Indoor Air Quality Assessment at the Library of the National Observatory of Athens, Greece

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ABSTRACT

Indoor environmental factors, such as microclimatic conditions (viz., the temperature and relative humidity) and pollutant concentrations, crucially affect the exhibits and artworks in a museum. To evaluate the air quality inside the library hosted by the Museum of Geoastrophysics of the National Observatory of Athens, a monitoring campaign was performed during summertime (August 2016). The findings were compared against scientifically accepted standards and recommended conditions for repositories and paperwork exhibition areas. The temperature and the relative humidity proved to be the most critical threats to the book collection, with the measured temperatures exceeding the recommended limits. Both parameters also displayed diurnal fluctuations, which are not recommended. Synergistically, these uncontrolled conditions contribute to book deterioration on a long-term basis, resulting in color and mechanical damage to the fibers and the growth of mold. Furthermore, despite only moderate infiltration, the library exhibited unacceptably high levels of pollutants, such as SO2, NO2 and O3, which also cause the embrittlement and discoloration of paper as well as a weakening or powdering of leather book covers.

Keywords: Microclimatic conditions; Air pollution; Indoor air quality; Books; Organic materials.

INTRODUCTION

It is well known that human activity has contributed to progressive deterioration of environmental conditions. Excessive air pollution in many cities especially those linked with aerosols (e.g., black carbon), acidic compounds (e.g., sulfur dioxide [SO2], nitrogen oxides [NOx], HNO3) and oxidants (e.g., ozone [O3], H2O2) affected historic and modern materials and significant damages have been observed in historical and cultural structures and monuments. Climate change accelerates the degradation due to increased temperature (T) or other extreme events such as flooding. The outdoor atmospheric conditions can also affect the indoor ones and consequently impact on degradation of collections exposed in museums. Indeed, indoor air quality (IAQ) at museums and historical buildings is considered in general as a major issue of concern for cultural heritage preservation (Ankersmit and Stappers, 2016). The exposure of artworks and materials to inappropriate temperature and relative humidity (RH) levels, as well as to gaseous and particulate pollutants emitted from either indoor or outdoor sources contributes to their decay. Under low air pollution conditions, direct effects on materials are rather limited, while in the case of long-term exposure to a heavily polluted environment, more serious effects, such as surface alteration, color change or even weakening of the material may occur (Brown et al., 2002; Andreopoulou-Magkou and Mariolopoulos, 2005; Zorpas and Skouroupatis, 2016). Simultaneously, the impact of the touristic activities on indoor cultural heritage areas should not be neglected (Worobiec et al., 2008). The indoor-outdoor interactions in general impact on the air quality of the storage or exposition areas. In this context, monitoring and controlling the indoor microclimatic conditions and the level of pollutants is of major significance and is priority for the conservation and preservation strategies implemented during exhibitions or materials storage.

Temperature and relative humidity are the most crucial risk factors for libraries and archival collections as they are...
potential catalysts of aging processes and their increase to extremely high levels favors the growth of insects (Adcock, 1998; Henderson, 2013; Sarantakos, 2013), especially in leather (Vujčić et al., 2017). An increase in T by 10°C, or even by 5°C for unstable materials could accelerate the chemical decay reactions’ rate even by a factor of 2 (Henderson, 2013). In general terms discoloration, fading and blackening could occur due to high temperatures. Hydroscopic archival collections (organic materials such as paper, leather and parchment) can readily absorb moisture from the environment resulting in the expansion of the material. Furthermore, according to Sterflinger (2010), high RH levels (above 55%) favor the development of mold and additional biological damages by microorganisms. In contrast, when the levels of relative humidity decrease, organic materials lose moisture content and tend to shrink. The previously described expansion and contraction of hydroscopic materials due to fluctuations of temperature and relative humidity can also lead to mechanical damage of the objects.

The presence of air pollutants in exhibition areas or storage rooms and under uncontrolled micro-environmental conditions could further determine the fate of book collections, mainly due to acidic hydrolysis processes (Daniel et al., 1990; Daniels, 1996; De Feber et al., 1998; Pavlogeorgatos, 2003; Tétreault, 2003). Paper and leather are among the materials seriously affected due to their sensitivity to acidic compounds. By considering the endogenous decay factors of vulnerable materials, such as the cellulose macromolecular or production properties of the paper (Dirksen, 1997; Adcock, 1998; Andreopoulou-Magkou and Mariolopoulos, 2005; Area and Cheradame, 2011; Kliafa, 2013), the long-term exposure to risk conditions are of great importance for such artworks or exhibits. Blades et al. (2000) mention that SO2 can cause embrittlement and discoloration of the paper and a weakening or powdered surface of the leather covers of books known as “red rot” when in combination with a presence of high RH and oxygen levels (Dirksen, 1997; Andreopoulou-Magkou and Mariolopoulos, 2005; Kite and Thomson, 2006). Specifically, SO2 can be absorbed onto cellulosic materials, such as paper, where it catalytically hydrolyzes to H2SO4·H2SO3 and H2SO4 (ASHRAE, 2015). Moreover, SO2 could react with leather, breaking down its molecular structure and weakening the material. As a result, it contributes to producing a powdery surface, which is easily abraded. Ozone, as a strong oxidant, causes fading of dyes and pigments and induces attack on organic materials (Morten, 2006). NO2 and O3 in humid environments enhance the SO2 uptake (Johansson and Lennholm, 2000; Johansson et al., 2000), catalyzing thus the hydrolysis reactions. Additionally, acidic or alkaline particulate matter (PM) favors the discoloration processes through deposition (Grau-Bové et al., 2016).

The current study, undertaken during August 2016, focuses on the IAQ at the library of the Museum of Geoastrophysics (www.noa.gr/museum) of the National Observatory of Athens (NOA). The museum is situated close to the center of Athens; therefore, the area is influenced by typical urban pollutants. Apart from local urban emissions (e.g., traffic), the Attica Basin is subjected to long-range transport and accepts burdens of contaminants of different origin (e.g., Gerasopoulos et al., 2009; Paraskevopoulou et al., 2015; Athanasopoulou et al., 2017; Fourtzio et al., 2017; Gratsea et al., 2017). Furthermore, the occurrence of heat waves (Founda and Giannakopoulos, 2009; Founda, 2011) should be taken into consideration, due to their synergy with indoor heating/cooling practices and interaction with emission sources and pollutants’ fate in the atmosphere as well. Despite the possible effects of the ambient conditions on the indoor environment, neither measurements nor installation of permanent monitoring equipment had been considered up to now for the library.

Our work aims to monitor and evaluate, for the first time, the temperature, relative humidity and air pollutant levels in the library room, to enable understanding of indoor-outdoor interactions with respect to natural and artificial ventilation of the building, and finally, to assist the museum authorities in undertaking tailored measures for the preservation of the exhibits. Also, in an effort to assess the risk related to the impact of IAQ on the library’s book collection, we compared our findings with already published reference or limit values and other available tools for evaluation of the micro-environmental conditions impact on cultural heritage (CH) artifacts.

METHODS

Description of the Museum Location and the Library

The Attica Basin, which includes Athens, is the most urbanized area in Greece, with 35% of the population of the country residing in the area using 52% of the private vehicles in the country (ELSTAT Annual Report 2014) therefore, resulting in increased local emissions. The Museum of Geoastrophysics of NOA is situated in the historical center of the city of Athens at the top of the Hill of the Nymphs, in close vicinity to the hill of the Acropolis (Fig. 1) and a relatively short distance (0.5–2 km) from the traffic-congested streets of the commercial center of Athens. The museum building is more than 170 years old, made of stone and hosts the library on the ground floor, where rare books, journals and other important manuscripts, even from the 16th century, are kept. The library is isolated from the rest of the museum and 1–3 staff members, including maintenance personnel, work in the room occasionally, but not simultaneously. There are no materials covering the floor of the room, the top portion of the walls that are close to the ceiling is decorated with paintings and on the roof there is a metallic remnant of an old opening mechanism used for sky observations. Closed windows, no lighting and occasionally operated air-conditioning system (for cooling or heating during meetings or guided tours) are the regular maintenance conditions. The windows are rarely opened for short periods, during working hours, to provide ventilation.

The building has been renovated since its inception in 1842 up to 2008, when it was converted into a museum, without interventions in the construction materials (stones). Despite the building renovation (e.g., roof restoration in 2008 and new shutters and wall painting in 2014), the books are kept under uncontrolled thermo-hydrometric conditions, without heating, ventilation, and air-conditioning (HVAC) system. Dust is deposited on the books, whereas fragility,
Discoloration, red rot in the leather cover pages, tide lines on the pages suggesting water migration, foxing and mold are further observed. The aforementioned degradation status makes thus necessary the investigation of the decay environmental factors to minimize the material destruction. Books are usually composed of various organic materials of plant and animal origin, resulting in a complex matrix that should optimally be preserved by taking into account the individual requirements of each component. Nevertheless, the book collection of the library can be considered uniform and the risk assessment is focused on paper (pages) and leather (covers), which are the main exposed materials. Other materials found in the library, such as wooden furniture (bookcases, desks, window frames and shutters) and the roof (paint and metal from a ceiling-opening mechanism) are not a part of this study with respect to their preservation, and thus possible implications on them will not be further investigated.

**Description of the Indoor Air Quality Monitoring Plan and Measurements**

The monitoring was conducted from 4 to 31 August 2016 (26 days) and the period was suitable for the evaluation in terms of atmospheric conditions. During August the regionally originated components (Theodisi et al., 2018; Stavroulas et al., 2019) dominate as a consequence of the summer atmospheric circulation which is quite stable with N/NE air masses accounting for 80% of the conditions. Moreover, due to the intensive photochemistry in summer and in absence of precipitation, the concentrations of the secondary pollutants (HNO₃, O₃, aerosols, etc.) could influence the quality of library collections in case of infiltration. They reach their maximum levels and consequently the impact is expected to be enhanced, considering also the high temperatures that could accelerate the decay processes.

For most of the period, the indoor equipment was operated without ventilation or cooling in order to study the targeted parameters’ variability under regular conditions encountered in the library as presented above (henceforth referred to as “background period”). On the 11th, 16th and 18th of August (2016), the air conditioner was operated for a period of 12 hours (8:00 a.m.–8:00 p.m.) in order to investigate the system performance and the variations under cooling conditions (henceforth referred to as “air-conditioned period”). On the 22nd, 24th and 26th of August (2016), ventilation took place by opening the windows from 9:00 a.m.–10:00 a.m. and 1:00 p.m.–2:00 p.m. (henceforth referred to as “natural ventilation period”). Each of the aforementioned sub-periods is accordingly identified in Tables S1 and S2 as BG, AC and V respectively. Despite the fact that during the measurements period the library was isolated for the purposes of our study, the selection of the test time frames was based on the working hours of the library personnel and the usual presence of visitors in the greater area of the observatory, when routine operation and organized daily tours could increase the possibility to open the windows or operate the cooling device. Apart from examining the library room as a whole, a glass-covered showcase table was selected for temperature and relative humidity control monitoring as it contains the most vulnerable publications (from the 16th century). A Rotronic MP101A-T7-W4W thermo-hygrometer, adjusted to an automated data-logger system, and a Tiny Tag TGP-4500 logger, were operated for the monitoring of relative humidity and temperature in the library and the showcase, respectively, collecting data at 5-minute intervals. The precision of the thermo-hygrometer was ±1% RH and ±0.3°C, while for the showcase logger the respective characteristics are ±3% RH and ±0.4°C at 20–40°C. Horiba Analyzers (360 Series) were used to monitor carbon monoxide (CO), nitrogen oxides, sulfur dioxide and ozone (CO, NOₓ = NO + NO₂, SO₂ and O₃ respectively) at 30-minute resolution. The detection limits of the analyzers are 50 ppb for CO and 0.50 ppb for the rest of equipment as provided by the manufacturer. Eight indoor particulate matter samples of less than 10-µm diameter (PM₁₀) were collected on quartz filters by means of a Partisol 2000 FRM sampler with a detection limit of 1.1 µg m⁻³. The filters were pre- and post-weighed in
the weighing room of the Atmospheric Chemistry Laboratory of NOA, with a 6-digit Mettler Toledo MX-5 balance (of 1-µg precision) operating under controlled conditions of temperature and humidity (20 ± 3°C and 40 ± 5% RH), for the determination of their mass concentration (Paraskevopoulou et al., 2014). The filters were afterwards analyzed by ion chromatography (ionic composition determination) and by a thermal optical transmission technique for organic and elemental carbon content (OC and EC respectively) at the laboratory of the Chemistry Department of the University of Crete (Novakov et al., 2005; Cavalli et al., 2010; Bougiatioti et al., 2013; Paraskevopoulou et al., 2014). The detection limit of the analysis was 0.26 and 0.05 µg C cm⁻² for OC and EC, whereas for the anions and cations ranges at 20 ppb and 10 ppb respectively. The reported concentrations were corrected for blanks. All of the equipment was calibrated and inter-compared prior to and/or after the measurements in order to ensure the quality of the results. The ambient meteorological and pollutant data that were used for this study are routinely collected at the Thissio Meteorological and Air Pollution Stations located at the central premises of NOA, situated 200 m and 10 m respectively from the museum.

RESULTS AND DISCUSSION

Temperature and Relative Humidity

In Fig. 2, the outdoor, indoor and showcase measurements of temperature and relative humidity are presented. The air-conditioned periods and the natural ventilation periods are marked with red frames and purple lines respectively. Each of these time slots was studied separately and the results of a basic statistical analysis are provided in Tables S1 and S2. The outdoor T during the campaign ranged between 21.7°C and 36.7°C, with the exception of the period of 13–16 August, when the average temperature was approximately 3°C lower, under the influence of strong northern winds (N, NE, NW direction). During the background period, the average indoor T was constantly higher by 2.4°C compared to relevant outdoor conditions. As shown in Fig. 2(a), on a diurnal basis the outdoor T was at a maximum at noon and was almost always higher compared to the indoor maximum values for the specific time frame. Nevertheless, the higher amplitude of the outdoor temperature variability resulted in constantly lower outdoor average levels. The stone walls of the library have high thermal inertia which means that during day the material accumulates the heat and later when the temperature drops, it balances the conditions leveling out the indoor variations. The temperature variability in the library and the showcase was similar, with lower levels of T by 1.1°C encountered in the showcase. During the air-conditioned period, the temperature in the library and the showcase decreased significantly compared to the outdoor conditions and reached even less than 25°C. According to Fig. 2(b), the indoor RH presented less variability compared

Fig. 2. Variability of (a) temperature and (b) relative humidity for outdoor conditions, the library and the showcase. Red frames and purple lines represent the air-conditioned and natural ventilation periods respectively. The 5-minute values are depicted.
to the outdoor levels, with observed significant difference in the showcase, which seemed to be independent from outdoor or indoor changes. The average background RH in the showcase was slightly higher than in the library (39% versus 36%), still reflecting an insignificant difference between the macro- and micro-environment of the library. The building hosting the library is old (middle of 19th century), made by stone, without interventions on the insulation material of the envelope to now dates and located in an open area enabling the direct impact of the current environmental conditions. Nevertheless, the structural features of the building (i.e., thick stone walls) maintain the RH at low levels and the hygric inertia ensures moisture balance by limiting relative humidity variations. The low RH variability in the library and the showcase, as well as the consequent smoothening of the short-term fluctuations could be attributed to the buffering capacity of the paper (Kupczak et al., 2018).

To better investigate the T and RH variability during the air-conditioned and natural ventilation periods, each case is magnified in Figs. 3 and 4 respectively. In Fig. 3(a), it is clearly depicted that during the air-conditioned periods (within the red frames) the temperature in the library decreases rapidly, in less than 1 hour, and it remains around 24°C as long as the air-conditioning system is in use. On the 11th of August, a sudden increase in T around noon is attributed to a short interruption of the air-conditioning system operation, with a lesser effect on the showcase’s temperature. At noon, the average deviation of the indoor conditions relative to the library and the showcase was in the order of 9–12°C and 8–12°C respectively, reflecting similar cooling capability of the air-conditioning system on both the library and the showcase. After the end of the AC period, the inner temperature recovered to outdoor conditions within an hour. It is also worth noting that while the showcase temperature is lower than in the library by 4% during background conditions, it remains slightly higher during the air-conditioned time slot by 3–5% (Table S1), demonstrating the slightly increased direct impact of the forced temperature change on the books on shelves relative to the isolated ones in the showcase. During the air-conditioned periods, the relative humidity in the library (Fig. 3(b)) remained unaffected with respect to its preceding level and higher or almost equal to the outdoor levels, while at background conditions, RH does not exceed the outdoor conditions due to its temperature dependence. In practice, the impact of the domestic air-conditioning system on the library humidity is not significant.

With respect to Fig. 3, Fig. 4 depicts each of the natural ventilation periods magnified for the case of temperature and relative humidity. The variability of the temperature (Fig. 4(a)) inside and outside the library is similar for the ventilation period, but with different rates regarding the temporal change. During the morning ventilation, indoor T was always higher by up to 2.5°C relative to outdoor. It was generally observed that the library temperature tends to decrease at the beginning of the ventilation as heat from the library is transferred out, but afterwards, the temperature is increased following the outdoor trend, but with a 30% lower rate. Midday levels are almost equal with less than a 0.5°C difference on average. Regarding RH in the library (Fig. 4(b)) for the ventilation period, there is no impact on the showcase variability as there was for the case of the air-conditioning operation. For the library, there is an insignificant RH increase at the beginning of morning ventilation due to penetration of the more humid outdoor air masses in the library and then it

Fig. 3. Maximized plots of (a) temperature and (b) relative humidity during the air-conditioned periods depicted in red frames on 11 August, 16 August, 18 August (top to bottom) for the period of 8:00 a.m.–8:00 p.m.
is gradually readjusted to almost stable levels throughout the course of ventilation. For the morning ventilation periods, indoor RH was always lower by around 7% compared to outdoor, whereas midday levels were equivalent.

**Indoor Gaseous and Particulate Pollutants**

In Fig. 5, the indoor concentrations of the gaseous pollutants NO, NO$_2$, SO$_2$, O$_3$ and CO are presented at 30-minute intervals, followed by the outdoor concentrations and the indoor/outdoor (I/O) ratio when simultaneous measurements were available. The air-conditioned and natural ventilation periods are also marked as done previously. Table 1 summarizes the findings of the parallel indoor-outdoor measurements, including PM$_{10}$ and the I/O ratio for each period. The common variability of both indoor and outdoor pollutant concentrations for O$_3$ and CO (Fig. 5) clearly indicates that the outdoor levels, as well as emission sources and processes, are driving the library air quality. The outdoor measurements of primary pollutants (CO) were characterized by a morning peak during the traffic rush hours (7:00–9:00 local time) and the increased evening and late night levels, driven by the boundary layer decrease (Alexiou et al., 2018). On the other hand, the photochemically produced O$_3$ levels were elevated around noon-time and influenced by the opening of the windows (as also observed by De Santis et al., 1992, for the case of the Galleria degli Uffizi in Florence). Increased levels of pollution were also observed a few days before and after the 15 August public holiday, possibly due to increased traffic (departure and return of Athens’ citizens). The relatively strong (> 5 m s$^{-1}$) north winds during 13–15 and 24–28 August also resulted in lower levels of the primary pollutants due to more efficient city ventilation processes. Indoor O$_3$ and CO was lower by 40% and 50%, respectively when compared to the outdoor levels during the background period and presented similar temporal variability. No significant changes on the pattern and the relative difference on both indoor and outdoor levels were observed during the air-conditioned periods (11$^{th}$, 16$^{th}$ and 18$^{th}$ of August). On the contrary, O$_3$ levels approach the outdoor values while windows were opened, with the relative difference of 8%, on average. In general, an I/O ratio > 1 reflects infiltration and/or additional indoor sources, while low I/O ratios correspond to low inflow (Krupińska et al., 2013). The average I/O ratio for both pollutants was < 1, indicating moderate infiltration and thus limited reactions on the material surfaces after deposition. I/O almost equal to unity (0.9) was observed for O$_3$ during the natural ventilation period attributed to the inflow of the outdoor-originated quantities. The enhanced I/O peaks that have been rarely observed (almost 2% of the observations) correspond to calculations for periods with low O$_3$ values (due to deposition or NO titration) which contribute to the observed high I/O peaks without significant qualitative impact on the results and the general conclusions regarding the O$_3$ impact.

Information about the 24-hour collected PM$_{10}$ filter samples is provided in Fig. 6. Similar to gaseous pollutants, the indoor levels were lower relative to outdoors and co-varied (Fig. 6(a)), with means of 19.9 µg m$^{-3}$ and 26.3 µg m$^{-3}$, respectively resulting in a 25% difference. The PM$_{10}$ I/O ratios for the whole period were lower than 1, ranging from 0.6 to 0.9 and the similar variability indicates that the main factor determining indoor PM$_{10}$ concentration is outdoor conditions, as in the case of gases. These values indicate the contribution of ambient sources in PM levels inside the library as reported elsewhere (Chianese et al., 2012). The significant indoor-outdoor differences of the 12$^{th}$ and 25$^{th}$ of...
Fig. 5. Indoor and outdoor temporal variability of gaseous pollutants followed by the I/O values when available. Red frames and purple lines represent the air-conditioned and natural ventilation periods, respectively.

August corresponds to days with mean wind speed higher than 5 m s\(^{-1}\), possibly denoting the slow response time of the building to the forced outdoor conditions, reflecting a kind of equilibrium between the indoor and outdoor relative to the infiltration capacity of particulates.

Apart from the particulate levels, the presence of specific chemical compounds in high concentrations can also be considered as a significant threat to book materials. For this reason and in addition to the main study, chemical characterization of the atmospheric aerosols collected in the library was performed and followed by a mass closure. Dust was calculated by calcium (multiplied by 8 according to Sciare et al., 2005) and particulate organic matter (POM) is equal OC multiplied by 1.8 (Stavroulas et al., 2019). The mass closure (Fig. 6(b)) was almost complete with unknown constituents of 5.4% and 5.9% for indoor and outdoor, respectively, which could be attributed to water (Theodosi et al., 2018).

The IC analysis shows that the species which seem to have similar levels both indoors and outdoors (Fig. 6(c)) are secondary species, such as sulfate (SO\(_4^{2-}\)) and nitrate anions (NO\(_3^-\)). Primary species, such as elemental carbon, sodium,
magnesium, calcium and to a lesser extent the photochemically produced oxalate ions (EC, Na⁺, Mg²⁺, Ca²⁺ expressed as dust and O₃, respectively), were found at higher levels outside, relative to the indoor library area. The most abundant species inside the museum was POM; and with dust and sulfates make up for almost 80% of the total mass with relative contributions of 37.1%, 21.1% and 20.4%, respectively. Enhanced levels of organic matter were also reported in other cultural heritage indoor environments (e.g., Cappitelli et al., 2009; Mascova et al., 2015). The predominant contribution of the sulfates, for the ionic components, is in agreement with findings at indoor cultural heritage environments (Cao et al., 2011; Xiu et al., 2015; Bartl et al., 2016; Uring et al., 2018); whereas, according to publications calcium-rich particles have been determined to dominate the indoor aerosol in museums depending on the wall material (Camuffo et al., 1999, 2001) or restoration and construction works (Gysels et al., 2004), without excluding outdoor sources (Gysels et al., 2002). The same stands for outdoors despite the prevalence of dust relative to POM with 42.5% against 22.6%. Outdoor soil re-suspension enhances the dust levels but these relatively big particles do not penetrate into the library, resulting thus in lower indoor levels of dust. The contribution (maximum < 5%) of the rest of the compounds is of less importance relative to these three factors (SO₄²⁻, POM, dust). By examining their absolute indoor and outdoor levels, important differences on the resulting I/O occurred (Fig. 6(c)). Higher-than-unity I/O was observed for POM, ammonium, potassium, and chloride, while sulfates and nitrates were close to unity. Emissions of organic material and microbial activity indoors could drive the enhanced levels of POM and ammonium. On the other hand, enhanced levels of chloride and potassium levels indoors could be associated with emissions from cleaning materials and dust, respectively. The source apportionment based on inter-correlations of such a short-term dataset provides relatively limited results. The resulting correlations were weak with the exception of sodium relative to magnesium (R² = 0.91 indoor and 0.94 outdoor) and sodium relative to chloride and magnesium indoor (R² > 0.86). Indeed, salts such as NaCl and MgCl₂ (Anaf et al., 2014) could be present indoors, denoting an impact of sea salt (transport for our case) or building materials, respectively (mortars according to Krupińska et al., 2013).

### Table 1. Statistics of the indoor and outdoor pollutants’ variability followed by their I/O ratio, when available, for each phase of the monitoring period. Values are given in µg m⁻³. BG, AC and V correspond to background, air-conditioned and natural ventilation periods, respectively.

| Pollutant | Statistics | Indoor | Outdoor | I/O |
|-----------|------------|--------|---------|-----|
|           |            | BG total | AC total | V total | BG total | AC total | V total | BG total | AC total | V total |
| NO        | min        | 0.9     | 1.1     | 1.7   | 0.8     | 2.7     | 60.8    | 0.1     | 0.1     | 0.7     |
|           | max        | 70.2    | 57.4    | 5.0   | 233.5   | 250.0   | 171.4   | 4.8     | 1.4     | 1.0     |
|           | avg        | 2.9     | 8.7     | 2.3   | 113.6   | 120.8   | 118.4   | 0.7     | 0.5     | 0.9     |
|           | stdev      | 4.8     | 15.0    | 1.0   | 39.6    | 62.5    | 29.8    | 0.3     | 0.3     | 0.1     |
|           | med        | 2.0     | 2.0     | 2.0   | 119.4   | 110.5   | 115.8   | 0.6     | 0.4     | 0.9     |
| NO₂       | min        | 4.3     | 6.2     | 8.1   | 72.6    | 60.2    | 46.7    | 11.3    | 12.2    | 10.3    |
|           | max        | 72.6    | 60.2    | 46.7  | 15.9    | 21.4    | 16.0    | 12.3    | 16.9    | 13.1    |
|           | avg        | 12.3    | 16.9    | 13.1  | 11.3    | 12.2    | 10.3    | 11.3    | 12.2    | 10.3    |
| SO₂       | min        | 2.4     | 2.4     | 3.4   | 23.3    | 10.0    | 11.5    | 4.7     | 4.2     | 5.3     |
|           | max        | 23.3    | 10.0    | 11.5  | 4.7     | 4.2     | 5.3     | 1.3     | 1.8     | 2.4     |
|           | avg        | 4.7     | 4.2     | 5.3   | 4.7     | 4.2     | 5.3     | 4.5     | 3.9     | 4.7     |
| O₃        | min        | 2.6     | 3.0     | 50.2  | 144.1   | 93.0    | 165.2   | 69.9    | 59.3    | 107.9   |
|           | max        | 144.1   | 93.0    | 165.2 | 69.9    | 59.3    | 107.9   | 30.6    | 30.1    | 27.2    |
|           | avg        | 73.7    | 69.2    | 106.0 | 73.7    | 69.2    | 106.0   | 119.4   | 110.5   | 115.8   |
|           | stdev      | 1.3     | 1.8     | 2.4   | 1.3     | 1.8     | 2.4     | 4.5     | 3.9     | 4.7     |
| CO        | min        | 49.3    | 49.3    | 73.9  | 1009.8  | 763.5   | 344.8   | 176.7   | 232.3   | 145.7   |
|           | max        | 1767.7  | 232.3   | 145.7 | 115.3   | 204.3   | 81.2    | 114.3   | 189.3   | 259.0   |
|           | avg        | 147.8   | 172.4   | 117.0 | 147.8   | 172.4   | 117.0   | 119.4   | 110.5   | 115.8   |
|           | stdev      | 1.5     | 6.7     | 25.9  | 1.5     | 6.7     | 25.9    | 13.6    | 24.4    | 38.1    |
| PM₁₀      | min        | 5.0     | 26.3    | 0.8   | 19.9    | 26.3    | 0.8     | 3.8     | 25.9    | 0.8     |
|           | max        | 20.5    | 26.3    | 0.8   | 3.8     | 25.9    | 0.8     | 19.9    | 26.3    | 0.8     |
|           | avg        | 15.5    | 26.3    | 0.8   | 15.5    | 26.3    | 0.8     | 20.5    | 25.9    | 0.8     |
|           | stdev      | 15.5    | 26.3    | 0.8   | 15.5    | 26.3    | 0.8     | 20.5    | 25.9    | 0.8     |
|           | med        | 15.5    | 26.3    | 0.8   | 15.5    | 26.3    | 0.8     | 20.5    | 25.9    | 0.8     |
Fig. 6. Indoor-outdoor relations of (a) the PM$_{10}$ mass concentration of filter samples on 24-hour basis, (b) the mass closure and (c) the mean chemical composition, over the experimental period.

**Risk Assessment of Temperature and Relative Humidity on the Books Collection**

The longer lifetime of paper material is achieved at low-moderate temperatures and moderate relative humidity levels (Adcock, 1998). The best practice is to regulate and stabilize the conditions, to the extent possible, as to avoid sharp fluctuations that put stress on the exposed materials. With respect to preservation, norms that nominate an optimum level or range of levels for the materials’ exposure conditions are applied, by making a compromise between the optimal
choices for conservation purposes and what is considered affordable. While the lowest acceptable humidity level for long-term storage of archival and library materials is, in general, under discussion and many reference levels or norms are used, the type of the material, the manufacturing process and the preservation state of the object, determine the selection of the applied limit values (Blades et al., 2000; Brown et al., 2002; Andreopoulou-Magkou and Mariolopoulos, 2005; Kite and Thomson, 2006). The limit values of 21 ± 1°C and 50 ± 3% RH, which were introduced in 1979 (La Fontaine, 1979), are still often considered to be the reference limits to avoid book deterioration (Table 2). The classic reference values for conservation conditions, according to Thomson (1994), are a temperature set to 20°C and a relative humidity of 50%. A slight change to 18°C and 45% RH (recommended by Davis, 2006) can significantly increase the lifetime of certain types of materials. Based on the best available knowledge and the specifications for collections included in the 2015 ASHRAE Handbook (American Society of Heating Refrigeration and Air-Conditioning Engineers, 2015), the limit values of 50% RH and a temperature range of 15–25°C can be adopted for sensitive materials. The tolerance is a bit higher for general collections, reaching 60% RH and temperatures within 20–30°C. The International Standard ISO 11799:2003, “Information and documentation—Document storage requirements for archive and library materials,” applies to the long-term storage of archive and library materials and also points out that repositories for such materials should be kept at a cool temperature and at a relative humidity below the point where microbiological activity occurs. Despite the relative unanimity about the decay of paper under constant T and RH, there is still discussion about the mechanisms that fluctuating environmental conditions impact on the chemical and physical properties of the specific substrate. In the review of Menart et al. (2011) degradation of paper under cyclic conditions of T and/or RH (Shahani et al., 1989; Bogaard and Whitmore, 2002; Panek et al., 2004) is reported, whereas the time spent under each condition is determinant for the impact on the material (Bigourdan and Reilly, 2002). Nevertheless, mild changes in T and RH could be buffered by books stored closely together (Henderson, 2007), as in our case.

In this study, the recommended range defined in ISO 11799:2003 are used in combination with the limitations recently published by Andretta et al. (2016) in accordance with UNI 10586:1997 (Table 2), leading to a combined range of 2–20°C and 30–60% RH, covering limitations for paper and leather. According to Fig. 2 and Table S1, temperature limits were exceeded during the background period in the library and the showcase, with values constantly above the upper limit of 20°C provided by the two aforementioned references. The minimum temperature in the library was also above the upper acceptable limit. Opposite to temperature, the indoor relative humidity fell within the proposed limits for paper preservation, but was lower than what is recommended for the preservation of the leather bindings of the books. Fig. 7 presents the 24-hour difference between the minimum and maximum of the measured indoor temperature and relative humidity (ΔT24 and ΔRH24 respectively). The air-conditioned and the natural ventilation periods are depicted within the frames in Fig. 7 and are excluded by the risk assessment as they correspond to forced conditions. Both tolerable daily changes of 1°C and 3% RH of the ISO 11799:2003 and 2°C and 5% RH according to Andretta et al. (2016) were considered. Regardless of the chosen norms, the indoor (library and showcase) gradient for temperature was above the limits during the majority of days. The RH gradient for the showcase was within the suggested limits, but exceedences were encountered almost every day for the library.

The Performance Index (PI) of the building, which expresses the percentage of time in which the microclimatic parameters of the library do not match the recommended values, is calculated in order to evaluate the indoor microclimatic quality (IMQ) (Corgnati et al., 2009). The values of both parameters, T and RH, obtained in the library and the glass-fronted showcase measured in 5-minute intervals were used in Fig. 8, where the green lines are the acceptable limits for storage according to ISO 11799:2003 (2–18°C and 30–60%) and the red lines are the acceptable limits according to Andretta et al. (2016) (14–20°C and 50–60%). In the optimal case, the pairs of T and RH should be within the colorful areas defined by these limits. Despite the fact that RH individually was in general considered acceptable, this synergistic tool highlights an important issue in our case. According to the findings, the conditions in the library and the showcase during the studied period are completely out

Table 2. Summary of preservation reference values for relative humidity and temperature for books and archival material. Text in italics corresponds to the norms that were utilized in this manuscript.

| Standard/Reference | Conditions/Material | Temperature | Relative Humidity |
|--------------------|---------------------|-------------|------------------|
| La Fontaine (1979) | Limits for deterioration of materials | 21 ± 1°C | 50 ± 3% |
| Thomson (1994)    | Classic reference conservation conditions | 20°C | 50% |
| Davis (2006)      | Updated recommended parameters | 18°C | 45% |
| ASHRAE (2015)     | Sensitive materials | 15–25°C | < 50% |
|                    | General collections | 20–30°C | < 60% |
| ISO 11799:2003 (archival book material) | Paper (optimum preservation) | 2–18 ± 1°C<sup>a</sup> | 30–45 ± 3%<sup>a</sup> |
|                    | Paper (staffed stack areas, items in regular use) | 14–18 ± 1°C<sup>a</sup> | 35–50 ± 3%<sup>a</sup> |
|                    | Leather | 2–18 ± 1°C<sup>a</sup> | 50–60 ± 3% RH |
| UNI 10586, Andretta et al. (2016) | Librarian artifacts | 14–20°C | 50–60% |
|                    | | ΔT<sub>24</sub> < 2°C | ΔRH<sub>24</sub> < 5% |

<sup>a</sup>Tolerable daily changes within the limits.
Fig. 7. Daily gradients (max–min) for (a) temperature and (b) relative humidity during the experimental period in the library. The black frames represent the days that the air library was either air-conditioned or naturally ventilated.

Fig. 8. Performance Index (PI) for the experimental period according to temperature and relative humidity measured in (a) the library and (b) the showcase in 5-minute intervals. The green lines are the extended acceptable limits for book materials storage according to ISO 11799:2003 (2–18°C and 30–60%) and the red lines are the limits according to Andretta et al. (2016) (14–20°C and 50–60%).

of control, demonstrating the poor capability of the building to regulate indoor conditions without an HVAC system, thus posing a risk to the collection of books. Over time, the high temperatures that have occurred in the room and the sharp daily gradients of both temperature and relative humidity could justify the observed discoloration and fragility of the books. It is worth noting that the books are stored under the specific environmental conditions for at least ten years, providing thus an acclimatization period for the evaluation of the historical climate (BS EN 15757:2010). Nevertheless, the current status of the books could also have been affected by the storage conditions prevailing before 2008 (i.e., before the reconstruction).

Risk Assessment of Air Pollution on the Book Collection

With reference to the currently recommended levels of key gaseous pollutants for collections included in the 2015 ASHRAE Handbook for sensitive materials, the limit values for NO₂ range from 0.09 to 4.89 µg m⁻³, for SO₂ from 0.1 to 1.05 µg m⁻³ and O₃ is less than 0.1 µg m⁻³. Taking into
concentration the general collection guidelines, the limits are set at 3.76–18.82, 1.05–5.24 and 0.98–9.82 µg m⁻³ for NO₂, SO₂ and O₃, respectively (Table 3). On the other hand, according to ISO 11799:2003, the concentration of pollutants in areas dedicated for books and archival material storage is set at higher levels even by one order of magnitude. According to Table 1, the average levels of NO₂ and SO₂ of 15.9 µand 4.7 µg m⁻³ respectively, are close to the ASHRAE guidelines for general collections but the min–max variability deviates significantly. Furthermore, our findings were within the limits of ISO 11799:2003 for SO₂ but extremely higher than the acceptable limit for O₃, regardless of the norms used and could be related to degradation of the leather components of the books. Concerning PM₁₀, no reliable conclusions could be deduced since there is no reference for the specific monitored fraction. The indoor levels of the gaseous species, which are higher than the suggested levels, may have a synergistic role with the thermo-hydrometric parameters, contributing to the decay of the books and their current status.

CONCLUSIONS

The temperature and relative humidity, as well as the concentrations of major air pollutants (viz., NO₂, O₃, SO₂, CO and PM₁₀), in the library hosted by the Museum of Geoastrophysics of the National Observatory of Athens were monitored for 1 month during the summer, a period representing conditions in this city when the primary pollution background is highly influenced by regional emission sources and which is associated with high temperatures and secondary pollutant formation. Measurements were performed both in the library room and outdoors to determine the indoor-outdoor interactions during natural and artificial ventilation of the building. Also, to assess the risk posed by the IAQ to the library’s book collection, we compared our findings to previously published reference values and applied existing tools for evaluating the effect of micro-environmental conditions on cultural heritage artifacts.

Higher mean temperatures were encountered inside the library and the showcase than outdoors, and similar diurnal profiles between these locations reflected the building’s inability to offset environmental changes. Operating the air conditioning decreased the temperature, but the effect of opening the windows was limited. On the other hand, the relative humidity was less influenced by the outdoor conditions and remained at almost stable levels in the showcase, regardless of the cooling method. Furthermore, the temperature continuously exceeded the recommended maximum limit of 20°C, whereas the relative humidity fell within the acceptable range for paper conservation. Nevertheless, the simultaneous investigation of both parameters using the performance index (PI) of the building revealed that conditions in the library and the showcase during the study period were consistently far from optimal and potentially damaging to the book collection. The books were also vulnerable to the intensive daily changes in temperature that occurred both during normal conditions and due to short periods of air conditioning.

Regarding the pollutants, the day-to-day variability of the I/O ratio may indicate changes in the air penetrating the building, which depends on factors such as the outdoor wind speed and the structural characteristics of the building. Although O₃ and dust infiltrated the library more easily when the windows were open, these risk factors were considered to be minor during the library’s normal operating conditions, which are defined as having closed doors and windows with a limited human presence. The average I/O ratio for both gaseous and particulate pollutants was less than 1, indicating low infiltration and minimal deposition processes and reactions on the materials’ surfaces. However, in absolute terms, the levels of ozone inside the library greatly exceeded any applicable limit for O₃, even though all of the other monitored pollutants displayed acceptable average concentrations. Nevertheless, the fluctuations in NO₂ and SO₂ should be taken into account, as they may be partially responsible for the observed discoloration, embrittlement and fragility of some of the books in the library.

Additionally, the atmospheric aerosols collected in the library were chemically characterized. The measured chemical species (viz., the major ions and organic and elemental carbon) and their I/O ratios can be divided into three categories: i) Primary species from both natural and anthropogenic sources, such as elemental carbon, sodium, magnesium and calcium, exhibited higher concentrations outside than inside the library (I/O < 1). ii) Secondary species related to long-range transport, such as SO₄²⁻ and NO₃⁻, exhibited an I/O ratio close to unity. iii) Lastly, POM, ammonium, potassium and chloride (related to organic material, microbial activity and indoor emissions from cleaning materials and dust) exhibited an I/O ratio above unity (i.e., I/O > 1).

According to our findings, outdoor conditions strongly influenced both the chemical profiles, especially for the gaseous species, and the microclimatic parameters in the library, demonstrating the poor ability of the building to regulate the indoor environment. We also evaluated the normal ventilation practices in the library and discovered that neither operating the air conditioning nor opening the windows for short periods of time affected the relative humidity indoors, which remained almost stable regardless of the conditions. As both the library and the showcase responded to forced temperature changes, the frequent use of a cooling device, which produces sharp fluctuations in the ambient temperature, is not recommended. Additionally, opening the windows at noon is not recommended because of the higher outdoor temperatures and the potential transport of photochemically produced, reactive pollutants, such as O₃. Instead, short periods of natural ventilation during the morning, which dissipate the heat load and increase the comfort of individuals inside the library, are preferred. At minimum, ideal improvements to the library environment include protective shelves that prevent the deposition of dust and other contaminants on the books. A continuously operated air-conditioning system should also be integrated into the environment to maintain the temperature within the recommended limits, to suppress sharp variations caused by outdoor conditions and to inhibit the degradation—thermal, primarily, and chemical and biochemical, secondarily—of the paper and leather components of the books. In summary,
the microclimatic conditions, which appear to be the crucial
decay factor at the library of the Museum of Geoastrophysics
of the National Observatory of Athens, should be regulated,
continuously monitored in the future and synergistically
investigated in order to evaluate their combined effects on
the book collection.

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DISCLAIMER

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be
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