# 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 16<sup>th</sup> 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<sub>3</sub>). 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<sub>2</sub>, O<sub>3</sub>) 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<sub>2</sub>, O<sub>3</sub> and SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (1.71 - 4.75 µg m<sup>-3</sup>) is above exposure levels recommended for paper based material (Table 1) and for leather book bindings (0.26  $\mu$ g m<sup>-3</sup>; [9]). Outdoor generated pollutants infiltrate into the BLH and the concentrations of harmful pollutants such as NO<sub>2</sub> and SO<sub>2</sub> 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  $\mu$ g m<sup>-3</sup> (Table 1; 4 ppb). However, and due to generally high "no observed adverse effect level" (NOAEL) for objects, concentrations below 100  $\mu$ g m<sup>-3</sup> are not considered mandatory [11]. In our study, concentrations of acetic acid were always above 100  $\mu$ g m<sup>-3</sup>.

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 <sup>-3</sup>	ISO11799/2003 [8]	NBS [7]
SO <sub>2</sub>	13 to 26	1
NO <sub>2</sub>		4.75
O <sub>3</sub>	10 to 20	26
Acetic Acid	<10	
Formaldehyde	<4.8	
Particles	50	
500 Acetic Ac	id (µg m-³)	Indoors
T		Outdoors
400 -		
300 -		
200 -		Ŧ
100 -		Т
o I I		
JUN 09 409 580109 Oct 09 100 Dec 09 Jan 10 10 Mar 10		

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

#### Pollutants from particulate infiltration

Indoor NH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> + HNO<sub>3</sub>). Indoor concentrations of HNO<sub>3</sub> 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<sub>3</sub>.

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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