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Environmental monitoring and evaluation of the indoor environment in the Baroque Library Hall of the National Library (Czech Republic)

Indoor Air Quality Assessment of the Baroque Library Hall

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Contents

Summary

This document is the Final Report of the project "Environmental monitoring and evaluation of tolerability of indoor environment in the Baroque Library Hall of the National Library" (CZ0046) and it hereby synthesizes the main results obtained by the Norwegian Institute for Air Research (NILU) and the activities performed in the project.

The project was carried out by the Institute of Chemical Process Fundamentals (co-ordinator; ICPF), the National Library of the Czech Republic (NL) and the Norwegian Institute for Air Research (NILU) as partners, and it was financed by the EEA/Norwegian Financial Mechanisms and the Ministry of Education, Youth and Sports of the Czech Republic.

The indoor air quality was evaluated based on measurements of single pollutant concentrations (NO_2, SO_2, O_3, NH_3, NHO_3, acetic and formic acids) and dosimetry (EWO-dosimeter). One of the main findings of the project is the seasonal differences measured in the Baroque Library Hall (BLH) of the National Library in Prague (Czech Republic). The building is naturally ventilated and, higher infiltration of outdoor pollutants and higher dilution of indoor pollutants were observed in winter than in summer. The seasonal variations were explained by higher air exchange rate (AER) as a consequence of indoor-outdoor temperature differences reaching a maximum during winter. In addition, gaseous pollutant sources were identified as outdoors, indoors or from infiltration of particles (i.e. ammonium nitrate) and subsequent evaporation forming gaseous pollutants (i.e. ammonia and nitric acid). The evaluation of the results indicates that there is some risk for the preservation of organic materials such as paper due to photo-oxidant effects, and to the impact of NO_2, SO_2 and acetic acid, which were measured at high concentrations.

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1 Introduction

Air pollution has become a main concern of our society due to its adverse effects on health, materials and ecosystems. The study of the effects of indoor air pollution on cultural heritage objects is receiving an increasing interest that has over the last decade focussed on the protection of items both in exhibition and storage.

The project "Environmental Monitoring and Evaluation of tolerability of indoor environment in the Baroque Library Hall of the National Library" (CZ0046) aimed to perform a detailed characterisation of indoor air pollution in the Baroque Library Hall (BLH) of the National Library in Prague (Figure 1). The study focused both on gaseous pollutants and particulate matter (PM), estimation of the contribution of outdoor and indoor sources and evaluation of the possible impacts of air pollution on books and manuscripts which could lead to degradation processes. This report will focus mainly on gaseous pollutants and on photo-oxidant effects of the environment on organic materials.

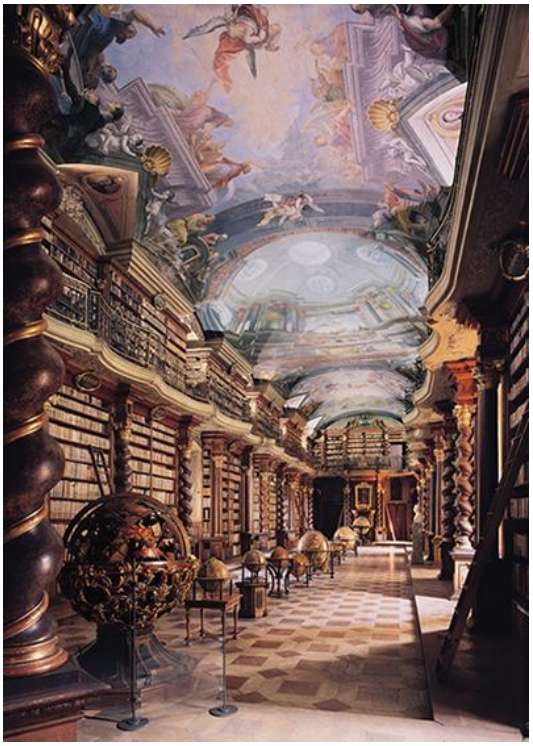

Figure 1: The Baroque Library Hall (BLH) of the National Library in Prague (Czech Republic).

In our study, measurements of NO_2, SO_2, O_3, NH_3, HNO_3 and organic acids (i.e. acetic and formic acids) were performed inside and outside the BLH by passive diffusion gas samplers. The study is one of few to measure and evaluate a range of pollutant concentrations both inside and outside a naturally ventilated historic building, with restricted personnel access, small groups of visitors and reduced number of activities which could influence the pollutant concentrations. The type of sampling location involves only a low number of variables which affect the indoor pollutant concentrations and indoor air quality. The study will contribute to the understanding of indoor air quality under natural ventilation. From the point of view of the protection of materials, libraries and archives are interesting places to study due to the homogeneity of material types they contain.

This report describes the methodology employed in the project to measure gaseous pollutants and the photo-oxidant effects of the environment. The results are evaluated concerning both material preservation and the behaviour of the naturally ventilated building envelope. In addition, some of the dissemination activities carried out during the project are described.

2 Methodology

2.1 Sampling Location

The BLH of the National Library in Prague (Czech Republic) is located in the Clementinum historical complex (50°5'067" latitude, 14°25'513" longitude, 190 m a.s.l.) in the Vlava Riven Valley (Figure 2). The historical complex is exposed to air pollution mainly from traffic. According to the 2008 Atlas of the Prague Environment the intensity of car traffic was about 24 200 cars on the main road adjacent to the library 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 of the Clementinum 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 (Figure 1).

Four locations inside the BLH, one indoor location in an adjacent storeroom and one outdoor location were selected for the measurements and the environmental evaluation (Figure 3).

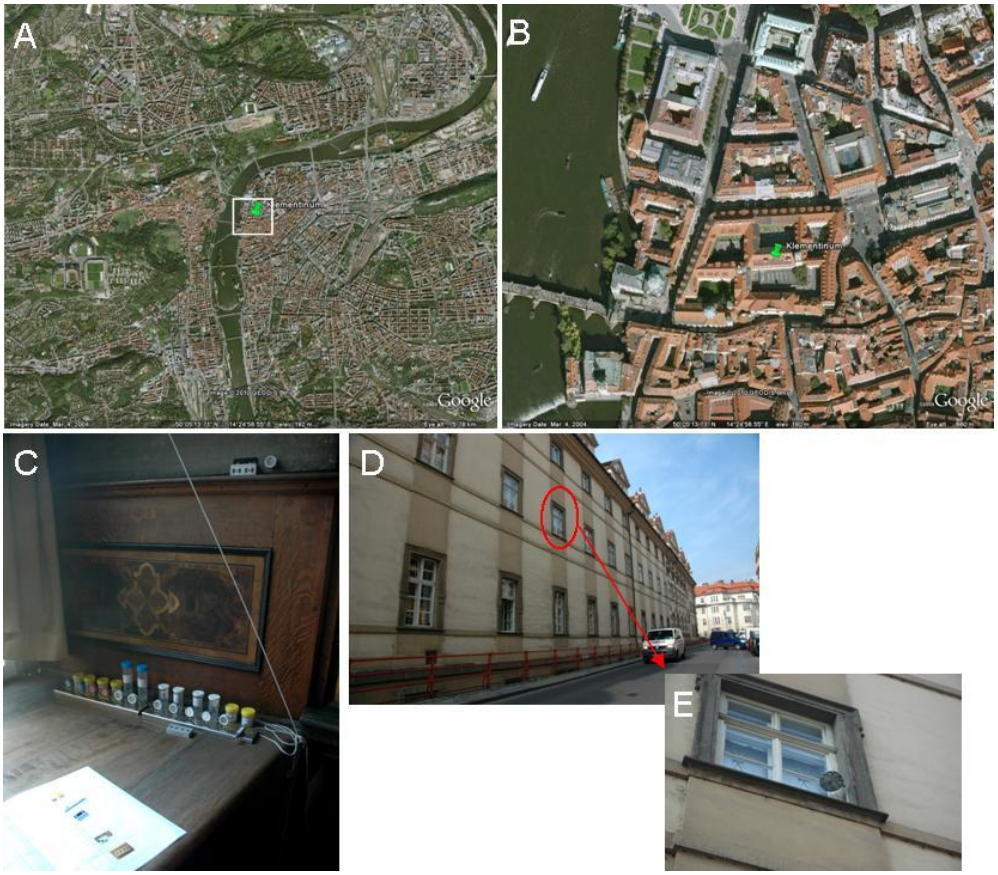

Figure 2: Location of the Clementinum historical complex in Prague (A and B). Indoor (C) and outdoor (D and E) sampling locations selected for the year measurement campaign.

2.2 Measurement Campaigns

Single pollutant gases concentrations were measured inside and outside the BLH, and the photo-oxidant effect of the environment was measured by dosimeter in the indoor environment. The measurements performed as part of the project were divided in two different measurement campaigns; 1) a nine-months measurements campaign; and 2) a seasonal measurement campaign (i.e. summer and winter).

Nine months measurement campaign
The nine months measurement campaign took place from the 1st of July 2009 to 30th of March 2010, when single pollutant measurements were monthly performed both indoors and outdoors (Figure 3). The main aim of the nine months measurement campaign was to perform a detailed characterization of the indoor environment, consequently the measurements included a wide range of gaseous pollutants such as NO_2, SO_2, organic acids (acetic and formic acids), NH_3, O_3, HNO_3 and VOCs.

The photo-oxidant effect of the environment was also evaluated by the EWO dosimeter and measurements were performed per period of three months.

Seasonal measurement campaign
Two measurement campaigns were performed at two different seasons in four different indoor locations (Figure 3) in order to evaluate possible variations. The first measurement campaign was carried out in July 2009 corresponding to summer while the second campaign was performed in January 2010, corresponding to the winter season. NO_2 and organic acids (acetic and formic) were selected as indicators of outdoor and indoor generated pollutants, respectively. The measurements lasted one month for the passive diffusion gas samplers and three month for the EWO dosimeter.

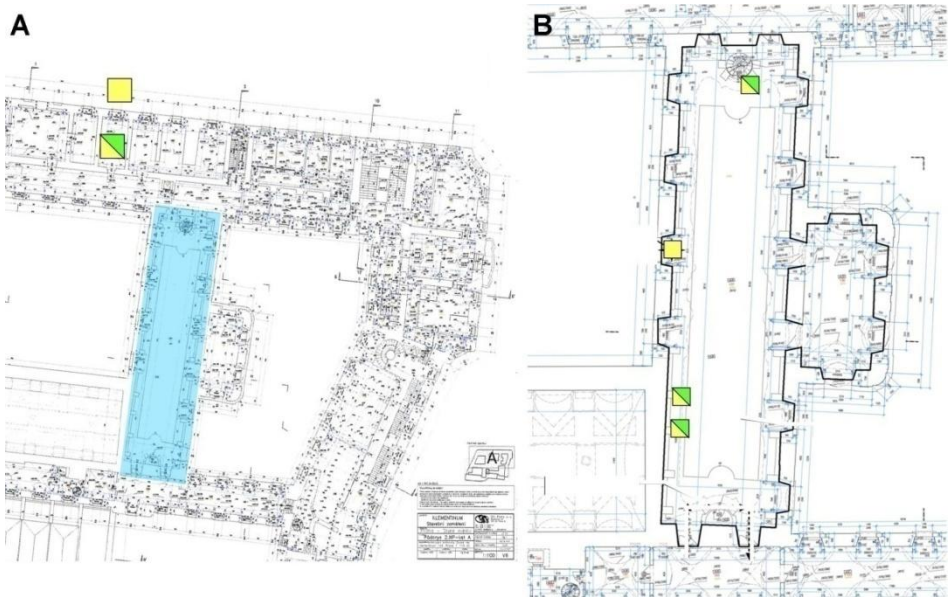

Figure 3: Sampling locations inside and outside the Baroque Library Hall. Yellow square: Year measurement campaign locations (IA and OA). Yellow/Green square: seasonal measurement campaign locations (ISS1, ISS2, ISS3 and ISS4).

2.3 Dosimetry

The photo-oxidant effects of the environment were measured by the Early Warning dosimeter for Organic materials (EWO) developed by the Norwegian Institute for Air Research (NILU; Figure 4; Grøntoft et al., 2010; López-Aparicio, et al., 2010a).

The EWO dosimeter is a synthetic polymer sensitive to climate parameters (i.e. temperature, RH and UV Light) and NO_2 and O_3, which are usually emitted outdoors and ventilated or infiltrated into the indoor environment. The environmental effect on the dosimeter polymer film is measured by photo-spectrometry as the change in UV absorption at 340 nm from before to after exposure. The relation between the EWO-response and the environment is based on a non linear dose response function found from the statistical analysis of the results obtained in one year measurement campaign. Two dose response functions for indoor locations outside (Equations 1) and inside enclosures (i.e. showcases; Equation 2) were defined (Grøntoft et al., 2010).

An evaluation of recommended response levels for the EWO dosimeter as compared to effects on organic cultural heritage objects was performed based on existing knowledge in conservation science about the effects of the single environmental parameters on the heritage objects. The results from measurements with the dosimeter are reported as values of increasing environmental impact ranging from one to five. The evaluation of the indoor air quality is performed for five different locations with different degree of protection, from archive to external store with no control (Table 1).

Equation 1

Equation 2

Table 1: Location - Tolerability diagram for the EWO dosimeter results (Grøntoft et al., 2006).

Determined expectation	LEVELS				
	1	2	3	4	5
Archive / Store	Expected environment (acceptable)	Environment could be better	Environment is poor	Something is wrong with control	Serious problem with building or control
Purpose built museum	Environment is very good	Expected environment (acceptable)	Environment could be better	Environment is poor	Something is wrong with control
Historic Building	Excellent environment	Environment is very good	Expected environment (acceptable)	Environment could be better	Environment is poor
Open structure	Dosimeter is not responding	Excellent environment	Environment is very good	Expected environment (acceptable)	Environment could be better
External store with no control	Dosimeter is not responding	Dosimeter is not responding	Excellent environment	Environment is very good	Expected environment (acceptable)

Figure 4: EWO dosimeter (left), passive diffusion gas samplers (middle) and VOC Tenax tube (right) used in the sampling campaign.

2.4 Passive diffusion gas samplers

Gaseous NO_2, SO_2, acetic and formic acids and NH_3 were measured by passive diffusion gas samplers from the Norwegian Institute for Air Research (NILU; Figure 4), whereas O_3 and HNO_3 were measured with passive diffusion gas samplers from the Swedish Environmental Institute (IVL). Two samplers of each compound were exposed during one month both indoors and outdoors, and each month samplers were exchanged for a new set. The indoor location was placed on a windowsill (Figure 2) whereas the outdoor sampling location was located on a window in an adjacent room, at the north side of the building (Figure 3).

The passive diffusion samplers consist of holder, steel net at the opening, Teflon filter and an impregnated filter to absorb the gas of interest. The filter of the NH_3-passive sampler is impregnated in oxalic acid, which is dissolved after exposures and the extracted nitric acid is determined by photometry. The mean concentration of NH_3 during the exposure time is estimated based on the quantity of extracted nitric acid, the diffusion constant for NH_3 and a factor based on the dimensions of the passive sampler. The filter of the SO_2-passive sampler is impregnated in an alkali, which is dissolved in an aqueous solution after exposure and the extracted sulphate (SO_4^{2-}) is determined by ion chromatography. A similar filter impregnated with an alkali solution and similar procedure is used for the determination of acetic and formic acid. For NO_2, the filter is impregnated in iodide (I-) and the formed nitrite (NO_2^-) is determined by photometry. The mean concentration of the different compounds is estimated in the same way as for NH_3, based on the quantity of extracted component, diffusion constant for the gas of interest and a factor based on the dimensions of the passive sampler. The passive diffusion samplers for O_3 and NHO_3 were analysed by the Swedish Environmental Institute (IVL).

The detection limit after one month of exposure is for NO_2 approximately 0.03 µg m^{-3}, for SO_2 it is 0.1 µg m^{-3}, for acetic acid and formic acid it is 0.5 µg m^{-3}, for NH_3 it is 0.5 µg m^{-3} and for O_3 and NHO_3 it is reported to be 1 µg m^{-3} and 0.02 µg m^{-3}, respectively.

Measurements of Volatile Organic Compounds (VOCs) were performed by Thermal Desorption VOC sampling tubes with Tenax TA sorbent and analysed by thermal desorption gas chromatography-mass spectrometry (GC-MS) at NILU.

3 Results and Discussion

The database with the results presented and discussed in this chapter is included in the Appendix A.

3.1 Photo-oxidant effects

The photo-oxidant effects of the environment on organic materials were measured with the EWO-dosimeter in the same location where the nine months measurement campaign was performed. From July 2009 to December 2010 the results were evaluated as acceptable for a "Purpose Built Museum" (i.e. Level 2; Figure 5). The measurement performed from January to March 2010 showed very low response of the EWO (Figure 5). There is reason to believe that some irregularities took place during January – March as this result is not consistent with the concentration of pollutants and / or climate parameters.

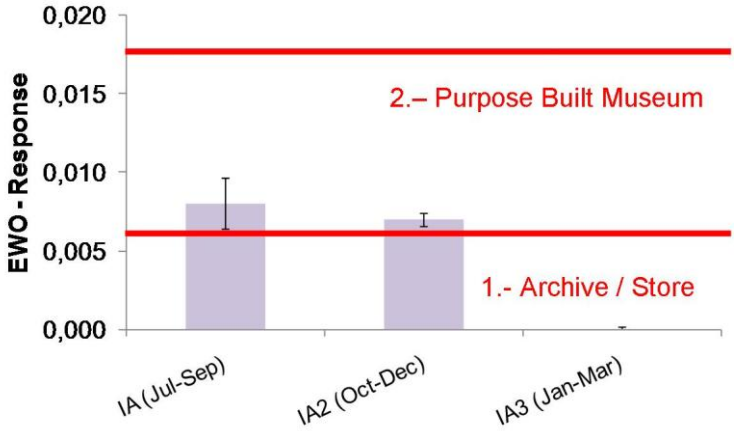

Figure 5: EWO response (ΔLight absorbance) obtained on the nine months measurements campaign (IA; Yellow square in Figure 3-indoors).

The photo-oxidant effects of the environment were additionally measured in summer and in winter (Figure 6) in four different indoor locations. ISS1, ISS2 and ISS3 are located inside the BLH (Figure 3), whereas ISS4 is located in an adjacent depository room. In summer 2009, the three locations inside the BLH were evaluated to be acceptable for a "Purpose Built Museum" whereas the depository room shows an acceptable environment for the an "Archive / Store" (Figure 6). In winter 2010, the EWO dosimeters do not show results after exposure in any of the four locations. As it was pointed out previously, there are reasons to assume that some irregularities occurred in the exposures intended from January to March, 2010. Therefore, these result would not be taken into account in further evaluations.

The indoor environment in the BLH of the National Library in Prague (Czech Republic) was evaluated as acceptable for a "Purpose Built Museum" concerning photo-oxidant effects of the environment on organic materials. The BLH may be defined as an archive or storage place, so the expected environment or level would be level 1. Therefore the evaluation of the results obtained with the EWO dosimeter indicates that the environment inside the BLH concerning the preservation of organic materials "could be better" (Table 1).

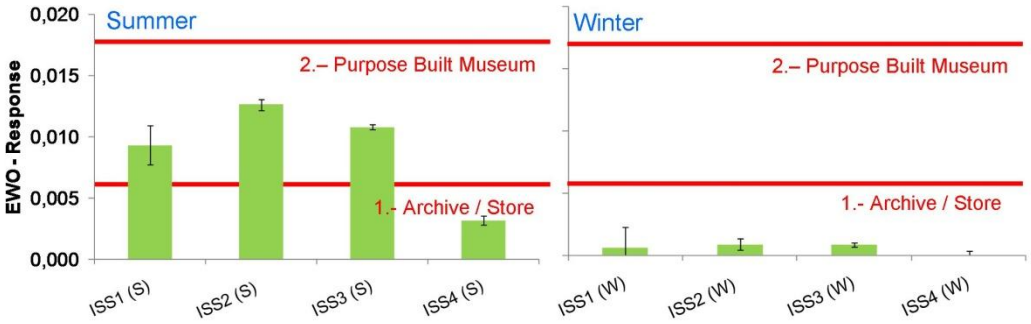

Figure 6: EWO response (ΔLight absorbance) obtained in summer and in winter in four different indoor locations.

3.2 Gaseous pollutants

Air pollutant concentrations measured indoors can be divided according to their origin as indoor and outdoor generated pollutants. The relationship of indoor and outdoor concentration (I/O ratio) provides indication of the possible source of the pollutant. In the absence of indoor sources, the indoor to outdoor pollutant concentration ratio is below 1, whereas with indoor sources, the I/O ratio is above 1. This chapter has been divided as outdoor generated pollutants, indoor generated pollutants and pollutant from particle infiltration, division based on the evaluation of relationship of indoor and outdoor pollutant concentrations (Table 2).

Table 2: Monthly indoor / outdoor concentration ratios in the BLH. R^2 represents the correlation coefficient of the linear regression between indoor and outdoor concentrations. n.r.: not relevant

	July'09	Aug'09	Sept'09	Oct'09	Nov'09	Dec'09	Jan'10	Feb'10	Mar'10	R^2
I/O (NO_2)	0,22	0,23	0,21	0,21	0,22	0,27	0,33	0,30	0,28	0,35
I/O (SO_2)	0,58	0,59		0,34	0,74	0,55	0,25	0,35	0,48	0,56
I/O (O_3)	0,10	0,11	0,13	0,22	0,28	0,30	0,27	0,18	0,21	0,53
I/O (NH_3)	2,19	2,29	0,99	1,31	0,75	0,69	0,82	0,72	0,64	0,10
I/O (NHO_3)	0,03	0,02	0,03	0,10	0,31	0,52	0,04	0,15	0,07	n.r.
I/O (Acetic acid)	17,45		18,99	14,65	16,74	13,94	6,48	5,54	17,29	n.r.
I/O (Formic acid)	7,61		14,08	7,62	25,47	9,02	3,46	2,23	6,05	n.r.

3.2.1 Outdoor generated

Concentrations of NO_2, O_3 and SO_2 obtained during the nine months measurement campaign are shown in Figure 7. The indoor and outdoor concentration of NO_2 varies between 9 and 17 µg m^{-3} and between 40 and 60 µg m^{-3}, respectively. The concentration of ozone measured inside the BLH varies between 2 and 5 µg m^{-3}, whereas outdoors concentrations vary between 8 and 43 µg m^{-3} (Figure 7). The concentration levels of SO_2 obtained indoors and outdoors vary between 1.71 and 4.75 µg m^{-3}, and 3 and 19 µg m^{-3}, respectively (Figure 7). NO_2, SO_2 and ozone are typical outdoor generated pollutants which infiltrate into the indoor environment. Their indoor / outdoor ratios below 1 confirm their outdoor origin and absence of indoor sources (e.g. cooking, smoking; Table 2).

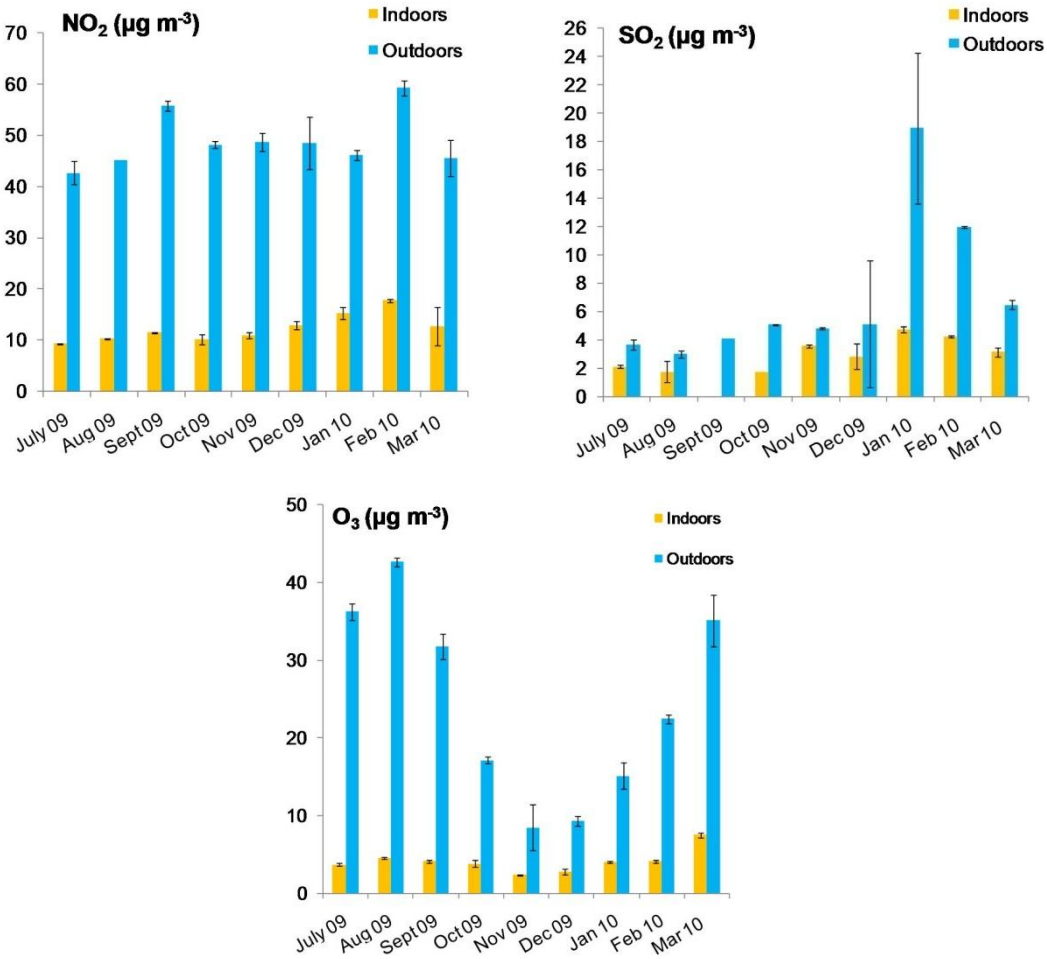

Figure 7: NO_2, SO_2 and Ozone concentrations monthly measured inside and outside the Baroque Library Hall.

The measurements performed inside the BLH show temporal variations in the infiltration behaviour of outdoor pollutants. The I/O ratios of NO_2 and O_3 slightly increase from summer to winter (Table 2; Figure 8), which indicates possible seasonal variations of the behaviour of the building envelope, such as higher infiltration of outdoor air in winter than in summer.

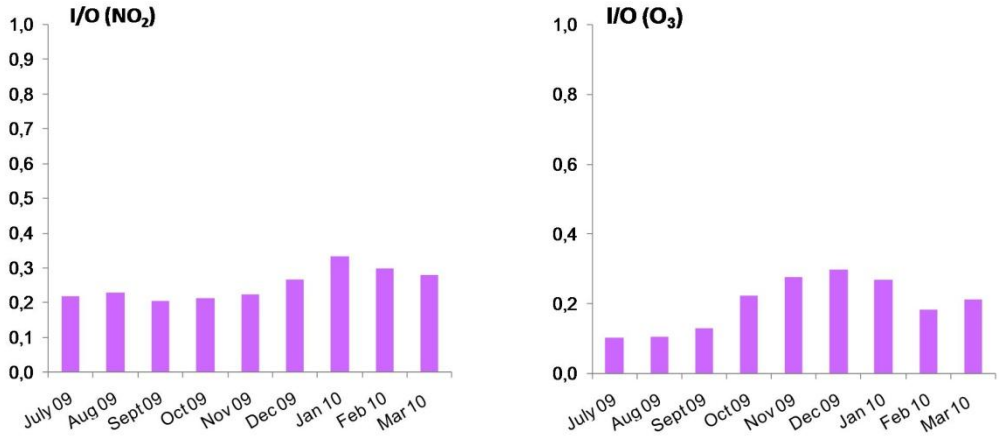

Figure 8: Indoor - outdoor ratios of NO_2 and Ozone concentrations.

3.2.2 Indoor generated

The concentration of organic compounds (acetic and formic acids) inside the BLH measured during the nine months measurement campaign reaches values up to 420 µg m^{-3} and 100 µg m^{-3} of acetic and formic acids, respectively, and its relationship with the outdoor concentration is typical of indoor generated pollutants (Figure 9). The I/O ratios of acetic and formic acids reach values up to 19 and 26 (Table 2), respectively. The indoor concentrations of acetic and formic acids decrease continuously from summer (July 2009) to winter (2010) and finally spring (March 2010). Differences in the regimen of ventilation of the building may explain these differences, such as higher ventilation and therefore higher dilution of indoor generated pollutants in winter than in summer. These results support the variation observed for outdoor generated pollutants in the previous chapter, which ratio indicates higher infiltration during winter.

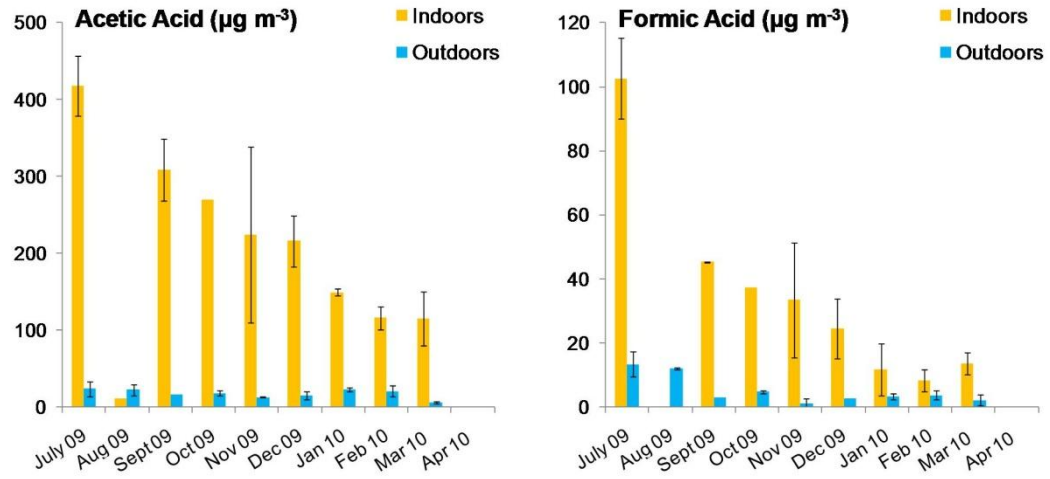

Figure 9: Acetic and formic acid concentrations monthly measured inside and outside the Baroque Library Hall.

Volatile organic compounds (i.e. C5 – C20 compouns) were measured in July 2009 by Tenax absorption tubes and subsequently analysed by gas-chromatography mass-spectrometry (GC-MS). Figure 10 shows the concentration of the most abundant compounds measured in the BLH. The total concentration of identified volatile organic compounds (TVOCs) was approximately 510 µg m^{-3}, which is slightly above the recommended values (i.e. 200-500 µg m^{-3}) for indoor environments by most standards and guidelines (http://www.aerias.org/DesktopModules/ArticleDetail.aspx?articleId=131). Some of the VOC measured in the BLH are associated with wood materials (e.g. α-pinene and toluene), insecticides (e.g. naphthalene) or it has been associated with the degradation of books and in particular cellulose degradation (e.g. furfural; Łojewski et al., 2010; Lattuati-Derieux et al., 2006).

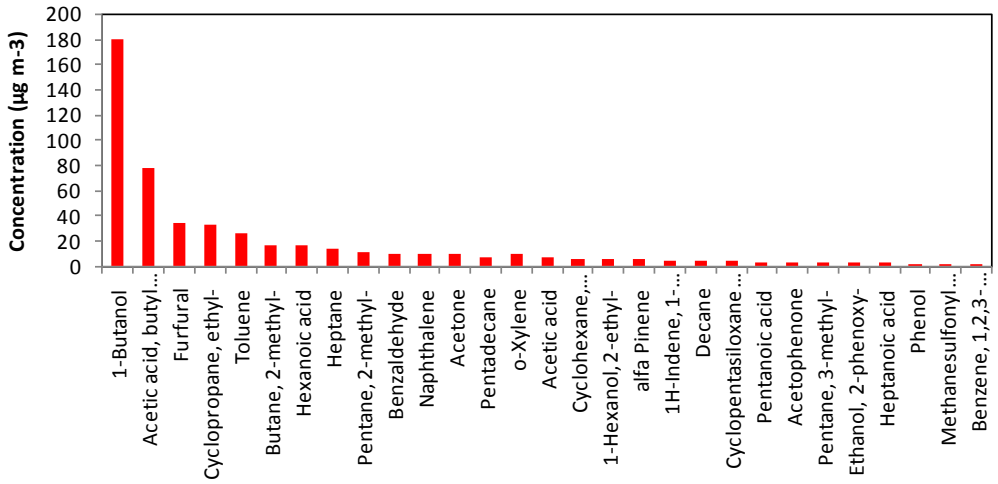

Figure 10: Concentration of volatile organic compounds measured in the BLH in July 2010.

3.2.3 Pollutants from particle infiltration

One of the most interesting relationships of indoor and outdoor air pollutant was observed for ammonia (NH_3). Indoor NH_3 concentration is higher than outdoor from July to October, whereas the opposite pattern is observed from November to March (Figure 11), although indoor and outdoor concentrations are comparable. Several studies have reported higher indoor than outdoor NH_3 concentration (Li and Harrison, 1990; Fisher et al., 2003) but to date and to our knowledge no studies show the opposite pattern.

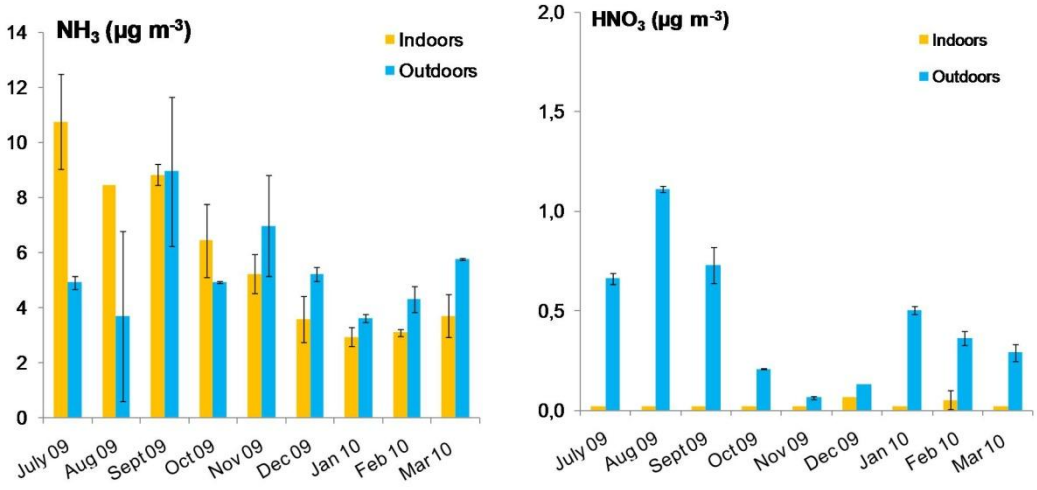

Figure 11: NH_3 and NHO_3 concentrations monthly measured inside and outside the Baroque Library Hall.

The I/O ratio varies from 0.64 to 2.29 (Figure 12) indicating possible indoor sources of gaseous NH_3. Ammonia is mainly associated with fertilizers, cleaning products, pets, human metabolic activities and smoking. Since these indoor sources were absent in the BLH, measured indoor concentration of NH_3 could

only be explained by another source. Indoor transformation of outdoor particles has been proposed as a possible indoor source for ammonia gas in several studies (Li and Harrison, 1990; Fisher et al., 2003).

The equilibrium between gaseous ammonia and nitric acid, and ammonium nitrate aerosol is defined by:

Equation 3

As ammonium nitrate moves from a cooler outdoor to warmer indoor environment, the equilibrium shifts towards the gas phase. Indoor concentrations of nitric acid are very low or below the detection limit (Figure 11), as obtained in other indoor studies (Suh et al., 1994; Fisher et al., 2003). A substantial loss of HNO_3 may explain the low or even negligible concentrations measured indoors, as HNO_3 may have been removed through dry deposition onto the indoor surfaces. This phenomenon may be considered to be a main concern for the preservation of books and manuscripts in the Baroque Library Hall as nitric acid is a strong acid which has harmful effects on cellulosic material (Tétreault, 2003).

The I/O ratio of ammonia varies along time supporting previous conclusions concerning seasonal variations. The I/O ratio of ammonia concentration decrease from summer to winter (Figure 11). Higher infiltration of ammonium nitrate in winter than in summer may explain the higher concentration of NH3 and higher I/O ratio observed in the BLH.

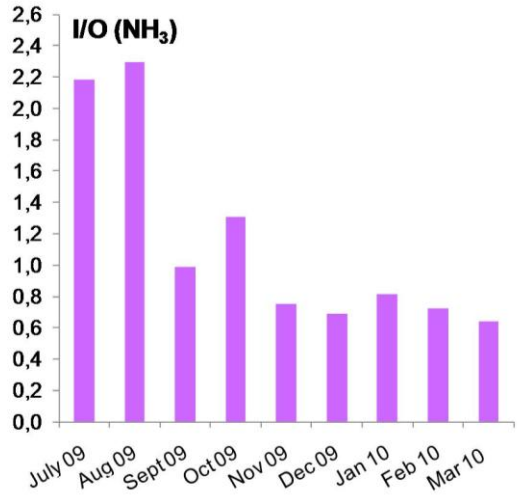

Figure 12: Indoor to Outdoor ratio of NH_3 concentration.

The indoor concentration of gaseous NH_3 and HNO_3 was interpreted by comparing the product of their concentrations to the equilibrium product expected from the gas-particle partitioning equilibrium constant. If the relative humidity (RH) is below the relative humidity of deliquescence (RHD) at any temperature, the partitioning constant Kp is calculated according to Finlayson-Pitts and Pitts (1986) as:

Equation 4

where unit of Kp is $(ppb)^2$ and T is temperature in Kelvin. The RHD is calculated as (Hammer and Wu, 1972):

—— Equation 5

If the concentration product of ammonia and nitric acid (ppb^2) is lower than the partitioning constant (Kp), then ammonia and nitric acids are the dominant species and the aerosol is not present or is being lost. Equal concentration product to Kp means that the gases are in equilibrium with ammonium nitrate aerosol, whereas concentration products greater than Kp would be obtained if the aerosol (i.e. ammonium nitrate) is forming. The present study indicates that the product of indoor ammonia and nitric acid concentration is lower than predicted by the gas-particle equilibrium at temperatures measured inside the BLH (Figure 13). This indicates that ammonia and nitric acids dominate and that the aerosol is not present or being lost indoors. In addition, ammonium nitrate was detected outdoors (Ondrackova et al., 2010) where the concentration products of gaseous ammonia and nitric acid show much closer conformity to theoretical equilibrium predictions at the measured outdoor temperatures (Figure 13). Outdoors gaseous ammonium and nitric acids are closer to equilibrium with ammonium nitrate aerosol and it seems that during the coldest months (i.e. December, January and February) the equilibrium slightly shifts to the formation of the aerosol (Figure 13).

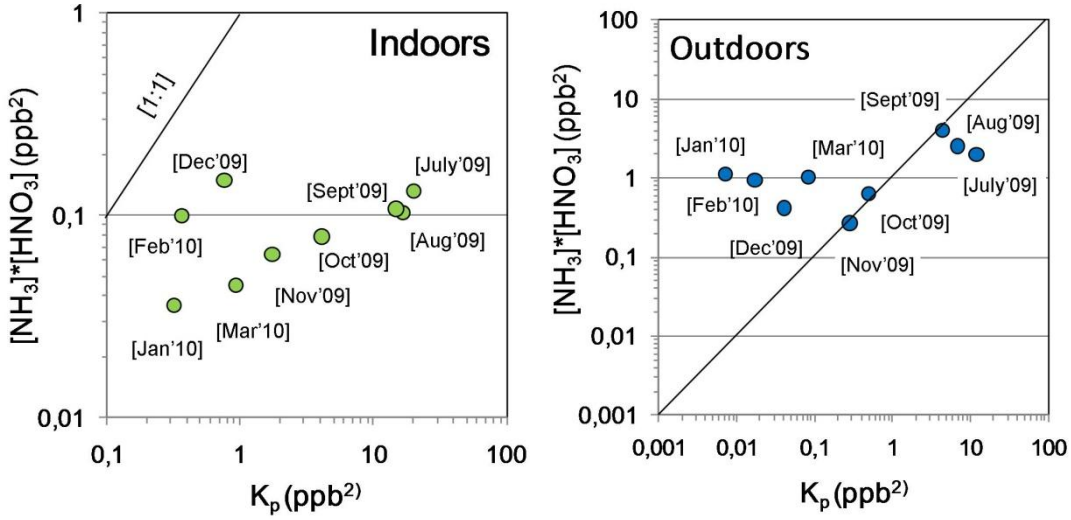

Figure 13: $[NH_3][NHO_3]$ indoor and outdoor concentration products vs. the predicted equilibrium constant at indoor and outdoor temperatures.

3.3 Seasonal variations of indoor air pollution

The results obtained during the nine-months measurement campaign indicated seasonal variations in gaseous pollutant concentration:

- The I/O ratios of NO_2 and O_3 increased from summer to winter indicating higher infiltration during winter than in summer (Figure 8);

- Organic acids (i.e. acetic and formic acids) concentrations decreased from summer to winter, indicating higher dilution processes during winter than in summer (Figure 9);
- Higher I/O ratio of ammonia was observed during winter than in summer (Figure 12). Higher infiltration of ammonium nitrate during winter would explain the observed I/O ration.

NO_2 and organic acids (acetic and formic acids) were measured in summer (July 2009) and winter (January 2010) in four additional indoor locations in order to evaluate possible seasonal variations. Indoor NO_2 concentration is much higher in winter than in summer, whereas the concentration of organic acids shows an inverse relationship (Figure 14). This results support previous hypothesis and the differences may be explained by higher air exchange rate (AER) during winter. Previous studies performed in naturally ventilated buildings have reported the opposite patterns, with a higher AER during spring / summer (Yocum, et al., 1971; Long et al. 2000). Activities such as the opening of windows and doors for increasing ventilation during warmer weather conditions explain a higher AER during summer. However, these activities do not take place in the BLH, which may explain the present results.

The BLH is a naturally ventilated building and so the air exchange rate is driven by the indoor-outdoor temperature differences. The intake of outdoor air depends on internal temperature variations (e.g. "stack effect") and on the pressure gradients imposed by wind flow (ASHRAE, 2005).

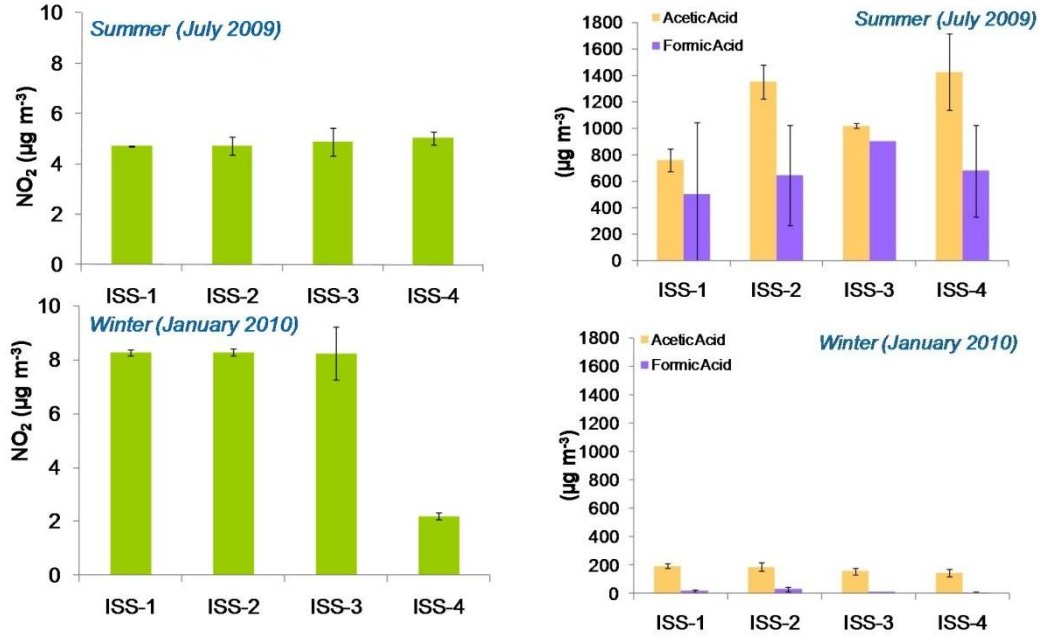

Figure 14: NO_2, acetic and formic acids concentrations measured in four indoor locations in summer (July 2009) and in winter (January 2010).

The temperature inside the BLH decreases gradually from summer to winter (Figure 15). The evaluation of indoor-outdoor temperature differences shows maximum values in winter (Figure 15), which causes pressure differences

between the inside and outside, and as a result outdoor air is drawn in, resulting in a higher flow rate according to the following expression (Walker, 2010):

Equation 6

where Q is the volume of ventilation rate (m^3/s), C represents a discharge coefficient, A is the flow area of inlet opening which equals the area of the outlet opening, g is acceleration due to gravity, h is the height or distance between inlet and outlet (m), T_I is the average temperature indoors (K) and T_O is the average temperature outdoors.

Winter marks a higher air exchange rate (AER) than summer in the BLH, allowing higher infiltration of outdoor pollutants (i.e. NO_2, ozone and SO_2) and higher dilution of indoor pollutants (i.e. acetic and formic acids).

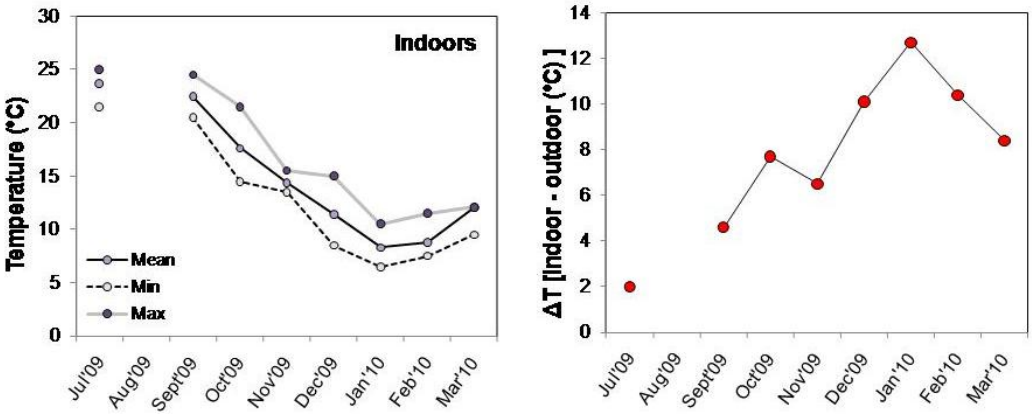

Figure 15: Monthly average temperature values inside the BLH (left) and indoor – outdoor temperature differences (right).

4 Evaluation of the indoor environment in BLH

The Baroque Hall of the National Library in Prague, apart from being a cultural heritage institution, is a long term storage location where books and manuscripts are collected, preserved and made available to the public. Therefore, air quality is a critical factor for the preservation of these objects.

The BLH may be classified as archive or library with natural ventilation, restriction of personnel access and reduced groups of visitors. The results obtained by EWO dosimeter indicate that the environment (i.e. synergistic effects of UV-light, T/RH, NO_2, O_3) may not be acceptable for the preservation of organic materials, and in this case, for paper-based material, as the results from the EWO dosimeter in the BLH were evaluated as acceptable for a purpose build museum (Figure 16).

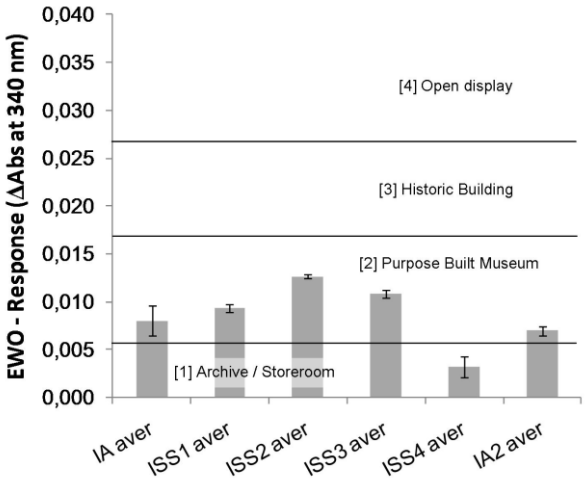

Figure 16: Evaluation of the photo-oxidant effects of the environment on organic materials (EWO-results). For locations see Figure 3.

The infiltration of ammonium nitrate into the indoor environment and a shift of the equilibrium to the gaseous phase, were proposed as mechanisms to explain the observed indoor concentration of ammonia. A consequence of this process is the lost of nitric acid from the air by deposition on surfaces. This deposition poses a high risk for the preservation of books and manuscripts, as nitric acid tends to remain absorbed on the surfaces (Febo and Perrino, 1991) and has adverse effects on paper-based materials (Tétreault, 2003).

According to ISO11799:2003, air in a repository or storage area should be kept free from air pollution; acidic and oxidizing gases and particles / dust. The effects of pollutants such as NO_2, O_3 and SO_2 on paper are well documented (Williams and Grosjean, 1990; Havermans, 1995; Johansson, 2000); and the main causes of paper deterioration are the breakage of glycoside linkages in cellulose by acid hydrolysis and deterioration by oxidation. The US National Bureau of Standard (NSB, 1983) suggests 4.75 µg m^{-3} of NO_2 (2.5 ppb) as a recommended limit value for exposure of paper based materials (Table 3). The concentration of NO_2 measured in the BLH is equal or above this value in all sampling locations (i.e. NO_2: 5 – 18 µg m^{-3}). Ozone is however below the exposure levels for paper based

material recommended by both NSB (1983; 26 µg m-3) and ISO11799:2003 (2003; 10-20 µg m^{-3}).

Table 3: Maximum limits of tolerance for air pollutants for archive and library materials (ISO11799/2003), recommended limit values for exposure of paper based materials by US National Bureau of Standard (NBS, 1983) and recommended values for museums, libraries and archives (ASHRAE, 2003).

Units: µgm^{-3}	ISO11799/2003	NBS	ASHRAE 2003 (µg m^{-3} . 1 yr)
SO_2	13 to 26	1	10
NO_2	9.5 to 19 (NOx)	4.75	10
O_3	10 to 20	26	10
Acetic Acid	<10		100
Formaldehyde	<4.8		
Particles	50		

Similarly to NO_2, the concentration of SO_2 measured inside the BLH is above (i.e. SO_2: 1.7 to ≈ 5 µg m^{-3}) exposure levels recommended for paper based material by US National Bureau of Standard (Table 3; < 1 µg m^{-3}) and for leather book bindings recommended by Larsen (1996; 0.26 µg m^{-3}). Outdoor generated pollutants infiltrate into the BLH and the concentrations of harmful pollutants such as NO_2 and SO_2 reach values which may pose a risk for the exposed books and manuscripts.

Indoor generated pollutants such as acetic acid were measured to be present at exceptionally high concentration in the BLH. Acetic acid can cause significant reduction in the degree of polymerisation of cellulose in paper (Dupond and Tétreault, 2000), and therefore its presence at high concentration inside libraries and archives is a concern. According to ISO11799:2003 (Table 3), the maximum limit of tolerance for acetic acid is 10 µg m^{-3} (Table 3; < 4 ppb). This value is in the lower range of typical outdoor background concentrations and higher concentrations are usually observed indoors, so it should be carefully considered. According to Tétreault (2003) and ASHRAE (2003), and due to generally high "no observed adverse effect level" (NOAEL) for objects, concentrations below 100 µg m^{-3} of acetic acids are not mandatory. In our study, concentrations of acetic acid were always above 100 µg m^{-3} and in summer the concentrations even reached values more than 10 times higher (e.g. 1 400 – 1 600 µg m^{-3}), similar to the values measured inside enclosures for art objects (Tétreault, 2003; López-Aparicio et al., 2010b). Therefore, the acetic acid may be a risk for the preservation of books and manuscript in the BLH.

The results obtained by EWO dosimeter and gaseous pollutants (NOx and SO_2) have been compared with results obtained in a previous study performed by SVOUM Ltd (Figure 17). The results of the EWO dosimeter exposed in 2008 in the BLH were evaluated as acceptable for a "Historic Building" (level 3). The results obtained during the projects were evaluated as acceptable for "Purposed Build Museum" (Level 2; Figure 16). This difference indicates that the environment has improved since 2008 concerning the photo-oxidant effects.

The NOx measurements included both NO_2 and NO, therefore the comparison with our measurements is not feasible. As an indication, the outdoor NOx concentration measured in July 2007 in three different locations varies between 45 and 58 µg m^{-3} (Figure 17). Similarly, the outdoor NO_2 concentrations measured in our study between July 2009 and March 2010 vary between 42 and 60 µg m^{-3}. This similitude between NOx concentration in July 2007 and NO_2 concentraions in 2009 (July-December) and 2010 (January-March) may indicate that the air quality around the Clementinum building has not improved.

Likewise indoor concentrations of NOx, NO_2 and SO_2 in 2007 (July), and 2009/2010 show similar values (Figure 7 and Figure 17) which may indicate that the indoor air quality has been very similar in the last three years.

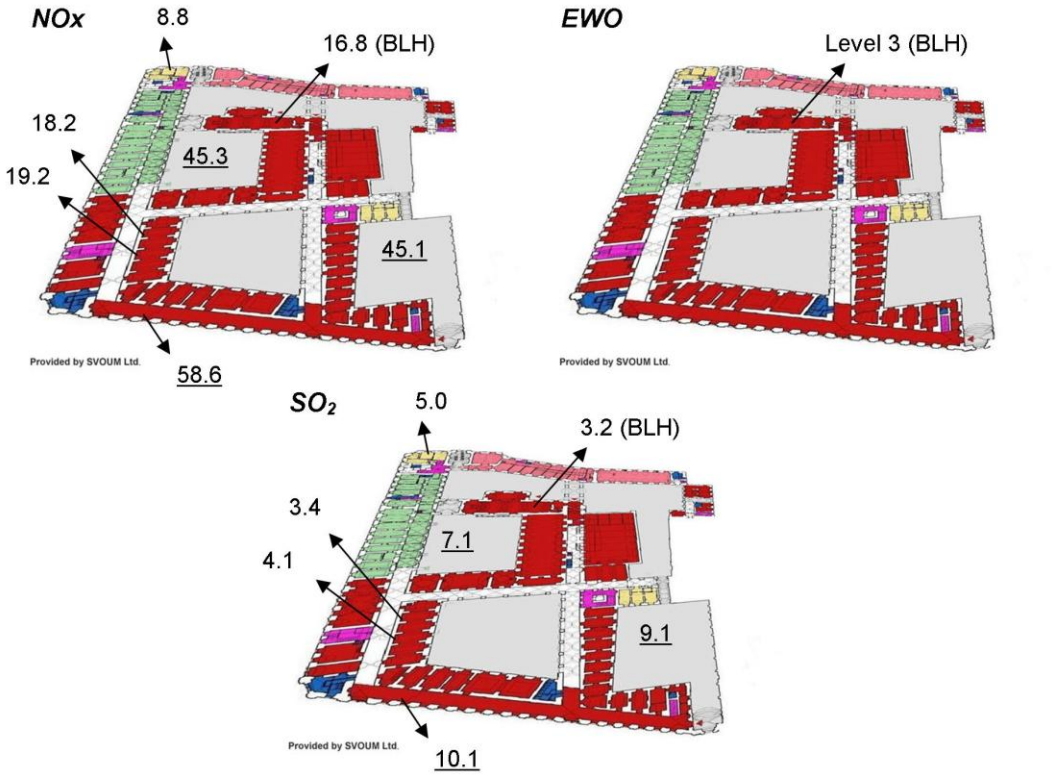

Figure 17: Results of the study performed by SVOUM Ltd in the Clementinum building and in particular in the Baroque Library Hall (BLH) in 2007 (NOx and SO_2) and in 2008 (EWO-dosimeter). Underlined numbers refer to outdoors concentration (Results courtesy of SVOUM Ltd).

6 Dissemination Activities

a. Poster presentation in the IAQ2010

The preliminary results of the project were presented as poster (Appendix B) in the 9th Indoor Air Quality Meeting which took place in Chalon-sur-Saône (France), 21th-23rd April, 2010.

b. Presentation in COSTD42 Final Conference

The main results of the project were presented at the COST Action D42 Final conference, "Impact of the Indoor Environment on the Preservation of our Moveable Heritage" which took place on 8-9 November 2010 in Trinity College Dublin (Ireland). The presentation and the extended abstract have been included in the Appendix C and D, respectively of this report.

c. Article in peer-review journal

An article synthesizing the main results of the project, titled "Relationship of Indoor and Outdoor Air Pollutants in a Naturally Ventilated Historical Building Envelope" and with S. López-Aparicio, J. Smolík, L. Mašková, M. Součková, T. Grøntoft, L. Ondráčková, J. Stankiewicz as co-authors is currently submitted in the journal "Building and Environment".

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Appendix A

Results Database

Table A-1: Results from the passive diffusion samplers during nine month measurements campaign.

		July 09	Aug 09	Sept 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10
NO_2 (μgm^{-3})										
Indoors	NO2 (I)	9,40	10,25	11,40	9,48	10,44	13,45	16,14	17,90	10,00
Indoors	NO2 (II)	9,18	10,41	11,57	10,94	11,27	12,40	14,52	17,58	15,37
Indoors	Average	9,29	10,33	11,48	10,21	10,86	12,92	15,33	17,74	12,69
	StdDev	0,15	0,12	0,12	1,03	0,59	0,74	1,14	0,22	3,80
Outdoors	NO2 (I)	41,15	45,27	55,07	48,63	47,54	44,94	45,40	60,37	48,05
Outdoors	NO2 (II)	44,28	45,27	56,52	47,71	49,98	52,13	46,86	58,25	42,99
Outdoors	Average	42,72	45,27	55,80	48,17	48,76	48,54	46,13	59,31	45,52
	StdDev	2,21	0,00	1,02	0,65	1,73	5,08	1,03	1,49	3,58
SO_2 (μgm^{-3})										
Indoors	SO2 (I)	2,19	1,26	0,00	1,70	3,65	2,19	4,61	4,16	2,90
Indoors	SO2 (II)	2,03	2,27	0,00	1,72	3,49	3,46	4,89	4,27	3,35
Indoors	Average	2,11	1,77	0,00	1,71	3,57	2,82	4,75	4,21	3,13
	StdDev	0,12	0,72	0,00	0,01	0,11	0,90	0,20	0,08	0,32
Outdoors	SO2 (I)	3,91	2,82	4,07	5,08	4,85	1,96	15,18	11,91	6,26
Outdoors	SO2 (II)	3,39	3,18	4,07	5,04	4,75	8,29	22,71	12,02	6,69
Outdoors	Average	3,65	3,00	4,07	5,06	4,80	5,13	18,95	11,96	6,47
	StdDev	0,37	0,26	0,00	0,03	0,07	4,47	5,32	0,08	0,30
O_3 (μgm^{-3})										
Indoors	O3 (I)	3,56	4,63	4,22	4,14	2,34	3,04	4,17	4,02	7,70
Indoors	O3 (II)	3,85	4,40	3,99	3,50	2,37	2,51	3,93	4,26	7,31
Indoors	Average	3,70	4,51	4,11	3,82	2,35	2,78	4,05	4,14	7,50
	StdDev	0,21	0,16	0,16	0,46	0,02	0,37	0,17	0,17	0,27
Outdoors	O3 (I)	37,00	42,27	30,64	16,80	10,54	9,78	16,29	22,85	37,48
Outdoors	O3 (II)	35,46	43,02	32,90	17,43	6,41	8,90	13,92	22,07	32,77
Outdoors	Average	36,23	42,64	31,77	17,11	8,47	9,34	15,11	22,46	35,12
	StdDev	1,09	0,53	1,60	0,45	2,92	0,62	1,68	0,55	3,33
NH_3 (μgm^{-3})										
Indoors	NH3 (I)	9,53		8,57	7,37	4,72	4,16	2,70	3,20	4,26
Indoors	NH3 (II)	11,97	8,45	9,10	5,50	5,75	3,00	3,19	3,02	3,14
Indoors	Average	10,75	8,45	8,83	6,44	5,23	3,58	2,94	3,11	3,70
	StdDev	1,72		0,37	1,32	0,72	0,82	0,34	0,13	0,79
Outdoors	NH3 (I)	5,08	5,87	10,87	4,91	8,27	5,39	3,71	3,97	5,75
Outdoors	NH3 (II)	4,75	1,50	7,04	4,94	5,67	5,03	3,50	4,63	5,80
Outdoors	Average	4,92	3,69	8,95	4,93	6,97	5,21	3,61	4,30	5,77
	StdDev	0,23	3,09	2,71	0,02	1,84	0,26	0,15	0,47	0,04
NHO_3 (μgm^{-3})										
Indoors	HNO3 (I)	0,02	0,02	0,02	0,02	0,02	0,07	0,02	0,02	0,02
Indoors	HNO3 (II)	0,02	0,02	0,02	0,02	0,02	0,07	0,02	0,09	0,02
Indoors	Average	0,02	0,02	0,02	0,02	0,02	0,07	0,02	0,05	0,02
	StdDev	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,05	0,00
Outdoors	HNO3 (I)	0,64	1,10	0,80	0,21	0,06	0,13	0,52	0,34	0,26
Outdoors	HNO3 (II)	0,68	1,12	0,67	0,21	0,07	0,13	0,49	0,39	0,32
Outdoors	Average	0,66	1,11	0,73	0,21	0,06	0,13	0,50	0,36	0,29
	StdDev	0,03	0,01	0,09	0,00	0,01	0,00	0,02	0,04	0,04

(Continued)

		July 09	Aug 09	Sept 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10
Acetic Acid (µgm^{-3})										
Indoors	AcAc (I)	445,19	11,43	280,06	270,25	305,48	192,94	153,13	126,91	140,72
Indoors	AcAc (II)	390,95		337,81		143,51	239,47	146,48	105,52	91,07
Indoors	Average	418,07	11,43	308,93	270,25	224,49	216,21	149,80	116,21	115,90
	StdDev	38,35		40,84		114,53	32,90	4,70	15,12	35,11
Outdoors	AcAc (I)	31,19	27,42	16,27	20,74	14,07	11,55	24,66	25,95	7,57
Outdoors	AcAc (II)	16,73	18,05		16,15	12,74	19,47	21,56	15,97	5,84
Outdoors	Average	23,96	22,73	16,27	18,44	13,41	15,51	23,11	20,96	6,70
	StdDev	10,22	6,62		3,25	0,94	5,60	2,19	7,06	1,22
Formic Acid (µgm^{-3})										
Indoors	ForAc (I)	111,49	0,00	45,49	37,38	46,26	18,10	17,48	5,89	11,19
Indoors	ForAc (II)	93,60		45,19		20,87	31,11	6,06	10,86	16,14
Indoors	Average	102,54	0,00	45,34	37,38	33,57	24,60	11,77	8,38	13,66
	StdDev	12,65		0,21		17,95	9,20	8,07	3,51	3,50
Outdoors	ForAc (I)	16,22	11,86	3,22	5,22	0,38	2,75	4,07	4,74	3,44
Outdoors	ForAc (II)	10,71	12,38		4,60	2,26	2,71	2,74	2,77	1,08
Outdoors	Average	13,47	12,12	3,22	4,91	1,32	2,73	3,40	3,76	2,26
	StdDev	3,90	0,37		0,44	1,33	0,03	0,94	1,39	1,67

Table A-2: Results from the passive diffusion samplers in the two-seasonal measurement campaign

(µg m$^{-3)}$	July 09	Jan 10	July 09	Jan 10	July 09	Jan 10
Location	***NO_2***	***NO_2***	***AcAc***	***AcAc***	***ForAc***	***ForAc***
ISS-1 (I)	4,71	8,17	822,15	204,39	121,58	10,38
ISS-1 (II)	4,70	8,34	700,19	182,31	884,73	23,21
ISS-1 aver	4,71	8,26	761,17	193,35	503,15	16,79
st.dev	0,01	0,12	86,24	15,61	539,63	9,07
ISS-2 (I)	4,97	8,36	1440,03	209,15	376,58	43,42
ISS-2 (II)	4,45	8,20	1261,82	167,36	912,08	20,45
ISS-2	4,71	8,28	1350,93	188,25	644,33	31,94
st.dev	0,36	0,12	126,01	29,55	378,65	16,24
ISS-3 (I)	4,50	7,55	1005,75	140,09	898,77	10,08
ISS-3 (II)	5,28	8,94	1029,20	173,36	900,22	12,21
ISS-3	4,89	8,25	1017,48	156,73	899,50	11,14
st.dev	0,56	0,98	16,58	23,52	1,03	1,51
ISS-4 (I)	5,22	2,30	1218,27	126,07	923,73	3,85
ISS-4 (II)	4,84	2,10	1628,42	163,94	429,62	12,71
ISS-4	5,03	2,20	1423,35	145,01	676,68	8,28
st.dev	0,27	0,14	290,02	26,78	349,38	6,26

Table A-3: Volatile organic compounds (VOCs) measured in the BLH

Baroque Library Hall _ July 09	µg/m3
1-Butanol	180,29
Acetic acid, butyl ester	78,26
Furfural	33,53
Cyclopropane, ethyl-	33,41
Toluene	25,98
Butane, 2-methyl-	16,18
Hexanoic acid	15,84
Heptane	14,08
Pentane, 2-methyl-	11,29
Benzaldehyde	9,95
Naphthalene	9,62
Acetone	9,38
Pentadecane	7,18
o-Xylene	9,80
Acetic acid	6,48
Cyclohexane, methyl-	6,04
1-Hexanol, 2-ethyl-	5,54
alfa Pinene	4,87
1H-Indene, 1-ethylidene-	3,94
Decane	3,87
Cyclopentasiloxane, decamethyl-	3,51
Pentanoic acid	3,37
Acetophenone	3,31
Pentane, 3-methyl-	2,85
Ethanol, 2-phenoxy-	2,77
Heptanoic acid	2,43
Phenol	2,05
Methanesulfonyl chloride	2,04
Benzene, 1,2,3-trimethyl-	1,85

Table A-4: Results obtained with the Early Warning dosimeter for Organic materials (EWO)

Location	Exposure	RH%	EWO-response	Level
IA	July-Sept	55	0,0069	
IA	July-Sept	55	0,0092	
IA (Jul-Sep)		55	0,0080	**2**
IA stdev			0,0016	
ISS1	July-Sept	55	0,0097	
ISS1	July-Sept	55	0,0090	
ISS1 (S)		55	0,0093	**2**
ISS1 stdev			0,0005	
ISS2	July-Sept	55	0,0125	
ISS2	July-Sept	55	0,0128	
ISS2 (S)		55	0,0127	**2**
ISS2 stdev			0,0002	
ISS3	July-Sept	55	0,0106	
ISS3	July-Sept	55	0,0111	
ISS3 (S)		55	0,0108	**2**
ISS3 stdev			0,0004	
ISS4	July-Sept	55	0,0039	
ISS4	July-Sept	55	0,0024	
ISS4 (S)		55	0,0032	**1**
ISS4 stdev			0,0011	
IA2	Oct-Dec	55	0,0067	
IA2	Oct-Dec	55	0,0073	
IA2 (Oct-Dec)		55	0,0070	**2**
IA2 stdev			0,0005	
IA3	Jan-Mar	55	0,0000	
IA3	Jan-Mar	55	0,0000	
IA3 (Jan-Mar)		55	0,0000	**1**
IA3 stdev			0,0000	
ISS1 (2)	Jan-Mar	55	0,0023	
ISS1 (2)	Jan-Mar	55	0,0000	
ISS1 (W)		55	0,0006	
ISS1 (W) stdev			0,0023	
ISS2 (2)	Jan-Mar	55	0,0011	
ISS2 (2)	Jan-Mar	55	0,0007	
ISS2 (W)		55	0,0009	
ISS2 (W) stdev			0,0003	
ISS3 (2)	Jan-Mar	55	0,0005	
ISS3 (2)	Jan-Mar	55	0,0012	
ISS3 (W)		55	0,0009	
ISS3 (W) stdev			0,0005	
ISS4 (2)	Jan-Mar	55	0,0000	
ISS4 (2)	Jan-Mar	55	0,0000	
ISS4 (W)		55	0,0000	
ISS4 (W) stdev			0,0000	

Appendix B

Poster presented at the 9th Indoor Air Quality Meeting, Chalon-sur-Saône (France) 21-23 April 2010

Indoor Air Quality in the Baroque Hall of the National Library in Prague – Preliminary Results

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Introduction

The Baroque Hall of the National Library in Prague is our object of interest. To assess the indoor environment for the preservation of books and manuscripts, a measurement campaign was designed and is currently ongoing. The measurements are performed:

- Monthly during one year in two locations (indoors and outdoors; Figure 1) and;
- In four additional indoor locations for sampling in two different seasons (Figure 1).

The environmental assessment will be based on the results obtained by EWO-dosimetry and pollutant concentrations obtained by passive diffusion samplers (NO_2, O_3, SO_2, acetic and formic acids, HNO_3, NH_3).

Results

EWO-dosimetry indicates that the environment inside the Baroque Hall is acceptable for the preservation of organic materials in a "purposed built museum" (Figure 2).

The results show infiltration of outdoor generated pollutants (Figure 3) and high concentration of indoor generated pollutants (Figure 4). The concentrations of NO_2 and SO_2 are above the values proposed as standard for preservation of paper based archival material by NBS (1983; NO_2: 5 µg m^{-3}; SO_2: 1 µg m^{-3}), and above the values proposed for museums, libraries and archival collections by ASHRAE (2003; 1 year; NO_2: 10 µg m^{-3}; SO_2: 10 µg m^{-3}).

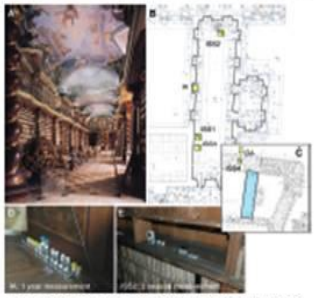

Figure 1: A: Baroque Hall of the National Library (Prague). B and C: Sampling locations; yellow square: locations of year measurement campaign; yellow/green square: locations of two-seasonal measurement campaigns. Blue area in C: Baroque Hall. D and E: passive diffusion samplers and dosimeter.

Seasonal differences are observed (Figure 5). Indoor NO_2 concentration is much higher in winter than in summer, whereas the concentration of organic acids shows an inverse relationship. This difference may be explained by higher ventilation during winter than in summer.

High concentration of NH_3 is observed inside the Baroque Hall, whereas the indoor HNO_3 concentration is below the detection limit (Figure 6). The indoor concentration of NH_3 may be explained by infiltration of NH_4NO_3 aerosol, which possibly moves from outdoors to the warmer indoor environment and the equilibrium shifts toward the gas phase.

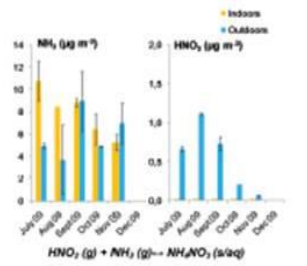

Figure 6: Indoor and outdoor concentrations of NH_3 and HNO_3 outside and inside the Baroque Hall.

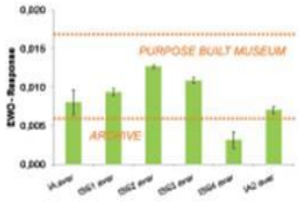

Figure 2: EWO dosimeter results obtained in the Baroque Hall.

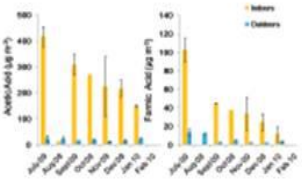

Figure 4: Acetic and formic acids inside and outside the Baroque Hall.

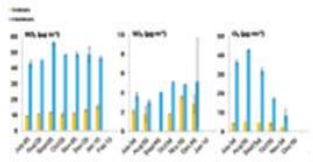

Figure 3: Concentration of NO_2, SO_2 and O_3 inside and outside the Baroque Hall.

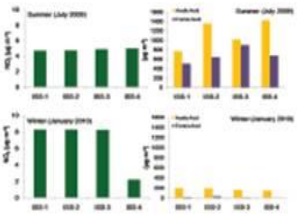

Figure 5: Seasonal differences in the concentrations of NO_2 and organic acids (acetic and formic acids) in the Baroque Hall.

Conclusions

- Concerning the protection of organic materials from photo-oxidant effects, the environment is "acceptable" for a "purpose built museum". However, the Baroque Hall of the National Library could be classified as an "Archive" in which case levels are not "acceptable".
- High concentration levels of NO_2 (> 10 µg m^{-3}) and SO_2 (>1 µg m^{-3}) were measured inside the Baroque Hall and may constitute a risk for the preservation of books and manuscripts.
- High concentration of NH_3 is measured indoors, whereas HNO_3 is below the detection limit. The source of NH_3 is uncertain but could be explained by infiltration of ammonium nitrate and shifting of the equilibrium to the gas phases. Possible loss of HNO_3 by surface deposition may explain the low concentration levels observed. If confirmed, surface deposition of HNO_3 may be a risk for the books and manuscripts.
- High concentrations of acetic and formic acids are observed in the Baroque Hall. Concentration levels similar to those reported inside enclosures (e.g. showcases) are observed on bookshelves during summer (i.e. acetic acid > 1000 µg m^{-3}).
- The preliminary results indicate seasonal variations. Higher infiltration during winter than in summer could explain the results obtained (i.e. NO_2 and organic acids). Further investigation in collaboration with the Baroque Hall is needed.

Acknowledgements

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Appendix C

Presentation at the COSTD42 Final Conference, Dublin (Ireland) 8-9 November 2010

Indoor and outdoor pollutants in a naturally ventilated historical building; the Baroque Hall of the National Library (Prague, Czech Republic)

Table of Content

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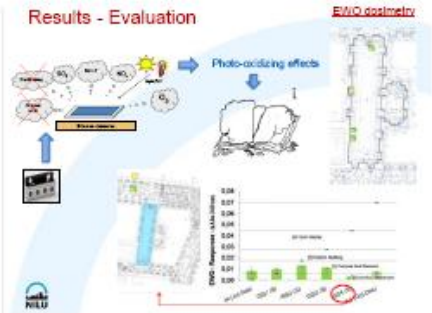
- Methodology
- Results - Evaluation
- Conclusions

Results - Evaluation

- Dosimetry – EWO dosimeter
- Gaseous Pollutants
  - Outdoor generated pollutants
  - Indoor generated pollutants
  - Gaseous pollutants from particle infiltration



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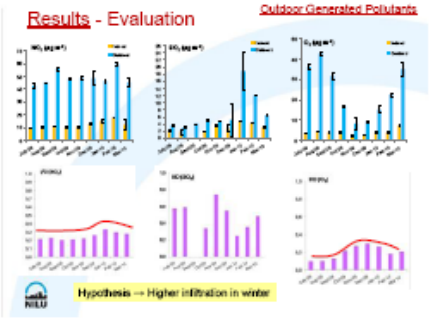
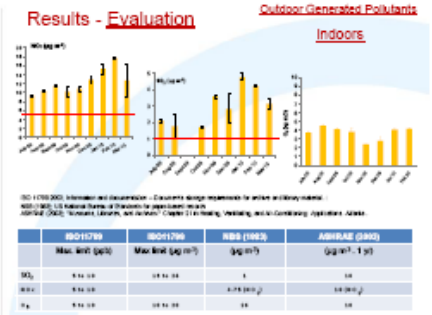
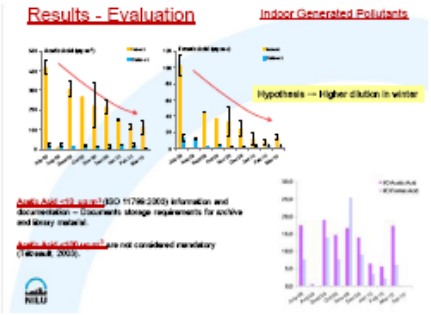
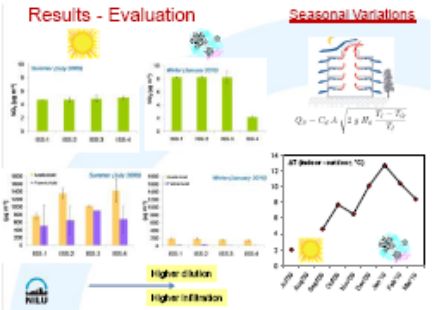
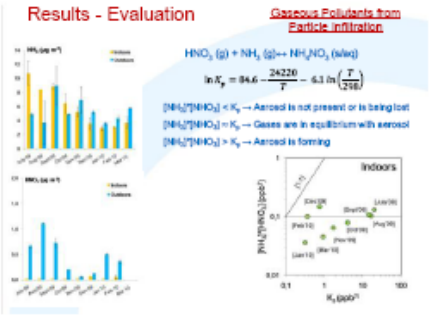
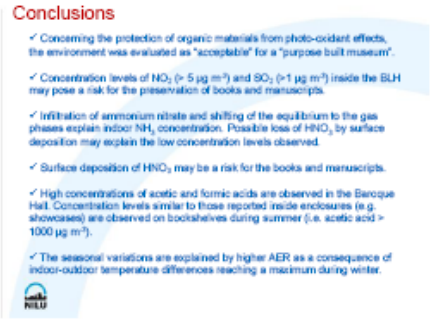

Results - Evaluation
Outdoor Generated Pollutants
Hypothesis → Higher infiltration in winter

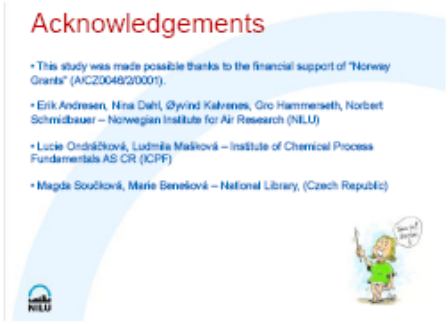

Results - Evaluation
Outdoor Generated Pollutants
Indoors


Results - Evaluation
Indoor Generated Pollutants
Hypothesis → Higher dilution in winter


Results - Evaluation
Seasonal Variations
Higher dilution
Higher infiltration


Results - Evaluation
Gaseous Pollutants from Particle Infiltration
Indoors


Conclusions
✓ Concerning the protection of organic materials from photo-oxidant effects, the environment was evaluated as "acceptable" for a "purpose built museum".
✓ Concentration levels of NO2 (> 5 µg m-3) and SO2 (>1 µg m-3) inside the BLH may pose a risk for the preservation of books and manuscripts.
✓ Infiltration of ammonium nitrate and shifting of the equilibrium to the gas phases explain indoor NH3 concentration. Possible loss of HNO3 by surface deposition may explain the low concentration levels observed.
✓ Surface deposition of HNO3 may be a risk for the books and manuscripts.
✓ High concentrations of acetic and formic acids are observed in the Baroque Hall. Concentration levels similar to those reported inside enclosures (e.g. showcases) are observed on bookshelves during summer (i.e. acetic acid > 1000 µg m-3).
✓ The seasonal variations are explained by higher AER as a consequence of indoor-outdoor temperature differences reaching a maximum during winter.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• Magda Součková, Marie Benešová – National Library, (Czech Republic)

Appendix D

Extended Abstract of the work presented at the COSTD42 Final Conference, Dublin (Ireland) 8-9 November 2010

Indoor Air Quality Assessment in the Baroque Hall of the National Library (Prague, Czech Republic)

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Summary: NO_2, O_3, SO_2, acetic and formic acids, HNO_3, NH_3 and VOC were measured inside and outside the Baroque Hall (BLH) during nine months. Additionally dosimetry was performed and NO_2 and organic acids were measured in two seasonal measurement campaigns in four indoor locations. Results show seasonal differences which correspond with different natural ventilation regimens. Pollutant sources were determined as indoors, outdoors or from infiltration of particles (i.e. ammonium nitrate) with a shift of the equilibrium to the gas phase (i.e. ammonia). The indoor pollutant concentrations were assessed to constitute some risk for the preservation of stored books and manuscripts.

Keywords: *indoor air quality, organic acids, library, paper, ammonia*

1 Introduction

The Baroque Library Hall (BLH) of the National Library in Prague (Czech Republic) is located in the Clementinum historical complex in the Vltava River Valley. The historical complex is placed in the city centre of Prague and is exposed to air pollution mainly from traffic emissions. According to the Atlas of the Prague Environment [1] the intensity of car traffic was about 24 200 cars on this main road adjacent to the library between 6 am and 22 pm during a working day. Due to the location of the historic building, one of the objectives of the study is to evaluate the influence of outdoor pollutants into the indoor environment.
The BLH was completed in 1726 and is situated in the centre of the Clementinum historical complex on the second floor. It is one of the finest interiors of the Clementinum and is 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 on original wooden shelves. Apart from the collection, the BLH is decorated with frescoes illustrating themes such as science and art. The historical building is naturally ventilated and the BLH in particular does not have a heater system.

2 Methodology

2.1 Measurement campaigns

The measurement campaigns were divided in two different types; 1) a nine months measurement campaign (July 2009 – March 2010); and 2) a two-seasonal campaign (i.e. summer and winter).
The main aim of the nine months measurement campaign was to perform a characterization of the indoor air pollution. Therefore a wide range of gaseous pollutants (i.e. NO_2, SO_2, acetic and formic acids, NH_3, O_3, and HNO_3) were measured indoors and outdoors on a monthly basis.
The two-seasonal measurement campaign was performed in July 2009 and January 2010 in four indoor locations, three inside the BLH and one in an adjacent room, in order to evaluate possible seasonal variations. NO_2 and organic acids (i.e. acetic and formic acids) were selected as indicators of outdoor and indoor generated pollutants, respectively. In addition, EWO-dosimetry was performed in both locations to assess the photo-oxidant effects of the environment on organic materials.

2.2 Analytical Procedure

Gaseous pollutants were measured by passive diffusion gas samplers [2] from the Norwegian Institute for Air Research (NILU; i.e. NO_2, SO_2, acetic and formic acids and NH_3) and from the Swedish Environmental Institute (IVL; i.e. O_3 and HNO_3). Two parallel samplers for each compound were exposed in the selected sampling locations during one month and replaced after exposure with a new for the next month. Those demounted were sent back for analysis to the respective laboratories. The

EWO-dosimeters were exposed during three months. The analytical procedure for the analysis of passive samplers and the EWO dosimeter can be found in [3-4].

3 Results and Discussion

3.1 Dosimetry

The EWO-dosimeter results obtained in the BLH, representing photo-oxidant effects on organic materials, were evaluated to be acceptable for a "Purpose Built Museum" (Fig. 1), whereas the result obtained in an adjacent room (ISS4) was evaluated to be acceptable for an "Archive / Storeroom" (Fig. 1). The BLH may be classified as archive or library with natural ventilation, restriction of personnel access and reduced groups of visitors. Thus the results obtained by EWO dosimeter indicate that the environment (i.e. synergistic effects of UV-light, T/RH, NO_2, O_3) may not be acceptable for the preservation of organic materials, and in this case, for paper-based material.

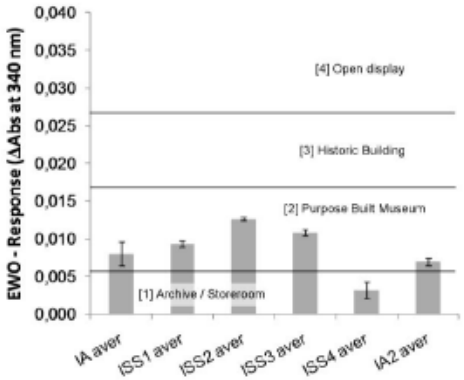

Fig. 1: EWO results obtained in the BLH.

3.2 Gaseous Pollutants

Pollutants from Outdoors Sources

NO_2, SO_2 and ozone are typical outdoor generated pollutants which infiltrate into the indoor environment. The indoor and outdoor concentrations of NO_2 and ozone measured in the BLH are shown in the Figure 2 (SO_2 showed similar pattern).

The effects of pollutants such as NO_2, O_3 and SO_2 on paper are well documented [5-6]; the main causes of paper deterioration are the breakage of glycoside linkages in cellulose by acid hydrolysis and deterioration by oxidation. The concentration of NO_2 measured in the BLH (Fig. 2) is equal or above recommended values for paper based materials (Table 1), whereas the concentration of ozone is below the recommended exposure levels for paper based material (Table 1). The indoors concentration of SO_2 (1.71 - 4.75 μg m^{-3}) is above exposure levels recommended for paper based material (Table 1) and for leather book bindings (0.26 μg m^{-3}; [9]). Outdoor generated pollutants infiltrate into the BLH and the concentrations of harmful pollutants such as NO_2 and SO_2 reach values which involve some risk for the exposed books and manuscripts.

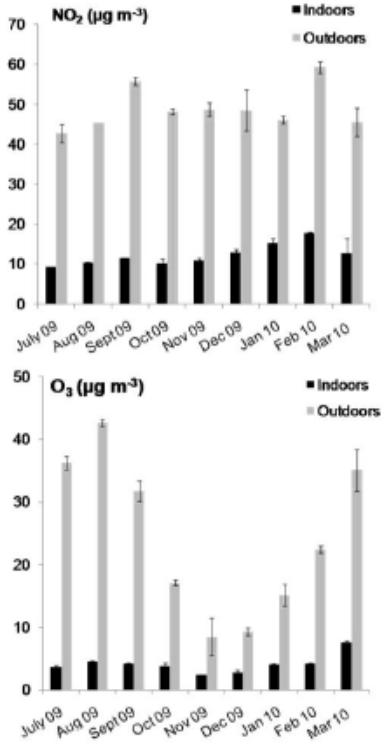

Fig. 2: Indoor and outdoor concentrations of NO_2 and O_3.

Pollutant from indoor sources

The indoors concentration of acetic and formic acids reach values up to 420 (Fig. 3) and 100, respectively. The indoor concentrations of organic acids decrease continuously from summer (July 2009) to winter (2010) and finally spring (March 2010).

Acetic acid can cause significant reduction in the degree of polymerisation of cellulose in paper [10], and therefore its presence at high concentration inside libraries and archives is a concern. The maximum limit of tolerance for acetic acid is 10 μg m^{-3} (Table 1; 4 ppb). However, and due to generally high "no observed adverse effect level" (NOAEL) for objects, concentrations below 100 μg m^{-3} are not considered mandatory [11]. In our study, concentrations of acetic acid were always above 100 μg m^{-3}.

Table 1. Maximum limits of tolerance for air pollutants for archive and library materials [8] and recommended limit values for exposure of paper based materials by US National Bureau of Standard [7].

Units: μgm^{-3}	ISO11799/2003 [8]	NBS [7]
SO_2	13 to 26	1
NO_2		4.75
O_3	10 to 20	26
Acetic Acid	<10	
Formaldehyde	<4.8	
Particles	50	

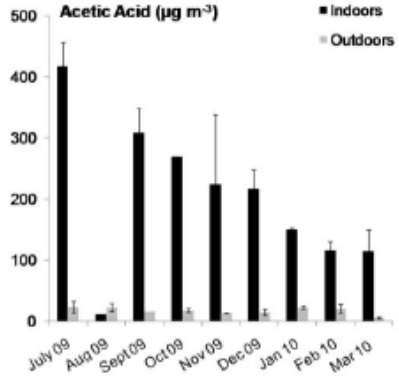

Fig. 3: Indoor and outdoor concentration of acetic acid.

Pollutants from particulate infiltration

Indoor NH_3 concentration is higher than outdoor from July to October (Fig. 4), whereas the opposite pattern is observed from November to March (Fig. 4), although indoor and outdoor concentrations are comparable. High indoor concentration of NH_3 in winter is explained by infiltration of ammonium nitrate from a cooler outdoor to warmer indoor environment, and a shift of the equilibrium towards the gas phase (NH_3 + HNO_3). Indoor concentrations of HNO_3 were very low or below the detection limit, which could be explained by a substantial loss by deposition on surfaces. This could pose a risk for the preservation of paper-based material in the BLH.

Seasonal variations

NO_2 and organic acids (acetic and formic acids) were measured in summer (July 2009) and winter (January 2010) in four additional indoor locations in order to evaluate possible seasonal variations (Fig. 5). Indoor NO_2 concentration was much higher in winter than in summer, whereas the concentration of organic acids showed the opposite relationship (Fig. 5). This difference may be explained by higher ventilation during winter than in summer. This hypothesis is supported by the results obtained during the continuous measurement campaign performed (July 2009 to March 2010), where an increase of the I/O ratio of NO_2 and O_3 was observed (Fig. 2) along with a decrease of the indoor concentration of organic acids (e.g. acetic acid, Fig. 3).

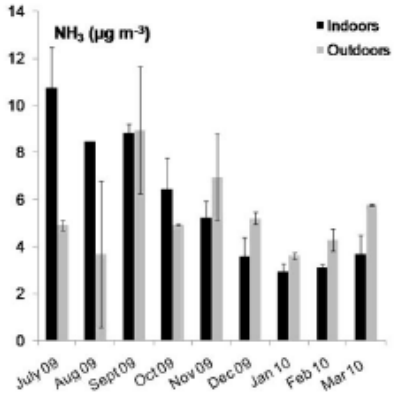

Fig. 4: Indoor and outdoor concentration of NH_3.

The BLH is naturally ventilated so the air exchange rate (AER) is driven by the indoor-outdoor temperature differences. The intake of outdoor air depends on internal temperature variations (e.g. "stack effect") and on the pressure gradients imposed by wind flow. The temperature inside the BLH decreases gradually from summer to winter, and indoor to outdoor temperature differences show maximum values in winter. This causes pressure differences between the inside and outside, and as a result outdoor air is drawn in.

Lower infiltration in summer involve higher concentration of acetic acid which reached values between 1 400 – 1 600 $\mu g\ m^{-3}$ (Fig. 5). These values are similar to those measured inside enclosures for art objects [7, 11]. Therefore, the acetic acid during summer may be a risk for the preservation of books and manuscript in the BLH.

4 Conclusions

Pollutant concentration measurements show seasonal differences; higher infiltration in winter than in summer. The seasonal variations are explained by higher AER as a consequence of indoor-outdoor temperature differences reaching a maximum during winter.

NO_2, O_3 and SO_2 show a clear outdoor origin, and could come from traffic emissions from the street adjacent to the historical complex where the BLH is located. Organic acids like acetic and formic acids show a clear indoor origin most probably from the building materials, such as the wooden shelves. The indoor concentration of gaseous ammonia is consistent with the

infiltration of ammonium nitrate from outdoors into the BLH and subsequent evaporation forming gaseous ammonia and nitric acid.

EWO-dosimetry indicates some risk for the preservation of organic materials due to photo-oxidant effects. Concentrations of NO_2, SO_2 and acetic acid are above the levels recommended in the available literature for the preservation of paper and leather bindings. In addition there is a risk that ozone and nitric acids deposit on the indoor surfaces, which constitutes a risk for the preservation of sensitive cultural heritage objects in the library.

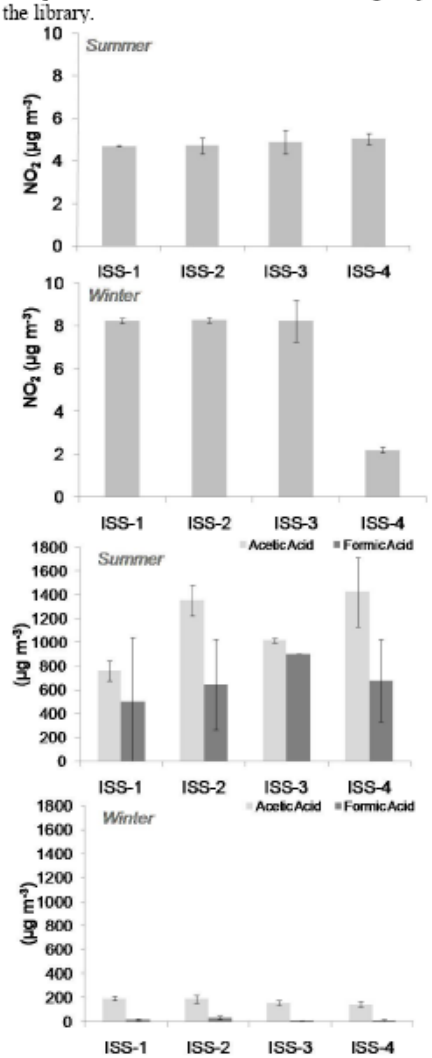

Fig. 5: Seasonal variations in the BLH.

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Environmental monitoring and evaluation of the indoor environment in the Baroque Library Hall of the National Library (Czech Republic) Indoor Air Quality Assessment of the Baroque Library Hall	Susana López-Aparicio NILU PROJECT NO. O-109067
AUTHOR(S) Susana López-Aparicio and Terje Grøntoft	CLASSIFICATION * A CONTRACT REF.

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ABSTRACT
Concentrations of NO_2, O_3, SO_2, acetic and formic acids, HNO_3 and NH_3 were measured inside and outside a historical building, the Baroque Library Hall (BLH) in the National Library in Prague (Czech Republic). The relationship between indoor and outdoor (I/O) concentration was investigated to assess the infiltration of outdoor generated pollutants. Outdoor and indoor pollution sources were determined and, infiltration of ammonium nitrate and a shift of the equilibrium to the gas phase were the reason for the high concentration of ammonia measured inside the BLH. A significant seasonal variation was observed and interpreted as a consequence of different infiltration regime associated with indoor-outdoor temperature differences, which in addition drives dilution processes of indoor generated pollutants. Based on the indoor air quality assessment performed in the BLH with regard to human and material exposure, there is reason for concern about material preservation and in particular paper at the BLH.

NORWEGIAN TITLE

Miljøovervåking og vurdering av innemiljø i den barokke bibliotekshallen i Nasjonalbiblioteket (Tsjekkia).

KEYWORDS		
Natural Ventilation	Indoor Air Quality	Archive

ABSTRACT (in Norwegian)
Konsentrasjonene av NO2, O3, SO2, eddiksyre, maursyre, HNO3 og NH3 ble målt innendørs og utenfor en historisk bygning, den barokke bibliotekhallen (BLH) i Nasjonalbiblioteket i Praha (Tsjekkia). Forholdet mellom innendørs og utendørs (I / O) konsentrasjoner ble undersøkt for å vurdere infiltrasjon av utendørs forurensninger. Utendørs og innendørs forurensningskilder ble funnet. Infiltrasjon av ammoniumnitrat og forskyvning av likevekten mellom partikkel og gassfasen mot gassfasen var årsaken til den høye målte konsentrasjonen av ammoniakk i BLH. Observert sesongvariasjon i innendørs konsentrasjoner ble forklart med ulike infiltrasjon og følgende fortynning av innendørs forurensninger på grunn av forskjeller i inne til ute temperaturer. Vurderingen av innemiljøet i BLH, gir noe grunn til bekymring for konservering av materialer, spesielt papir, i BLH.

** Classification*
A Unclassified (can be ordered from NILU)
B Restricted distribution
C Classified (not to be distributed)

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