameters including ambient temperature and relative humidity were measured in all archives, both indoors and outdoors, by TinyTag data loggers (Gemini, U.K.).

The mass of PM was obtained from weighing each filter/foil before and after sampling with a microbalance with ± 1 μg sensitivity (Sartorius M5P, Data Weighing Systems, USA). The weighing was performed at $20(\pm 1)^\circ\text{C}$ and $50(\pm 3)\%$ relative humidity with samples pre-equilibrated at these conditions for at least 24 h. The PM₁ and PM₁₀₋₁ fractions from the BLPI data were estimated by summing concentrations at stages 1–6 and adding 50% at stage 7 for PM₁ and at stages 8–9 and 50% at stages 7 and 10 for PM₁₀₋₁.

Teflon filters and BLPI samples were further analysed using ion chromatography (IC) and particle-induced X-ray emission spectrometry (PIXE). The IC analyses were provided using a Dionex ICS-5000 (Thermo Scientific, USA). The samples were extracted using ultrapure water with conductivity below 0.08 $\mu\text{S}/\text{m}$ (Ultrapur, Watrex Ltd., Czech Rep.) for 0.5 h using an ultrasonic bath and 1 h using a shaker. The solution was filtered through a Millipore syringe filter with 0.22 μm porosity. The filtered sample was then analysed for both anions (SO_4^{2-} , NO_3^- , Cl^- , NO_2^- , Br^- , H_2PO_4^-) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+}) in parallel. The anions were detected with an anion self-regenerating suppressor (ASRS 300) and an IonPac AS11-HC (2×250 mm) analytical column. The cations were detected with a cation self-regenerating suppressor (CSRS ULTRA II) and an IonPac CS18 (2×250 mm) analytical column. Separation of anions was conducted using 25 mM KOH as an eluent at a flow rate of 0.38 ml/min and cations using 25 mM methanesulfonic acid at 0.25 ml/min. The PIXE analyses were performed using a 3 MV Tandem accelerator (High Voltage Engineering Europa, Netherlands) (Havránek et al., 2009). The PIXE provided concentration data for up to 22 elements (Al, Ba, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Se, Si, Sr, Ti, Tl, V, Zn, and Zr). Quartz filters were analysed for organic and elemental carbon (OC and EC) by a thermal–optical method (EC/OC analyser Model 4, Sunset Laboratory, USA) using the EUSAAR_2 temperature protocol (Cavalli et al., 2010). All data were corrected for blanks (16 unexposed Teflon and 16 unexposed Quartz filters and 48 Nuclepore foils).

The minimum detection limit (MDL) was calculated as three times the standard deviation of the blanks. The mass concentration MDL was 0.2 $\mu\text{g}/\text{m}^3$ for Teflon filters and 0.1 $\mu\text{g}/\text{m}^3$ for Nuclepore foils. The MDLs for both EC and OC were 0.2 $\mu\text{g}/\text{m}^3$. MDLs for other analysed species were below 10 ng/m^3 (Table A.1 in supplementary materials).

Using this approach, mass, ionic, elemental and EC/OC PM₁ and PM₁₀ indoor concentrations, and mass, ionic and elemental size distributions and estimations of PM₁ and PM₁₀₋₁ from BLPI for indoor and outdoor environments were obtained.

3. Results and discussion

3.1. Mass concentration

Indoor and outdoor mass size distributions were bimodal with a minimum at approximately 1 μm in all cases. The fine particle mode was set at approximately 0.2–0.3 μm and the coarse mode at approximately 2–5 μm for both indoor and outdoor particles. A typical example is shown in Fig. 2. The results showed that the fine mode corresponded to the PM₁ fraction and that the coarse mode corresponded to the PM₁₀₋₁ fraction.

We found that the PM₁ and PM₁₀₋₁ indoor mass concentrations strongly correlated with the indoor BLPI data (PM₁: $R^2 = 0.96$, PM₁₀₋₁: $R^2 = 0.95$, $n = 24$), and therefore both data from impactors and indoor PM measurements were used for comparison of indoor/outdoor PM concentrations. The results are shown together with indoor PM₁ and PM₁₀₋₁ samplings from Prague in Fig. 3. As observed, the mass concentrations of indoor PM were always lower than the outdoor ones due to the penetration and deposition losses and absence of indoor sources. At all localities outside of Prague the submicrometre fraction dominated, constituting more than 80% of the indoor and more than 75% of the outdoor PM. From Fig. 3, it can also be observed that the indoor PM₁ and PM₁₀₋₁ concentrations in Prague were strongly reduced by the filtration system.

3.2. Mass closure

Aerosol chemical mass closure was performed for fine (PM₁) and coarse (PM₁₀₋₁) size fractions. For mass closure, nine aerosol components were considered (Maenhaut et al., 2002): (1) organic matter (OM), which was estimated to be 1.6 OC in urban archives (Třeboň, Teplice, and Prague) and 2.1 OC in the rural archive (Zlatá Koruna) (Turpin and Lim, 2001); (2) EC; (3) sulphate; (4) ammonium; (5) nitrate; (6) crustal matter = $1.16(1.90\text{Al} + 2.15\text{Si} + 1.41\text{Ca} + 1.67\text{Ti} + 2.09\text{Fe})$, where the factor 1.16 is used to compensate for the exclusion of MgO, Na₂O, K₂O, and H₂O from the crustal mass calculation (Riley and Chester, 1971); (7) trace elements, which is the sum of the mass of all non-crustal/non-sea-salt elements measured by PIXE (S and K were excluded from this sum); (8) non-crustal K = $K - 0.6 \text{ Fe}$ (Chan et al., 1997); and (9) sea salt, estimated to be $\text{Cl} + 1.4486\text{Na}$, where 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water (Chan et al., 1997).

The average percentage contribution to the indoor fine and coarse PM for the nine aerosol types are reported for every archive given in Table 2. The sums of all included components were on average $95(\pm 13)\%$ and $115(\pm 38)\%$ for PM₁ and PM₁₀₋₁, respectively.

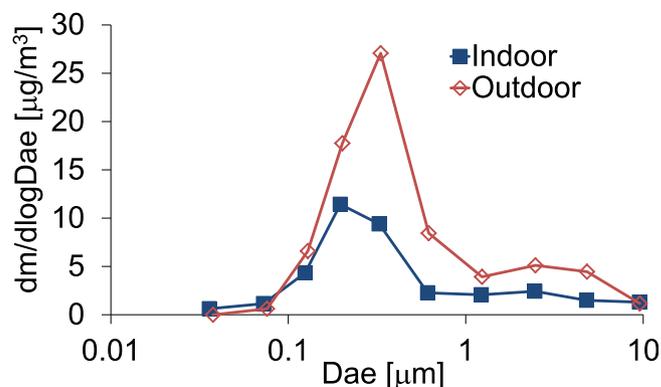


Fig. 2. A typical example of mass size distributions of indoor and outdoor particles observed during the spring campaign in the archive in Zlatá Koruna.

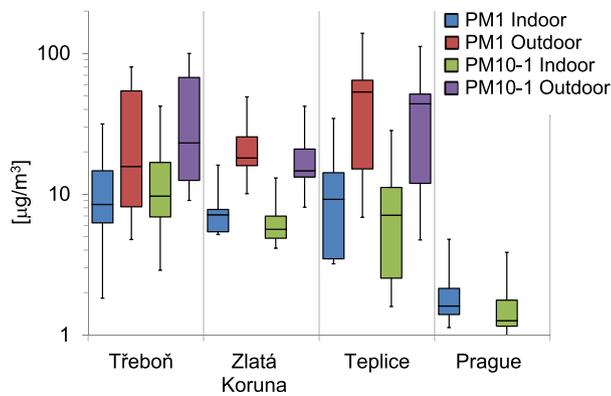


Fig. 3. Annual mass concentrations of fine (PM1) and coarse (PM10-1) fractions collected in the indoor and outdoor environment of the archives. The median is drawn as a horizontal line inside the box. The vertical hinges represent data points from the lower to the upper quartile (i.e., 25th- and 75th-percentiles). The whiskers represent minimum and maximum.

Table 2

The annual average percentage contribution and the associated standard deviation of the aerosol mass for the nine aerosol components for the PM1 and PM10-1 fractions measured in the indoor environment.

	Třeboň	Zlatá Koruna	Teplice	Prague
Fine (PM1)				
OM	55(±20)%	80(±13)%	48(±17)%	70(±18)%
EC	11(±4)%	9(±3)%	12(±7)%	16(±16)%
Sulphate	11(±8)%	8(±4)%	14(±11)%	6(±5)%
Nitrate	1(±1)%	1(±0)%	0(±0)%	0(±2)%
Ammonium	5(±3)%	3(±2)%	5(±4)%	3(±2)%
Crustal matter	3(±4)%	2(±1)%	2(±2)%	8(±6)%
Trace elements	0(±0)%	0(±0)%	1(±1)%	1(±1)%
Non-crustal K	0(±0)%	1(±1)%	1(±1)%	0(±0)%
Sea salt	0(±0)%	1(±1)%	0(±0)%	1(±1)%
Total	87(±14)%	105(±11)%	83(±8)%	104(±9)%
Coarse (PM10-1)				
OM	52(±33)%	78(±39)%	57(±27)%	81(±38)%
EC	4(±3)%	2(±2)%	2(±2)%	2(±2)%
Sulphate	9(±8)%	9(±8)%	5(±4)%	12(±12)%
Nitrate	3(±3)%	6(±8)%	1(±1)%	8(±16)%
Ammonium	3(±3)%	3(±3)%	1(±1)%	4(±5)%
Crustal matter	35(±17)%	42(±36)%	15(±12)%	11(±13)%
Trace elements	0(±0)%	0(±1)%	3(±3)%	4(±4)%
Non-crustal K	1(±1)%	1(±1)%	0(±0)%	1(±1)%
Sea salt	1(±1)%	1(±1)%	1(±1)%	3(±4)%
Total	108(±25)%	141(±40)%	85(±22)%	126(±43)%

It should also be mentioned that water was not included in the sums (except for that which is associated with crustal matter). However, considering the uncertainties of the analysis, the difference from 100% is probably not very significant.

The results showed that the dominating component of both fine and coarse indoor PM was OM, which represented approximately 50–80%. In the fine fraction, the next most abundant components were EC and sulphate, and in the coarse fraction crustal matter, the next most abundant components were sulphate and nitrate. Further ionic equivalent ratios of sulphate, nitrate, and ammonia corresponded to ammonium sulphate and nitrate in fine PM (Fig. A.1 in supplementary materials). In the indoor environment fine nitrate was detected only when indoor temperature decreased below 5 °C (winter in Třeboň – see Table A.2 in supplementary materials). In archives equipped with heating systems (Zlatá Koruna, Teplice and Prague), the indoor fine nitrate practically disappeared, which indicates a shift in equilibrium towards the gas phase caused by higher temperatures indoors (Andělová et al.,

2010; Lunden et al., 2003).

3.3. Sources of indoor PM

The indoor/outdoor concentration ratio determined from impactor samples was lower than 1 at every location for all analysed chemical compounds (Fig. 4). This indicates that particles detected inside have their sources predominantly outside the archives. Further, the I/O ratio mostly increased with increasing temperature difference between indoor and outdoor air. This was probably due to higher pressure gradient produced between the inside and outside, resulting in higher penetration indoors (Walker, 2014).

3.3.1. Major components

Seasonal variations in PM1/PM10 ratios of the six major components are shown in Fig. 5, where values close to one indicate a presence predominantly in the fine fraction. The organic compounds were found mainly in the fine fraction during spring, autumn and winter, and also partly in the coarse fraction in summer. This may indicate, in addition to secondary organic PM, combustion as a source of OM and a higher contribution of biogenic emission during the summer (Hueglin et al., 2005). The contribution of combustion can also be supported by EC found predominantly in the fine particles. The typical sources of combustion PM are traffic and biomass burning. For traffic emissions, high EC concentrations in total carbon (TC = EC + OC) are typical (Chiang and Huang, 2009; Handler et al., 2008; Nguyen et al., 2010), whereas a low EC/TC ratio in the fine fraction may indicate contributions from biomass burning (Gelencsér et al., 2007; Fine et al., 2001; Rau, 1989) or secondary organics (Turpin and Huntzicker, 1995). Seasonal variations of EC/TC ratios are shown in Fig. 6. The highest values of EC/TC ratios were found during the autumn in all naturally ventilated archives and was probably due to lower emissions from local heating than in winter (and spring in Teplice – see Table A.1 in supplementary materials) and lower photochemical activity than in spring (in Třeboň and Zlatá Koruna) and summer. Other sources of EC/OC include campfires in Zlatá Koruna (mainly OC) and higher traffic intensity (mainly EC) during the summer tourist season. The EC/TC ratios were usually higher in both urban libraries (Třeboň and Teplice) than in the rural archive (Zlatá Koruna), likely due to the higher traffic intensity in the towns. In the filtered and isolated archive (Prague), the EC/TC ratios were relatively stable during the whole year, likely due to constant indoor sources (visitors, degradation of books etc.).

Fig. 5 also shows that sulphate, nitrate and ammonium were

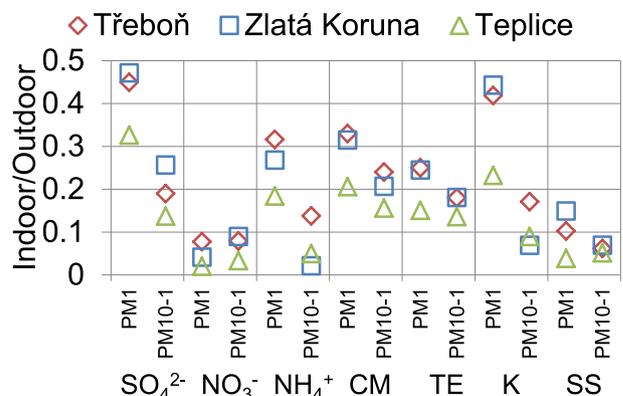


Fig. 4. Annual average indoor/outdoor ratios of sulphate, nitrate, ammonium, crustal matter (CM), trace elements (TE), non-crustal K (K), and sea salt (SS).

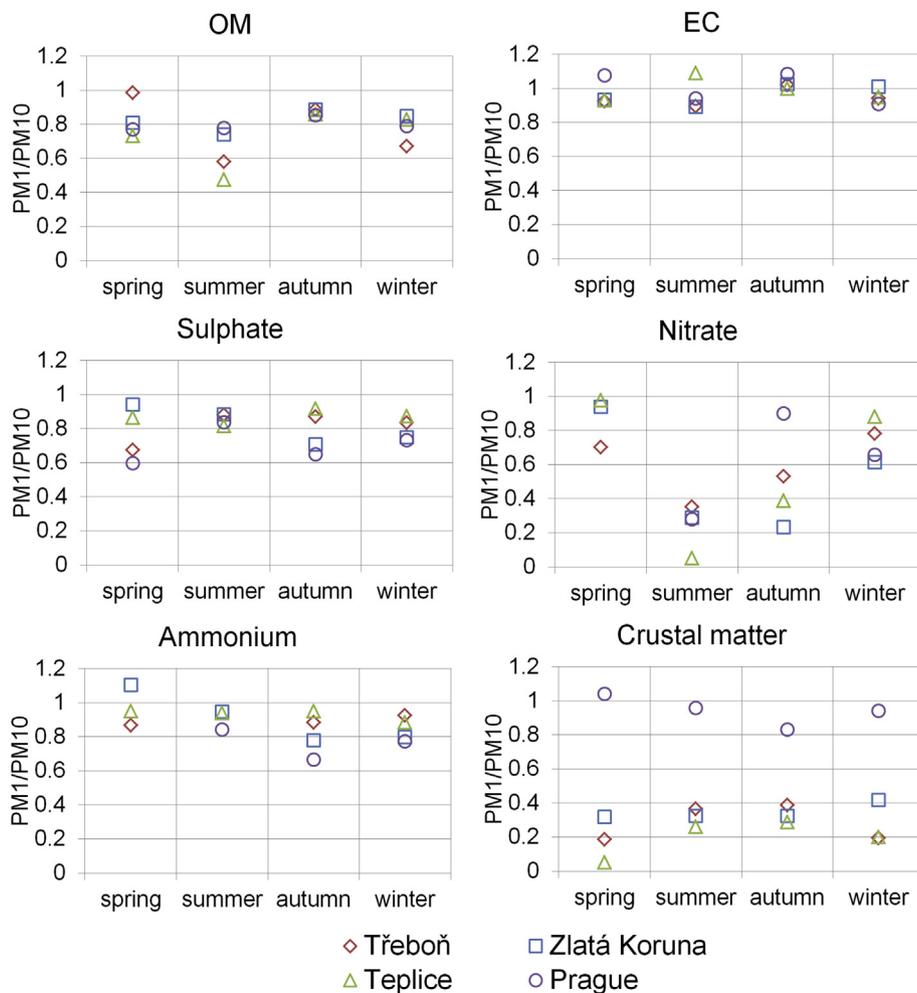


Fig. 5. PM1/PM10 ratios of the six major components in the indoor environment.

observed mainly in the fine fraction. These ions, typical for secondary inorganic PM, originated probably from the regional background or long range transport (Viana et al., 2008). In summer, some nitrate was present in the coarse fraction, which may be due to reactions between nitric acid and crustal matter and sea salt (Finlayson-Pitts and Pitts, 1999; Mamane and Gottlieb, 1990). Crustal matter was found mainly in the coarse fraction; however, in the Prague's archive, it was found mostly in fine PM, which was due

to the very low coarse particle concentrations.

3.3.2. Minor components and trace elements

Non-crustal K, sea salt and trace elements contributed averages of less than 1% each to the total mass of the indoor PM. However, indoor concentrations of some trace elements can be considered to be markers of specific PM sources.

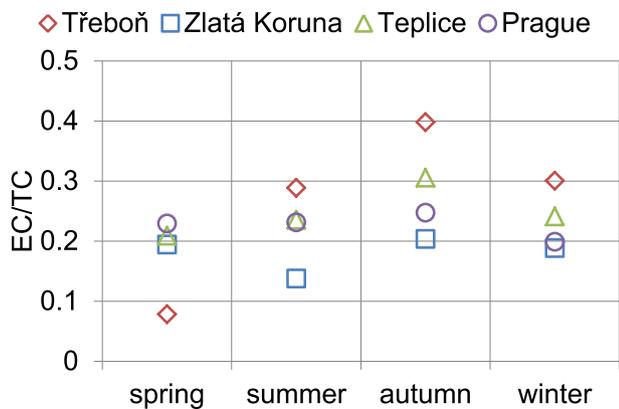


Fig. 6. Ratios of EC/TC in PM1 in the indoor environment.

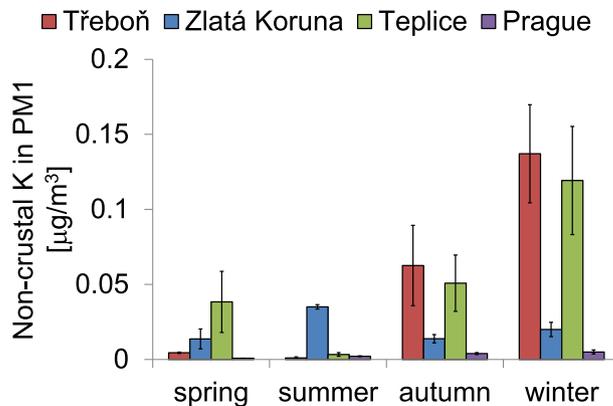


Fig. 7. Average concentrations and associated standard deviations of non-crustal K in PM1 in the indoor environment.

The seasonal variation of non-crustal K in the fine fraction is shown in Fig. 7. K is a typical marker of biomass burning (Calloway et al., 1989; Fine et al., 2001; Johansson et al., 2003; Rau, 1989), which constitutes approximately 3–15% of the mass of dry wood (Miles et al., 1996). The results indicated that during the cold seasons, domestic heating was an important source of PM in the indoor environment of both of the naturally ventilated urban archives (Třeboň and Teplice) but also in the rural archive (Zlatá Koruna). During the summer, the concentrations were negligible at all localities except for the archive in Zlatá Koruna, which shows emissions from fires in the close camp to be an important outdoor source of indoor PM. In the archive in Prague, concentrations of these particles were again strongly reduced by the filtration system. These results correspond to the observed lower EC/TC ratios in the urban archives during winter (local heating) and in the rural archive during summer (campfires).

Cu in the coarse fraction is a typical marker of traffic emissions (Viana et al., 2008). It originates from brake abrasion or from the abrasion of various engine parts (Hjortenkrans et al., 2007; Sanders et al., 2003; Sternbeck et al., 2002; Wählín et al., 2006). The seasonal variation of indoor coarse Cu concentrations revealed that traffic was a very important source of PM in the indoor environment of both of the naturally ventilated urban archives (Třeboň and Teplice), but the concentrations were negligible in the filtered urban archive (Prague) (Fig. 8). In the rural archive (Zlatá Koruna), the influence of traffic was observed only during the summer tourist season. In the archives in Třeboň and Teplice, slightly higher coarse Cu concentrations were found during the summer, which could also be a result of the tourist activity. These results can also clarify the higher EC/TC ratio in Třeboň in summer than in spring. It should be mentioned that Cu can also be used during spring as a major component of fungicides (Mirlean et al., 2007), but no influence of this type of source was detected.

Concentrations of trace metals in the fine fraction were usually negligible at all locations except for the archive in Teplice (Fig. 9). In the indoor environment of this archive, significantly higher concentrations of some elements (Cr, Mn, Ni, Pb, Sr, Ti, and Zr) were observed during the whole year. These metals are typical markers for industrial pollution (Minguillon et al., 2012; Passant et al., 2002; Querol et al., 2002, 2007; Tsai et al., 2007; Zhou et al., 2004).

Ca and Si particles represented approximately 10–15% and 5% of coarse PM in all archives indoors and outdoors, respectively. Coarse Ca–Si-rich particles are a typical marker for indoor activities originating mainly from the degradation of building materials. In many indoor environments strongly influenced by visitors, these particles

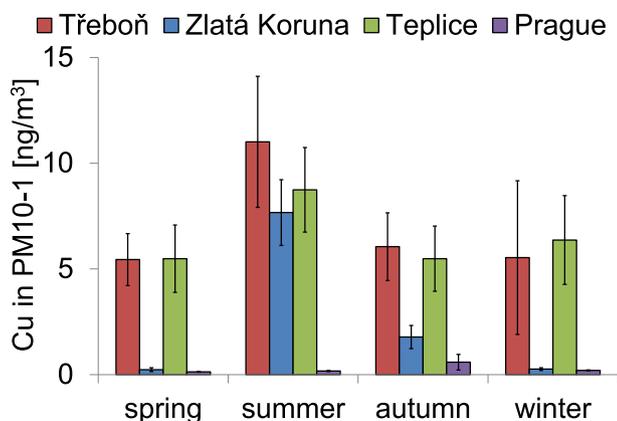


Fig. 8. Average concentrations and associated standard deviations of Cu in PM10-1 in the indoor environment.

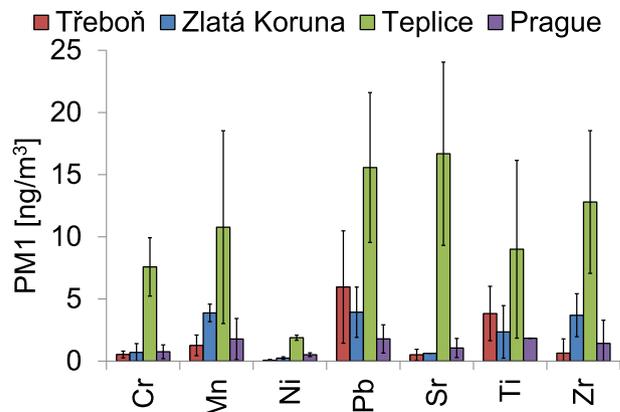


Fig. 9. Annual average concentrations and associated standard deviations of Cr, Mn, Ni, Pb, Sr, Ti, and Zr in PM1 in the indoor environment.

were identified as the most abundant aerosol type (Camuffo et al., 1999, 2001; De Bock et al., 1996; Godoi et al., 2008; Gysels et al., 2002). These results showed the activities of the staff to be a source of coarse particles in the indoor environment.

3.4. Potential effects of PM on archival materials

Chemical compounds found in the indoor PM can be considered to be potentially threatening to the preservation of archives. OM represented the major part of the total indoor PM (on average 67%). These particles have a high potential to damage surfaces by soiling (Baer and Banks, 1994; Brimblecombe and Grossi, 2004), but some organic compounds are hygroscopic and may cause moistening (Hatchfield, 2002). EC, which constituted 12% of the indoor particles on average, can also cause soiling and darkening of surfaces (Baer and Banks, 1994; Brimblecombe and Grossi, 2004). In addition, EC may serve as an adsorbent of gaseous pollutants (Springmann et al., 2009). Ammonium sulphate, which represented approximately 10% of the indoor PM, can induce bloom on varnish (Brimblecombe, 1990). Moreover, ammonium sulphate is hygroscopic (Seinfeld and Pandis, 2006) and has a high potential to cause moistening (Hatchfield, 2002). S-rich particles constituted more than 10% of indoor PM. Oxidation of these particles to sulphuric acid may cause discolouring (Larson, 1957). Coarse particles, which represented approximately 20% of the indoor PM, may damage materials by abrasion (Nazaroff and Cass, 1991). On average, 26% of the indoor coarse fraction was constituted by crustal matter. These particles, in addition to abrasion can also cause soiling (Baer and Banks, 1994; Brimblecombe and Grossi, 2004). Additionally, Fe-rich particles, which represented approximately 2% of the coarse fraction, can play a catalytic role in the oxidation of sulphur dioxide to sulphuric acid (Thomson, 1965), which causes discolouring.

These results showed that all of the particles found indoors can be considered to be potentially threatening to the stored materials. Approximately 85% of the total indoor PM has a high potential to cause soiling, more than 20% may serve as a centre of moisture condensation or adsorption of gaseous pollutants, approximately 20% may cause abrasion, and approximately 15% can damage colours.

4. Conclusions

The current paper presents the characterisation of PM collected indoors and outdoors at four types of archives during the different seasons of the year. The measurements were carried out at locations representing different outdoor environments: (1) rural (Zlatá

Koruna), (2) small town (Třeboň), (3) industrial area (Teplice), and (4) large city (Prague). Three of the selected archives were naturally ventilated (two equipped with heating systems: Zlatá Koruna, Teplice and one non-heated: Třeboň). One archive was equipped with a ventilation and filtration system (Prague). Indoor activities in all of the archives were very limited.

In all cases, the submicrometre fraction dominated. The major component of both fine and coarse indoor PM was organic matter. In the fine fraction, the next most abundant components were EC and sulphate, and in the coarse fraction crustal matter, the next most abundant components were sulphate and nitrate. The considered components explained 95(±13)% and 115(±38)% of the gravimetric indoor PM in the fine and coarse size fractions, respectively. The chemical compositions indicated that indoor PM has a high potential to cause soiling, abrasion, chemical degradation and moistening of stored archives.

The results showed that the most important source of indoor PM in the archives was penetration from outdoor air. In both of the naturally ventilated archives in towns (Třeboň and Teplice), the influence of urban sources such as road traffic and domestic heating was evident. Furthermore, in Teplice, some industrial pollution was observed. In the rural archive (Zlatá Koruna), emissions from camp fires and traffic during the tourist season were detected. The results also showed activities of the staff as an indoor source of coarse particles. In the archive in Prague, the concentration of PM was strongly reduced by the filtration system. From the point of view of conservation, it became clear that the air quality in archives could be improved by employing filters with higher collection efficiency in the HVAC system, but this solution can be very expensive.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.02.049>.

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