



CHARACTERIZATION OF AIRBORNE PARTICLES IN THE BAROQUE HALL OF THE NATIONAL LIBRARY IN PRAGUE

FULL PAPER

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To determine the composition of particulate matter (PM) in the Baroque Library Hall, size-resolved sampling has been performed during three intensive campaigns in spring, summer and winter 2009. Particles were collected and segregated into 10 size fractions (0.025 - 10 µm) using two Berner type Low Pressure Impactors that sampled the indoor and outdoor environment in parallel. The collected samples were analysed gravimetrically, by Ion Chromatography (IC) and Particle Induced X-Ray Emission (PIXE) giving mass, ionic, and elemental size distributions. Simultaneously, total suspended particles (TSP) were collected on quartz filters, that were later analysed for elemental (EC) and organic carbon (OC). In addition, indoor and outdoor gaseous ammonia and nitric acid were measured using passive diffusion samplers. Typical mass size distributions were bimodal with the minimum at about 1 µm, with lower concentrations indoors and submicron range shifted to smaller particles. The results of IC revealed that ammonium sulphate and nitrate form about 30% of outdoor and about 20% of indoor mass of submicron fractions of PM, with indoor nitrate concentrations decreasing to zero. Most of the ammonium nitrate evaporated after penetration indoors probably due to higher indoor temperatures and fast surface deposition of gaseous nitric acid. This process also increased indoor concentrations of ammonia and could also explain a shift of indoor size distributions to smaller particles.

1 Introduction

Particulate matter (PM) in cultural heritage buildings such as museums and libraries represents different degrees of risk to materials. Particles not only cause soiling but are abrasive, provide sites for surface reactions and have the potential to damage artefacts due to their hygroscopic nature.¹ Particles can be generated indoors by various processes such as cooking, smoking, heating, material deterioration, produced and/or resuspended by visitors or during cleaning, or pene-

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trate from the outdoor environment. The important contribution comes from accumulation mode particles (0.1 – 1 μm). Particles of such sizes enter most easily through the shell of buildings² and have the lowest deposition velocities.³ In urban environments this mode predominantly contains primary particles emitted from combustion sources and secondary particles formed by ammonium sulphate and nitrate, complex mixtures of organics and elemental carbon.^{4,5} These species not only cause soiling,⁶ but due to their hygroscopic nature can enhance deterioration of materials.¹ In addition, ammonium nitrate can evaporate after penetration indoors, generating gaseous ammonia and nitric acid. Deposition of gaseous nitric acid on indoor surfaces, including the objects and artefacts, can then further drive ammonium nitrate evaporation, leading to increased concentrations of ammonia indoors.^{7,8} Both ammonia and nitric acid can damage works of art in museum environments.^{9,10}

There are several studies reporting higher indoor ammonia concentrations than outdoors.^{8,11-15} To explain it, some indoor sources for ammonia were suggested such as human metabolic activities, use of cleaning products or smoking in addition to possible evaporation of ammonium nitrate infiltrated from outdoors.¹¹ Many investigators also observed that indoor concentrations of nitric acid were substantially lower than those outdoors,^{12,16-18} or even negligible.¹⁵ The low HNO_3 indoor concentrations were attributed to the deposition on indoor surfaces. Some studies also found lower concentrations of ammonium nitrate in the indoor environment.¹⁹⁻²¹ This was apparently due to higher temperatures indoors compared to outdoor conditions causing ammonium nitrate to decompose after penetration indoors.²¹

Several authors observed the effect of air exchange rate on indoor levels of nitric acid. Salmon et al.¹⁶ measured nitric acid concentrations in indoor and outdoor air at five museums in southern California. At a museum with high infiltration of air through open doors and windows, the indoor nitric acid levels were up to 69% of those outdoors. In a second museum with a very low air exchange rate, high internal recirculation, and activated carbon filtration indoor nitric acid concentrations of about 1% of those outdoors were found. Brauer et al.¹² measured indoor and outdoor concentrations of inorganic acidic aerosols and gases during summer and winter in the area of Boston. Higher indoor/outdoor ratio of nitric acid was observed during summer and lower during winter, probably due to elevated air exchange rates during the summer and reduced air exchange rates during the winter period. Hisham

and Grosjean¹⁷ measured gaseous pollutants at nine southern California museums. Indoor levels of nitric acid varied substantially from levels comparable to outdoor ones at locations with high air exchange rate to low levels in more confined settings such as storage rooms, where deposition to walls and collections, as well as lower air exchange rate could be expected. The dynamics of indoor ammonium nitrate aerosol was modelled by Lunden et al.^{7,22} and Hering et al.²³ The results showed that ammonium nitrate evaporates at time scales comparable to air exchange, generating gaseous ammonia and nitric acid. The uptake of nitric acid on indoor surfaces reduces gas phase levels and further drives the evaporation of ammonium nitrate.

In this study we report the size resolved mass concentration and ionic composition of PM sampled both indoors and outdoors at the Baroque Library Hall of the National Library in Prague. The detailed characterization, including elemental and EC/OC composition is part of a future contribution.

2 Experimental

2.1 Measurement Site

The indoor and outdoor aerosol particle measurements were carried out during three intensive campaigns: 10-17 March, 14-21 July, and 23 November – 2 December 2009 in the Baroque Library Hall of the National Library (Clementinum Historical Complex). The Clementinum (50°5'06.7" latitude, 14°25'51.3" longitude, 190 m a.s.l.) is located in the Vltava River valley. It is a historical complex of buildings covering more than 20,000 m² and it is the second largest complex of buildings in Prague after the Prague Castle. The Clementinum is exposed to air pollution from local sources but mainly to traffic due to its situation adjacent to a main road (i.e. Křižovnická street). According to the Atlas of the Prague Environment²⁴ the intensity of car traffic was about 24,200 cars on this main road between 6 am and 22 pm during a working day in 2008.

The Library Hall was completed in 1726 and is situated in the centre of the Clementinum on the second floor. It is one of the finest interiors and constitutes an excellent example of the baroque style. The library holds approximately 20,000 theological books written in different languages dating from the 16th century until recent times and stored in original wooden shelves. Apart from the collection, the Hall is decorated with frescoes illustrating themes such as science and art. Concerning the ventilation, the Library Hall does not have an

HVAC system, i.e. ventilation of the Hall proceeds through cracks and small openings in the building, windows, and doors. The Hall is 39 m long and 9.4 m wide with an arched ceiling, in the lowest point 8.3 m and in the highest point 9.6 m high. Along the western and eastern side of the Baroque Hall double glass windows are situated covered by curtains, 8 of size 2 x 3.3 m and 8 of size 1.3 x 1.8 m. On the east side, the Library Hall is connected with a study room by two open doorways covered with curtains (4.1 x 1.9 m). The study room is 11.2 m long and 5.7 m wide with an arched ceiling, in the lowest point 7.4 m and highest point 9.3 m high. There are 4 double glass windows covered by curtains of size 2.2 x 6.3 m. In the Baroque Hall, there are 4 entrance doors, 2 on the north side and 2 on the south side. On the north side the entrances lead from the hallway, which serves as a storage room and as an entrance used by librarians and restorers. On the south side a door leads from the foyer of the Baroque Hall and serves as an entrance and exit for visitors. Visitors enter the Hall in groups of max of 25 people accompanied by a guide, and tours run only along the south side of the Hall. Sightseeing tours take place every day from 10 am and finish differently in different months (XI., XII. at 4 pm; I., II., III., X. at 5 pm; IV., IX. at 6 pm; V. at 7 pm; VI., VII., VIII. at 8 pm). From Monday till Thursday the tours start every hour and from Friday to Sunday every half-hour. A scheme of the Baroque Library Hall is shown in Figure 1.

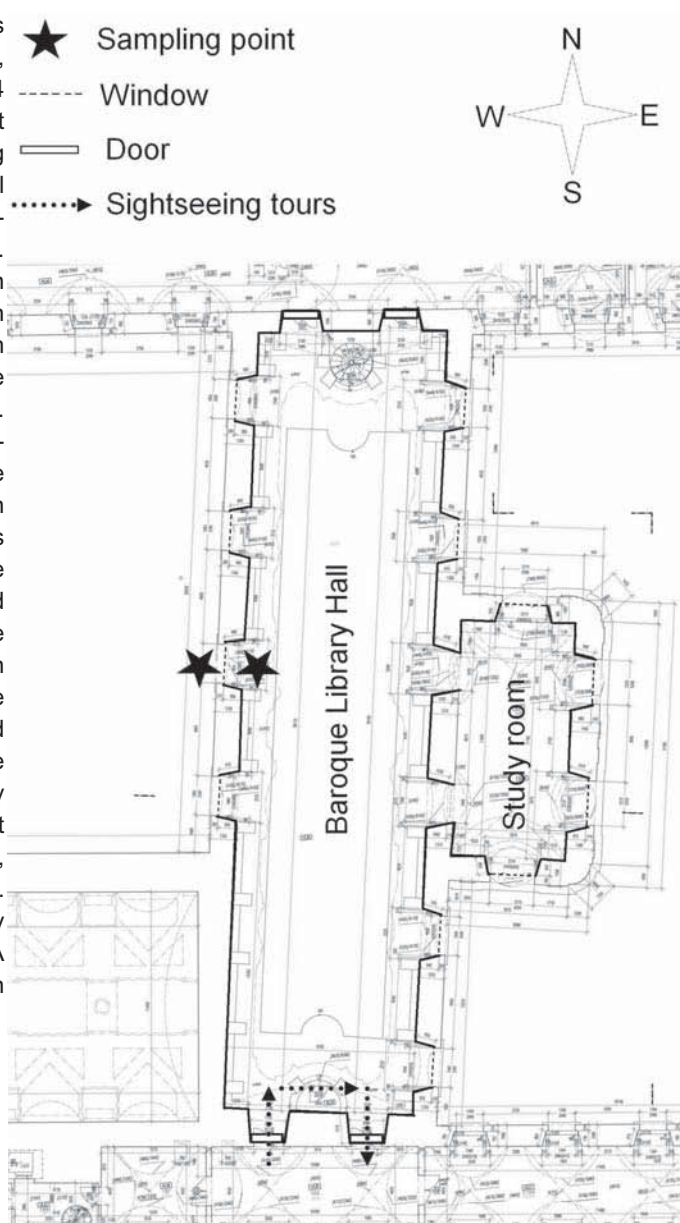


Figure 1: The scheme of Baroque Library Hall where the measurements were performed.

2.2 Particulate Matter Sampling and Analysis

The sampling of particulate matter was performed using two Berner type Low Pressure Impactors (BLPI, 25/0.018/2, Hauke, Austria), collecting and separating particles into 10 size fractions with aerodynamic cut diameters ranging from 25 nm to 10 μm . Both impactors were situated inside the library at a distance of about 1.5 m from the window. Indoor samples were taken at the height of about 1.5 m above the floor, outdoor samples were taken using sampling train extended using a wooden panel fixed in the window frame. Both impactors were equipped by the same type of inlet. Prior to the measurements the impactors were compared by parallel atmospheric aerosol sampling and satisfactory agreement was found. The samples were deposited on Nuclepore foils greased by Apiezon L vacuum grease to reduce

particle bounce. In total, three size-segregated samples were collected from both indoors and outdoors during each campaign. The mass size distributions were calculated considering the mass of particulate matter deposited on the individual stages (given by the difference of the weight of the foil at this stage after and before sampling), the volume flow rate (25 L/min) and the total time of sampling. The foils were weighed on Sartorius M5P microbalances, Germany, with a sensitivity of 1 μg in a weighing room equipped with temperature and humidity sensors. The relative humidity was in the range of 20 - 40%. The size-segregated samples were further analysed by ion chromatography (IC). The analyses were provided using the setup by Watrex Ltd., Czech Rep., with columns Watrex IC Anion II 10 μm 150 x 3 mm for anions and Alltech universal cation 7 μm 100 x 4.6 mm for cations. The conductivity detector used in this

setup was a SHODEX CD-5. Impactor samples were extracted by mixture of 0.5 ml of methanol and 4.5 ml of ultrapure water (Ultrapur, Watrex Ltd.) for 0.5 h using ultrasonic bath and 1 h using a shaker. The filtered sample was then analysed for anions and the next day for cations. The sample solutions for cation analysis were stored in the fridge prior to the analysis. The ions Cl^- , NO_2^- , NO_3^- and SO_4^{2-} , were analysed as main anions and Na^+ , NH_4^+ , K^+ , Zn^{2+} , Mg^{2+} and Ca^{2+} as main cations.

2.3 Passive Diffusion Samplers

Gaseous NH_3 and HNO_3 were measured by passive diffusion samplers from the Norwegian Institute for Air Research (NILU) and the Swedish Environmental Institute (IVL), respectively. Two samplers of each compound were exposed during one month both indoors and outdoors. The indoor location was the same selected for particulate matter sampling (Figure 1) whereas the outdoor sampling location was located on a window in an adjacent room, at the north side of the building.

3 Results and Discussion

3.1 Mass size distributions

Indoor and outdoor mass size distributions were bimodal with the minimum of about $1 \mu\text{m}$. The fine particle mode was of about $0.2 \mu\text{m}$ for indoor PM and about $0.3 \mu\text{m}$ for the outdoor PM. The coarse mode was of about $2 - 5 \mu\text{m}$ for both indoor and outdoor particles. Typical examples are shown in Figure 2a-c. In all cases the fine particle mode ($<1 \mu\text{m}$) dominated, contributing to mass concentrations on average by 70% during the spring, 55% during the summer, and 65% during the winter campaigns. The characteristic differences between both distributions were (1) the fine particle mode of indoor PM was shifted to smaller sizes compared to the outdoor ones, and (2) the mass concentrations of indoor PM was lower than outdoor concentrations. The same behaviour we already observed in a similar study dealing with characterization of indoor and outdoor aerosols in a suburban area of Prague.²¹ The observed differences might result from the combination of penetration and deposition losses, indoor sources and indoor aerosol dynamics.²⁵ Penetration and deposition losses decrease indoor PM concentration, indoor sources increase indoor PM concentration while aerosol processes such as coagulation, hygroscopic growth or particle evaporation change the particle size and therefore also particle size distribution.

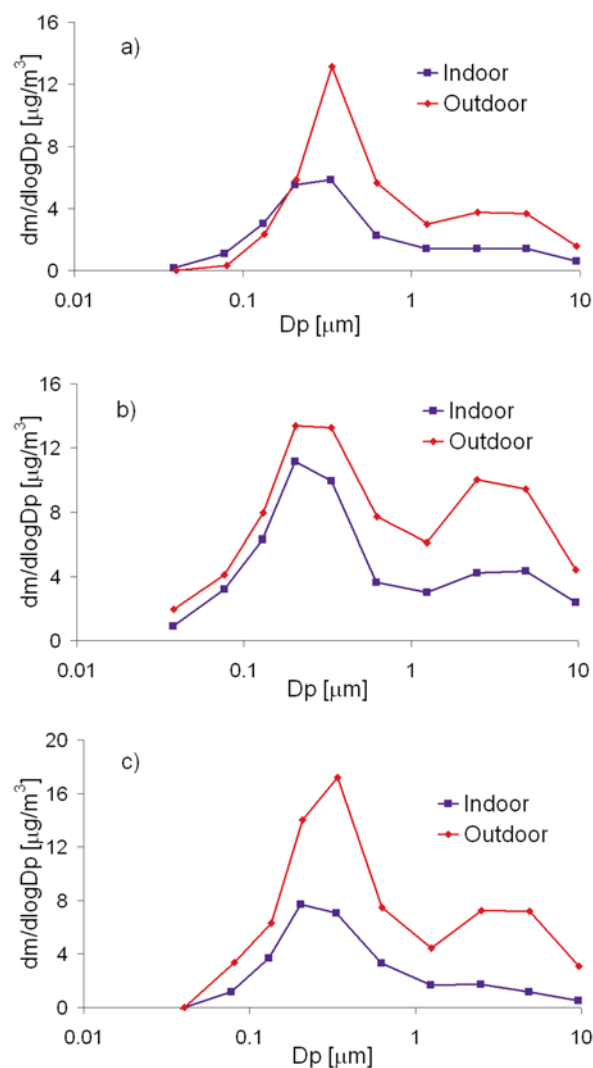
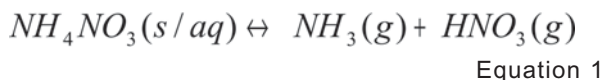


Figure 2: Typical examples of mass size distribution of indoor and outdoor aerosol particles, a) 12.3.2009, b) 15.7.2009, c) 26.11.2009.

3.2 Ionic size distribution

The ion chromatography revealed that the major water-soluble inorganic components of the fine particle mode were sulphate, nitrate, and ammonium with the composition corresponding to ammonium sulphate and ammonium nitrate. Both compounds formed up to 30% of outdoor and up to 20% of indoor mass of the submicron PM. The typical indoor and outdoor mass size distributions of sulphate, nitrate and ammonium ions are shown in Figure 3a-c. As can be seen, the ammonium nitrate practically disappeared in submicron fractions of indoor PM. The large decrease in indoor nitrate concentration compared to those measured outdoors clearly indicates a shift in equilibrium toward the gas phase, caused by higher temperatures indoors,⁴ (equation 1) that can be further driven by deposition of gaseous nitric acid on indoor surfaces.⁷



This can be supported by the results obtained from passive diffusion sampler measurements where indoor concentrations of gaseous nitric acid were below the detection limit during the whole period (Figure 4). The evaporation of ammonium nitrate indoors could also explain higher concentrations of ammonia measured indoors. But, combined effect of ammonium nitrate evaporation and penetration of ammonia from the outdoor air should be considered (Figure 5). The evaporation of ammonium nitrate in the indoor environment leading to the shift of mass size distribution to the smaller particle sizes was also observed in a previous study.²¹ Figure 2a-c also shows a shift in the mass size distribution of indoor sulphate and ammonium to smaller particles. This effect, already observed in a previous study,²¹ was apparently caused by a shrink of aerosol particles after evaporation of ammonium nitrate.

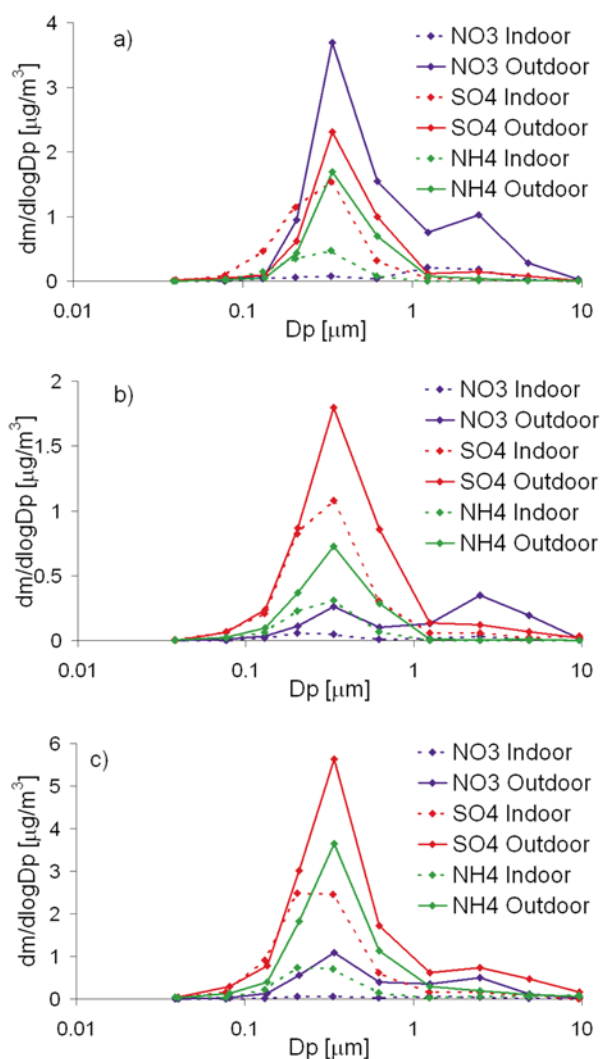


Figure 3: Typical examples of indoor and outdoor mass size distributions of sulphate, nitrate, and ammonium, a) 12.3.2009, b) 15.7.2009, c) 26.11.2009.

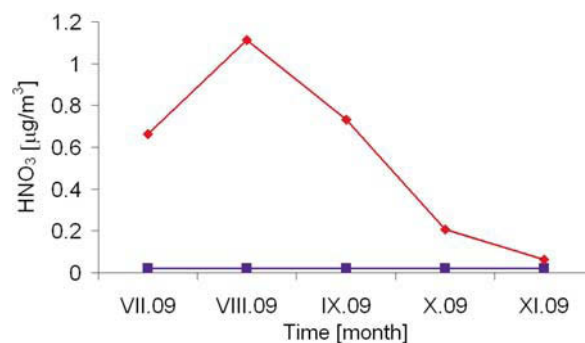


Figure 4: Time series of gaseous nitric acid concentrations measured by passive diffusion samplers during the whole period. The value for each month represents the averages obtained from two passive diffusion samplers.

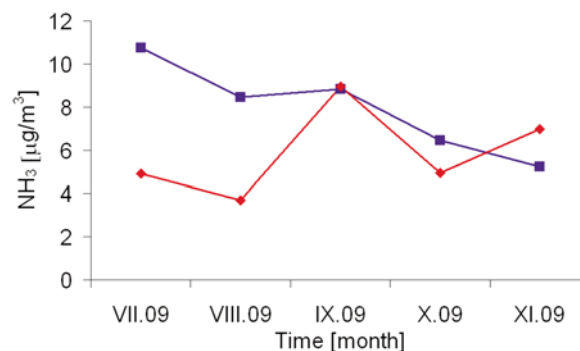


Figure 5: Time series of ammonia concentrations measured by passive diffusion samplers during the whole period. The value for each month represents the average obtained from two passive diffusion samplers.

4 Conclusions

The current paper presents the characterization of aerosol particulate matter (PM) collected indoors and outdoors of the Baroque Library Hall of the National Library in Prague during three intensive campaigns in the spring, summer, and winter of 2009. The particles were sampled by two low pressure BLPI impactors separating particles into 10 size fractions from 25 nm to 10 µm and further analyzed gravimetrically and by ion chromatography. In parallel to PM sampling indoors and outdoors, gaseous ammonia and nitric acid were measured using passive diffusion samplers. The IC analyses revealed that the major water-soluble inorganic components of the fine particle mode were sulphate, nitrate, and ammonium, with indoor nitrate concentrations decreasing to zero and a shift of mass size distribution of indoor sulphate and ammonium to smaller particles. It was apparently caused by evaporation of ammonium nitrate after penetration indoors. This process also increased indoor concentrations of ammonia and led to deposition of gaseous nitric acid on indoor surfaces.

5 Acknowledgement

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6 Literature

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