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**DIPLOMA THESIS:**

# Indoor-outdoor air quality interrelation at museum environments: The case of the Museum of Geoastrophysics at N.O.A

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*To my grandparents*

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**Abstract**

Nowadays, the problem of Indoor Air Quality (IAQ) has received crucial concern regarding the cultural heritage deterioration. The natural decay of materials and artworks exposed to non-controlled environmental conditions of temperature and relative humidity or exposed to gaseous and airborne particulate pollutants, either emitted indoors or penetrating from the outdoor environment, could be accelerated. As a result, monitoring and controlling the indoor microclimatic conditions (temperature and relative humidity) and the level of indoor pollution is of major importance for the applied conservation and preservation techniques of cultural heritage.

The present study focuses on the measurements of airborne particulates and gaseous pollutants (NO, $NO_2$, $SO_2$, CO, $O_3$ and PM10 and determination of their content in OC, EC and ions), as well as the thermo hydrometric conditions indoors and outdoors of the Library of the Museum of the Geoastrophysics of the National Observatory of Athens which hosts books from the $16^{th}$ century. The scope of the thesis is to measure, evaluate and define the threats of the existing pollutants, temperature and relative humidity for the materials met indoor.

To evaluate the air quality inside the museum a monitoring campaign was performed during summer-time period from 4 to 31/8/16. The experimental period was separated into 3 different periods. The *background days* where there was a monitoring of the library indoor according to the usual conditions, the *air condition days* where the air was conditioned for 8 hours and the *ventilation days* where natural ventilation took place for two hours a day (morning and midday). The Library was exposed to gaseous pollutants and the microclimate conditions, temperature and relative humidity, proved to be the most crucial threats for the book collection. Temperature and relative humidity indicated that for the study period the measured levels were out of the recommended limit values, presenting also a wide range of fluctuations. This could possibly pose impact on books in long term basis, leading to possible cracking of the paper, breaking of the fibers, damage by embrittlement and warping of the cover. Furthermore, pollutants such as $SO_2$, NOx and $O_3$ presented to be higher than the acceptable limits, which can also lead to embrittlement and discolorance of the paper and weakening or powdered surface to the leather covers of books. To sum up, given that the cultural value of those exhibits is huge and their sensitiveness to environmental conditions is quite high, extensive monitoring for longer period and evaluation of the findings is suggested in order to obtain an integrated knowledge of the possible threats under extreme weather conditions (cold or heat waves) that seem to influence the indoor air quality of the Library.

# 1. INTRODUCTION

Indoor air quality in historical buildings and museums is receiving growing concern nowadays. Air pollutants contribute significantly to the deterioration of library and archival materials. The exposure of artifacts to gaseous pollutants, airborne particles (emitted indoor or penetrating from the outdoor environment), as well as monitoring and controlling the indoor microclimatic conditions (temperature and relative humidity) is of major importance for the applied conservation and preservation of cultural heritage materials.

The long term serious effects, such as surface deterioration, color change and even weakening of the material may occur, especially for items composed of vulnerable materials like wood, paper, leather. Gaseous contaminants especially sulfur dioxide, nitrogen oxides, ozone catalyze harmful chemical reactions that lead to the formation of acid in materials. Particulate matter as well, creates discoloration deposition of reactive species such as acidic particles and alkaline particles. Thus, paper and leather are seriously affected due to their vulnerability to damage caused by acid. Paper becomes discolored and brittle. Lack of relative humidity can cause break and make the material fragile while high humidity can contribute to the development of mold and to the existence of microorganisms on exhibits. As far as the temperature is concerned, this can discolor, fade or blacken the paper.

This study will focus on the book collection of the Library of the Museum of Geoastrophysics of the National Observatory of Athens (NOA). We will try to define the Air Quality factors that could contribute to or even accelerate the decay processes. We will also refer information about the reasons triggered the study of the specific monument. The study has been divided into 8 chapters.

- *Chapter 1 Introduction*: Information about the area of interest and its historical value is provided. The scope of the study is also introduced along with the description of the parameters inducing the need of monitoring.
- *Chapter 2 Theory*: Air pollution and indoor pollution issues are briefly described.
- *Chapter 3 Book materials and Environment*: The possible impacts on cultural heritage artifacts, with emphasis on organic materials such as book type collections are discussed.
- *Chapter 4 Experimental*: The design of the experimental part is provided with details about the monitoring techniques and datasets that have been acquired in and out the Library of the Museum of Geoastrophysics of the National Observatory of Athens.

- *Chapter 5 Results of thermo hydrometric parameters*: The results of temperature and relative humidity in the Library are described and correlated with the ambient meteorological conditions in order to investigate the Indoor/Outdoor relations.
- *Chapter 6 Results of pollution measurements*: The results of the Library Indoor Air Quality (IAQ) in the aspect of the pollution (particulate and gaseous species) are studied. The Indoor to outdoor ratio (I/O) is investigated relatively to the ambient air pollution levels.
- *Chapter 7 Impact of Indoor Air Quality on the book collection*: The datasets of temperature, relative humidity and pollution are combined and an approach of risk assessment of the IAQ into the decay of the books collection is performed.
- *Chapter 8 Conclusions*: The findings of the study are compiled and future plans are set.

### 1.1 Historical information about the National Observatory of Athens

The National Observatory of Athens, founded in 1842, is the first scientific research institute in Greece and one of the oldest research institutes in Southern Europe. The construction of NOA was financed by the national benefactor Georgios Sinas, a successful banker in Vienna and ambassador of Greece in Austria, who was influenced by both Prokesch-Osten, the Austrian ambassador in Athens and the Greek-Austrian physicist and astronomer Georg Constantin Bouris. Bouris became the first director of Athens Observatory, and was also involved in the construction of its first building. The original Observatory building was based on a project presented by Eduard Schaubert and designed by the Danish architect Theophil Hansen.

The hill of the Nymphs, where the Observatory was selected to be built, is one of the seven hills of Athens, a sanctuary of the Nymphs in antiquity (Fig 1.1). It is also next to the Pnyka hill, where one of the early Observatories of the 5th century was located and where Meton's Heliotropion was placed. The hill of the Nymphs is aligned with one of the most celebrated and best preserved meteorological/astronomical observatories, the Tower of the Winds, also the emblem of the Royal Meteorological Society. The building was completed in 1846. The Observatory of Athens foundation ceremony took place in June 26 1842, the day of a Solar Eclipse.


**Fig.1.1** The National Observatory of Athens depicted on postal card of 19th century (National Observatory of Athens, 2016)

Nowadays, the following research themes are covered by NOA: a) astronomy, astrophysics and space sciences by the Institute of Astronomy, Astrophysics, Space Applications and Remote Sensing (IAADET), b) air quality, environmental monitoring, meteorology, natural disasters, climate and climate change by the Institute for Environmental Research and Sustainable Development (IERSD) and c) the physics of the Earth's interior and territorial deformations with remote sensing methods, seismology, geophysics, volcanology, satellite geodesy and marine seismology by the Geodynamic Institute (GI). The three Institutes of NOA are staffed by highly qualified scientific personnel and contribute to basic and applied research in areas of numerous scientific fields, while providing social services of strategic importance to the country.

## 1.2 The historical Library of the Museum of Geoastrophysics of the National Observatory of Athens

As mentioned above, the National Observatory of Athens is the first scientific research institute in the Greek State since its establishment in 1828, created at the same time keen interest within the country as well as abroad. This interest led to the creation of NOA Library, through donations of books and journals. The historical NOA Library is today hosted on the ground floor of Sina’s building, where rare books, journals and other important issues such as those of the first season of typography are kept (Fig. 1.2).

**Fig. 1.2**The NOA Library (National Observatory of Athens, 2016)

The period  in which head of the institution was Aiginitis (1890-1934), a large influx of magazines and books was held together with a systematic exchange of data and publications among respective institutions from all around the world. Through the years, attempt was made cataloguing 6685 volumes and 1802 books of which 22 are books of 16th and 17th century. Among them, there are many first editions of classical works of Aragon, Bessel, Buffon, Gauss, Laplace and others. Yet in the library today, several old books are preserved, such as the historical edition of Copernicus of 1536 '*De Revolutionibus Orbium Coelestium'*. In Figure 1.3 some pages of the valuable astronomical and scientific books accommodated in the Library of the museum are presented.

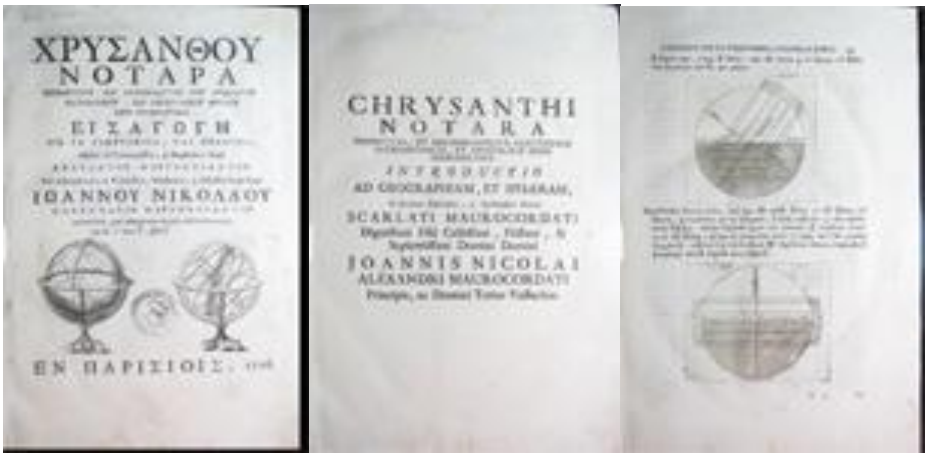



**Fig. 1.3** Pages from "Introduction in the Geographical and Global" by Chrysanthos Notaras, 1716, Paris (www.noa.gr/museum)

### 1.3 The location of the museum

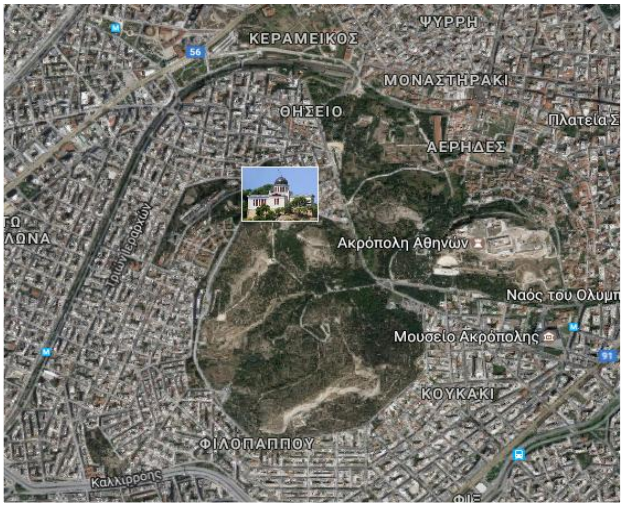



**Fig. 1.4** The location of the museum

The museum is situated in the historical center of the city of Athens (Fig.1.4). The Attica basin is defined by the mountains Egaleo, Poikillo, Parnitha, Penteli and Hymettus, while the coastline of the Saronic Gulf is its southern boundary. The geomorphology and topography of the basin and the fauna of these mountains are of enormous importance in climate parameters. The climate in the basin is a typical Mediterranean, with mild winters and hot dry summers. Furthermore, the basin is the most urbanized area in Greece, while 35% of the total population of the country resides in Attica and the 33% of all the country houses are in Attica, as well (ELSTAT 2014 census). Other factors affecting the climate of Attica are the number of cars as 52% of the private vehicles of the whole country are in this region (ELSTAT 2014 census) and the destruction of peri-urban forests. All these factors have created serious environmental problems as PM, ozone, NOx and often increased inversion of air temperature, etc. Regarding the position of the National Observatory of Athens, it is located in the top of Nymphs hill, a rocky hill of Athens, opposite the Temple of Thission and Acropolis, near (0,5-1,4 km) from traffic congested boulevards of Athens (Piraeus, Stadiou,Syngrou, Ermou. Athinas).

### 1.4 Scope of the study

The Sina building has been renovated quite a few times (building construction for roof restoration in 2008 and new shutters and wall painting in 2014 as well) since 1842 up to 2008 when it was converted into a museum. Nevertheless, the books kept in the library (in uncontrolled hydrometric conditions, without HVAC system) have been recorded but not conserved. Additionally most of them are mounted on book shelves instead of suitable display cases. The museum is actually situated in the center of the city of Athens; therefore the area is influenced by urban pollution. The Attica basin is subjected to long range transport and accepts influences by different sources of contaminants. Furthermore, the last five years during winter the levels of pollution were elevated mainly due to wood burning in domestic

heating systems, so a new source of pollution has been raised and could also influence the Library in case of infiltration occurs. Extreme weather conditions, cold or heat waves, may also encountered throughout the year. Despite the possible effect of both air quality and weather that also may affects the interior of the building, no effort has been done to investigate the interactions. Considering the status described above *this study focuses* on the following points:

- Monitoring of temperature, relative humidity and major air pollutants levels ($NO_x$, $O_3$, $SO_2$, CO, PM10 and chemical composition) in the Library room.
- Monitoring, to the level this was feasible, the same ambient parameters. Data from the meteorological station of NOA and the Air Pollution Station of NOA at Thissio will be used, since both are situated in the close vicinity of the museum.
- Correlating the indoor and outdoor (ambient) data in order to investigate the interaction of the environment with the library.
- Providing a risk assessment related to the impact of the Indoor Air Quality (IAQ) on the book collection of the library.

# 2. THEORY

According to the World Health Organization in 2015 the term “air pollution” refers to the contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere. Household combustion devices, motor vehicles, industrial facilities and forest fires are common sources of ambient air pollution. Pollutants of major public health concern include particulate matter, carbon monoxide, ozone, nitrogen dioxide and sulfur dioxide.

Air quality (indoor and outdoor) is considered to be one of the crucial environmental issues. The major culprits are the combustion processes in industries, transport, households and agriculture. The combustion processes are responsible for the emissions of various substances, having an adverse impact on the environment and human health. These are gases such as carbon monoxide (CO), nitrogen oxide (NO) and sulfur dioxide ($SO_2$), volatile organic compounds (VOCs) and particulate matter (PM). All the substances mentioned above are mostly primary pollutants as they are directly emitted in the air from different sources. Other substances, such as tropospheric ozone ($O_3$) and nitrogen dioxide ($NO_2$), are formed by chemical reactions in the air, known as secondary pollutants which stem from atmospheric reactions and transformations of primary pollutants.

Besides the negative effects on health and the environment, pollution is also harmful to many materials. At a low degree of air pollution, direct effects on materials are rather limited, but for long term exposition, more severe effects such as surface alteration, color change or even weakening of the material, may occur (Zorpas and Skouroupatis, 2015). As a consequence, it is important that vulnerable materials with a historical or cultural value must be kept under controlled atmospheric conditions. Environmental parameters such as, relative humidity, environmental temperature and atmospheric pollution can deteriorate several cultural exhibits and have a large impact on their proper preservation.

## 2.1 Major air pollutants produced outdoors

The term air pollutant refers to a substance suspended in the air that can be harmful to humans and the general ecosystem. It can be in the form of solid particles, liquid droplets or gases. The major pollutants, which are measured in this research, are described below.

***Nitrogen oxides ($NO_X$, $NO_2$, NO)***

Nitrogen oxide (NO) and nitrogen dioxide ($NO_2$) belong to the most significant air pollutants. Their role is important in the formation and destruction of tropospheric ozone. $NO_2$ is a reddish-brown gas with a characteristic sharp, biting odor. It is formed by the reaction of oxygen with nitrogen at high temperatures during combustion or lighting strikes. Specifically, nitric oxide is a principal by-product of combustion processes, arising from the high-temperature reaction between $N_2$ and $O_2$ in the combustion air and from the oxidation of organically bound nitrogen in certain fuels such as coal and oil (Flagan et al., 1988). The reactions 1.1, 1.2 are responsible for the oxidation of $N_2$ by the $O_2$ in combustion air. The first one is highly temperature sensitive and it has high activation energy in order to break the strong $N_2$ bond. Due to this high energy, the reaction proceeds at a slower rate than the combustion of the fuel (thermal NOx).

$$N_2 + O \rightarrow NO + N \quad (1.1)$$

$$N + O_2 \rightarrow NO + O \quad (1.2)$$

The second major NO formation combustion pathway is the oxidation of organically bound nitrogen in the fuel, such as coals and oil (fuel NOx) (Flagan et al., 1988). As far as the secondary pollutant $NO_2$ is concerned, $NO_2$ is associated with burning processes (emissions from cars, trucks and buses, power plants, and off-road equipment). NOx gases are formed whenever combustion occurs in the presence of nitrogen. In areas of high motor vehicle activities, the amount of nitrogen oxides can be very distinguishable. Emissions are dominated by fossil fuel combustion at northern mid-latitudes and by biomass burning in the tropics. In the atmosphere NOx reacts with volatile organic compounds (VOCs) and carbon monoxide to produce ground-level ozone through a reaction mechanism. In addition, agricultural fertilization and the use of nitrogen fixing plants also contribute to atmospheric NOx, by promoting nitrogen fixation by microorganisms Like sulfuric acid, nitric acid contributes to acid deposition and to aerosol formation.

As far as the human health effects are concerned, NOx concentrations can reduce visibility and increase the risk of acute and chronic respiratory diseases, such as emphysema or bronchitis. Moreover, NOx emissions can cause global cooling through the formation of OH radicals that destroying in that way methane molecules, countering the effect of greenhouse gases. Furthermore, NOx contributes to the brownish haze seen over congested

areas and to acid rain. Due to their vulnerability to dissolve in water, $NO_X$ can form acids which cause metal corrosion and fading and deterioration of fabrics.

### *Sulfur dioxide ($SO_2$)*

Sulfur dioxide ($SO_2$) is a colorless gas. $SO_2$ is formed from the oxidation of sulfur contained in fuel as well as from certain industrial processes that utilize sulfur-containing compounds. It reacts on the surface of a variety of airborne solid particles; it is soluble in water and can be oxidized within airborne water droplets to form sulfuric acid ($H_2SO_4$), which falls as acid precipitation or "acid rain".

Sulfur dioxide is released into the atmosphere mainly from anthropogenic activities, from stationary point sources, stationary fuel combustion and industrial processes (primarily smelting) and from natural sources, such as volcanic activity. Fossil fuels, including coal, oil and to a lesser extent gas, contain sulfur in both organic and inorganic form. Stationary fuel combustion includes all boilers, heaters, and furnaces found in utilities, industry, and commercial/ institutional and residential establishments (Flagan et al., 1988).

Sulfur dioxide can cause breathing difficulties causing constriction of the airways of the lung. This effect appeared to occur in people suffering from asthma and chronic lung disease. Furthermore, it reduces visibility and it is toxic to plants. Specifically, $SO_2$ deposits on trees, lakes, soils and monuments leading to their deterioration and adverse effect on aquatic life. It dissolves in water, forms an acid contributing to acidification of soils and waters and subsequent loss of biodiversity, often at locations far removed from the original emissions.

### *Carbon monoxide (CO)*

Carbon monoxide (CO) is a colorless, odorless gas. It is formed by incomplete combustion of carbon containing fuels. The major source is road transport, vehicle exhaust, with residential and industrial combustion making significant contributions. Moreover, cigarette smoking and emissions from natural sources such as volcanoes and wildfires contribute to its formation.

Carbon monoxide reduces ability of red blood cells to carry oxygen to body cells and tissues. This leads to headache and anemia. Low exposures can aggravate cardiac ailments, while high exposures cause central nervous system impairment or death. WHO suggests that the exposure in high carbon monoxide concentration (100 $mg/m^3$) should be less than 15 minutes in short term peak exposure, 1 hour in excess exposure (WHO, 2011). At high levels it causes coma, irreversible brain damage and death. It also plays a role in the generation of ground-level ozone.

***Ozone ($O_3$)***

Ozone ($O_3$) is a secondary pollutant and it is not emitted directly into the air. It is a bluish gas, soluble in water that is created in the troposphere by chemical reaction of NOx and VOCs in the presence of heat and sunlight (Fig. 2.1).

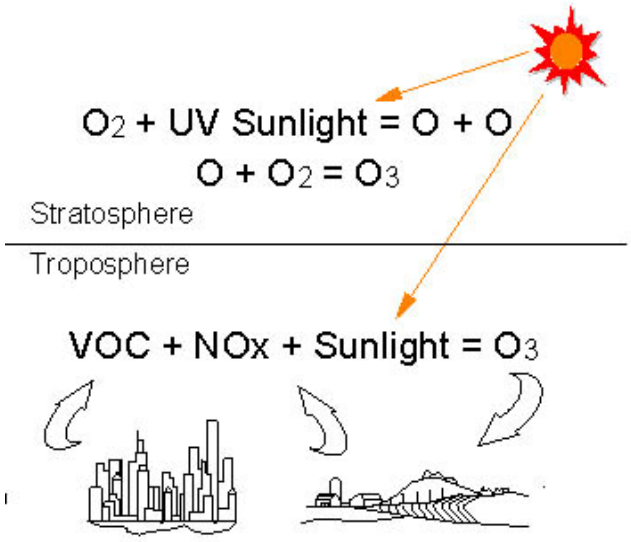



**Fig.2.1** Ozone formation (Chameides, 2010)

Ozone can irritate lung airways leading to inflammatory reactions. It is also able to cause wheezing and coughing especially among those with respiratory and heart problems. Repeated exposure can cause permanent lung damage increases incidence of respiratory symptoms, respiratory hospital admissions and mortality. Ozone can cause irritation to eyes. Ozone damages leaves of trees and other plants. It decreases the ability of plants to produce and store food, and reduces crop yield. It also affects buildings and building materials.

***Particulate Matter (PM)***

Particulate matter (PM) is composed by liquid and solid particles, suspended in the atmosphere through various natural and anthropogenic processes. The term “aerosol” is often used synonymously with PM. An aerosol includes both the particles and all vapor or gas phase components of air.

The types of PM differ depending on their shapes and sizes, chemical composition, optical properties and emission sources. Natural aerosols are emitted into the atmosphere by natural processes such as sea spray, volcanoes eruptions, windblown dust from arid and semi-arid regions, terrestrial biomass burning and others. Meanwhile, manmade aerosol are generated from combustion or emission from industrial, welding, and vehicle exhaust or

produced intentionally for commercial uses (i.e. flame reactor aerosol that produces nanoparticles) (Dayou et al., 2014).

As it mentioned above, particles are either emitted by ejection directly into the atmosphere (primary aerosol production), or formed in the atmosphere from precursor gases by physical and chemical processes (secondary aerosol production). Moreover, they are often produced by atmospheric gases reacting and condensing, or by cooling vapor condensation (gas to particle conversion), such as organic particles from oxidation of $SO_2$ (Huang, 2009). As for their dimensions, particulate matter is divided into fine and coarse particles. Fine particles have diameters less than 1 μm, while coarse particles are the largest aerosols with diameters higher than 1 μm. Sometimes the size of 2.0-2.5 μm is set as the threshold for characterization of fine and coarse particles. Figure 2.2 shows their number and volume density distribution. The size of aerosols is an important factor concerning their lifetime and chemical interactions in the atmosphere. Fine particles are emitted through combustion processes or are formed in the atmosphere from chemical processes taking place in precursor gases. Coarse mode particles are emitted in the atmosphere with mechanical processes (e.g. windblown dust) and dry deposition is the most effective removal process, due to their larger size (Nikitidou, 2013).

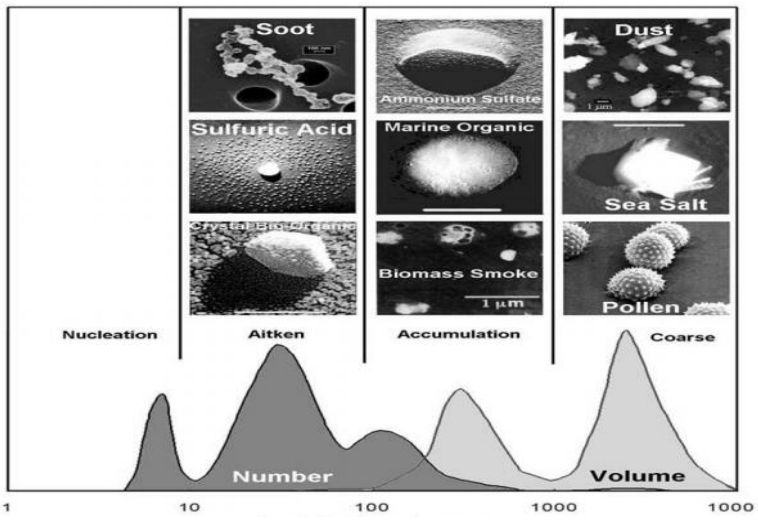



**Fig 2.2** Idealized number and volume distribution of atmospheric aerosols (Huang, 2009)

Particulate matter can reduce visibility and cause a variety of respiratory problems. It is also linked to cancer. Particles, smaller or equal than 10 μm can be inhaled into the deepest parts of lugs. Fine particles more than 2.5 μm are capable to pass from the lugs into the blood

supply. It can also corrode metal as well as it is capable to erode building and sculptures, and soil fabrics.

### 2.2 Sources of air pollutants

The sources of air pollutants can be classified into two major categories depending on the locations, activities or other factors responsible for their emissions.

**Anthropogenic (man-made) sources.** The anthropogenic sources are mostly connected with burning of fuels. These can be mobile sources, such as motor vehicles and stationary sources such as manufacturing facilities, factories, furnaces and other types of fuel burning devices. Moreover, fumes emitted from paints, sprays, varnishes and last but not least waste deposition strategies in landfills which are responsible for methane generation.

**Natural sources.** These sources are nature generated. They are related to volcanic eruptions with the production of sulfur, chlorine and ash particles. Also, to wildfires releasing smoke and carbon monoxide to the atmosphere, sea sprays and dust storms.

### 2.3 Major air pollutants indoors

According to Environmental Protection Agency (EPA) 2017, Indoor Air Quality (IAQ) is referred to the air quality within and around buildings and structures, related to the health and comfort of building occupants. The term indoor air is usually referred to nonindustrial indoor environments: office buildings, public buildings (schools, hospitals, museums) and private dwellings.

Indoor pollutants generated within the building of a museum, mostly originate from the out gassing of structural and decorative materials, heating plants, activities of visitors and staff. In special cases, the materials that artifacts are made of or exhibited by, such as glass or the construction of a showcase, emit significant amounts of polluting gases. Consequently, the pollutant accumulation is higher indoors.

Indoor pollutants can be classified in the following categories:

- Human activities within the building
- Pollutants emitted from materials
- Pollutants produced by HVAC systems.

***Pollutants emitted from human activities***

The quality of the air in a building is strictly related to the kind of use of the indoor space as well as to the activities of its inhabitants. For example, smoking and cleaning affect directly IAQ and result to the increase of pollutant accumulation.

***Pollutants emitted from materials***

Structural materials and equipment consist, as well, indoor polluting sources. Equipment of a building, such as carpets, furniture, paints, varnishes, emit pollutants, depending on their chemical composition which can play an important role in IAQ levels. Besides, the use of low emissivity materials can lead to the reduction of emergency ventilation and therefore of the building energy consumption.

Furthermore, the organic compounds such as acetic acid, formic acid and formaldehyde tend to be the most damaging, causing corrosion of metals and calcareous materials, and sometimes attacking pigments, paper and textiles (Blades et al., 2000).

- Acetic acid is given off by wood, wood products and certain adhesives and sealants.
- Formic acid is emitted from some woods and when oil-based paint dries.
- Formaldehyde is emitted chiefly from glues and binders in particleboard and composite materials.

All these materials are frequently used in the construction and fitting out of museums, galleries, archives and libraries. Usually but not always, galleries and storerooms have sufficient ventilation to keep carbonyl concentrations at low levels in the rooms themselves. The big problems tend to arise in closed storage containers and display cases, where carbonyls from their construction materials, finishes, adhesives or contents can build up in concentration.

***Pollutants introduced by HVAC Systems***

The term HVAC (Heating Ventilation Air Conditioning) refers to equipment that provides heating, cooling, ventilation and humidity control in order to create and maintain the comfort conditions inside a building. In addition, a well designed HVAC system via pressure control and filtration isolates and removes contaminants and odors in indoor environment, ensuring indoor air quality. Very often though, the HVAC system is responsible for increasing the concentration of indoor pollutants and therefore to poor air quality in the internal environment of a building.

## 2.4 Main mechanisms that control indoor environment

The change rate of indoor pollutant concentrations is mainly guided by the outdoor air pollution, the transport between the indoor and outdoor environments and the deposition of indoor surfaces (Fig.2.3). The transport between them is controlled by the ventilation rate which represents the tightness of the building shell, cracks, etc. and depends on the pressure field inside and outside the microenvironment (Halios and Helmis, 2007). Specifically, this rate (α) is expressed with air changes per hour ($h^{-1}$) and depends on the structural features of the building, the meteorological conditions and the indoor conditions and habits of the people and staff inside the building. Moreover, there are processes that occur on surfaces including heterogeneous reactions and the direct deposition, these are expressed with the parameter of deposition velocity (Vd). This parameter is defined as the ratio of the pollutant flux to a surface to the free stream concentration (Nazaroff and Cass, 1986).

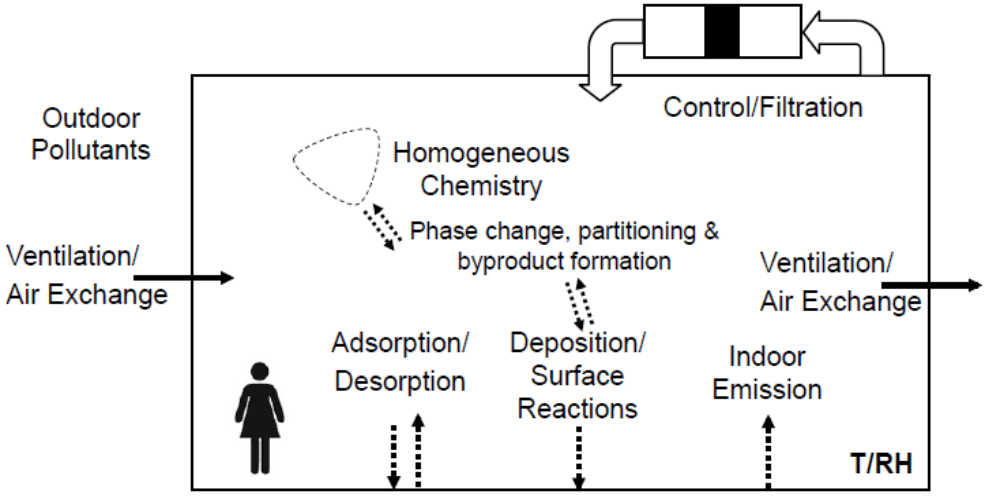



**Fig.2.3** Emission, transport and control of pollutants (Stephens, 2014)

# 3. BOOK MATERIALS AND ENVIRONMENT

## 3.1 Paper and Leather

### 3.1.1 Paper

Paper, is a heterogeneous mixture of plant material such as cellulose, hemi-cellulose, lignin and other components. Depending on the raw material used for its production method, the time and the use for which it is intended, the paper may contain various components (Zervos, 2015).

**Fig.3.1** Cellulose fibers (Gertz)

The natural cellulose is an organic compound with formula $[C_6H_{10}O_5]_v$. The chains of cellulose, because of their chemical composition and their formation, have a strong tendency to agglomerate, creating high class areas (crystallinity). The areas where there is a big parallelism of the cellulose macromolecules, crystalline regions are formed. Thus, the remaining areas are classified as amorphous. The mobility of the chains in the amorphous regions provides flexibility to the paper, while the stabilization of the crystalline chains provides strength and elasticity (Klemm et al., 1998). The hemicelluloses are polysaccharides that play an important role in linking the paper fiber during manufacture (Hon, 1981), but act as photosensitizers in the paper exposure to light, absorbing energy and triggering photochemical reactions. Natural lignin is a polymer which is sensitive to UV light and to the oxidative action of air oxygen. Lignin also acts as an antioxidant, protecting cellulose.

Background paper produced before 1850, often called paper from rags (rag paper) and contains almost exclusively cellulose, and very small amounts of hemicelluloses and lignin (Fig. 3.1). Especially cotton papers consist almost exclusively of very good quality cellulose. The rags of paper, due to the high content of good quality cellulose, the pH of the gelatine contains usually has good resistance to aging (Barrett, 1989). Paper that has been produced since 1850 has been made from wood pulp. Wood, besides cellulose and hemicelluloses, contains large quantities of lignin. Thus, this paper, according the pulping method may contain from traces of lignin until significant amounts of lignin. Also, it usually contains rosin and aluminum sulfates which makes it acidic. The lower the pH and the normally worse quality of cellulose containing make it chemically unstable and low resistance to aging (Wilson, 1970).

The paper is a hygroscopic material and in usual conditions (temperature 20-25ºC and 50-60% relative humidity) absorbs about 5-10% of its weight in water, while this percentage can reach 25 to 27% when relative humidity becomes 100% (Zervos, 2015) . The cellulose ability to absorb water vapors is significantly affected by the way of its drying. With water absorption, the paper swells. Furthermore, it is worth mentioning than high relative humidity levels can create growth of mold and mildew, cockling of paper and parchment, flanking ink, warping of the covers of books and leads to biological damages by organisms. Low relative humidity makes the archival collection brittle and susceptible to cracking.

### 3.1.2 Leather

Leather is durable and flexible material created by tanning animal rawhide and skin, often cattle hide. The uses of leather range from clothing to bookbinding or furniture covering. It is produced by processing vyrsas (pelt, rawhide) of mammals and consists mainly of a protein, collagen. Desirable properties of skin (strength, softness and flexibility) achievable by the tanning step of the process, making it immune to the action of microorganisms. The skin consists of entangled bundles of protein fibers, which can change their relative positions as the skin is alive. When it dies, the fibers shrink and stick together (Zervos, 2015). Essentially, the purpose of tanning is the fiber separation by means of the chemical treatment and their lubrication, so that they can move one relative to the other. So skin that has been tanned properly retains the properties of elasticity, durability and wears resistance. Moreover, it continues to breathe by allowing water vapor to pass through but remained relatively impermeable.

The natural fibers of leather break down with the passage of time. Acidic leathers are particularly vulnerable to red rot (Fig. 3.2), which causes powdering of the surface and a change in consistency. Damage from red rot is aggravated by high temperature and relative humidity. Exposure to long periods of low relative humidity (below 40%) can cause leather to become desiccated, irreversibly changing the fibrous structure of the leather. Chemical damage can also occur from exposure to environmental factors, including ultraviolet light, ozone, acid from sulfurous and nitrous pollutants in the air, or through a chemical action following any treatment with tallow or oil compounds. Both oxidation and chemical damage occur faster at higher temperatures.

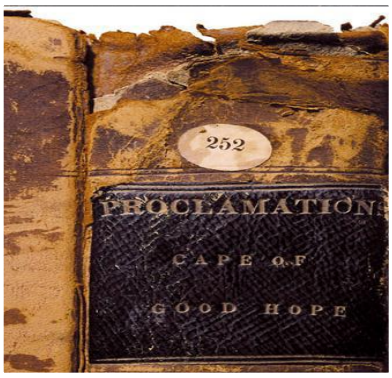



**Fig.3.2** Formation of red rot (Zervos, 2015)

### 3.2 Air pollution in libraries

Temperature, relative humidity and air quality all affect the long life of libraries and archival collections. In this chapter, the effects of these factors will be discussed concerning cultural heritage materials, especially library archrivals, collections and materials of the exhibition areas.

#### 3.2.1 Gaseous pollutants control in Libraries

Pollutants contribute significantly to the deterioration of library and archival collections. There are many gaseous pollutants that have been identified as dangerous posing a risk to book collections and archival materials. Damage to artifacts is cumulative and irreversible. Either exposure is long term with low levels of pollutants or short-term exposure with high pollutant concentrations, both can cause damage to objects. Especially with organic materials (e.g., papers, textiles, animal skins), all damage is not immediately visible.

According to Janusz Czop in *Air pollutant depositions in museums* (2007), air pollutants are divided in two categories depending on their origin, if they are internal, generated within the building or external, coming from outdoors (Fig. 3.3). The two groups subdivided, both of them, in gaseous and particles respectively. Gaseous contaminants, especially nitrogen oxides, sulfur dioxides and ozone are responsible for catalyzation harmful chemical reactions that form acid in materials. This process contributes to the creation of serious problems for papers and leathers, which are sensitive to damages caused by acid. Paper becomes discolored and brittle, and leather becomes weak and powdery (Ogden, 2007). Particulates, especially soot, abrade the materials, soil and disfigure them.

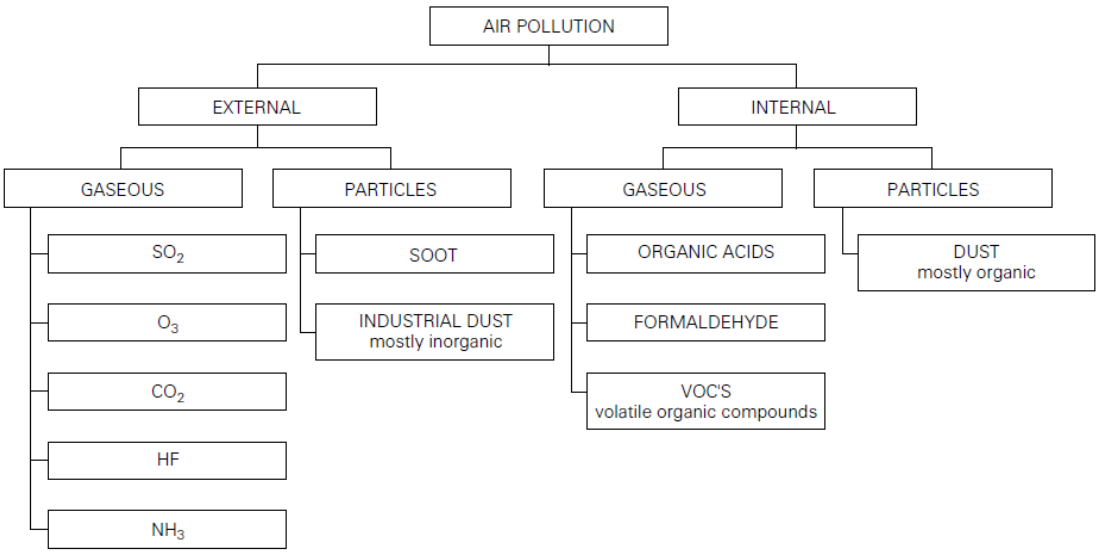



**Fig. 3.3** Two groups of air pollution (Czop, 2007)

The natural aging of paper is attributed to both endogenous and exogenous factors (Area and Cheradame, 2011). The cellulose macromolecules' properties and the industrial processes of paper production belong to the endogenous parameters. The conservation conditions (temperature, humidity, illumination), the contamination of the air with pollutants and the use of books consist the exogenous contributors. The degradation of the paper could be chemical (acid or enzymatic hydrolysis, alkaline degradation and oxidative degradation), thermal (due to temperature levels and variations) and radiation induced decay (exposure to UV/Vis radiation). The role of air pollution is crucial. The presence of air pollutants could be critical for the fate of the book collection, especially in exhibition areas or storage rooms with uncontrolled micro-environment parameters, mainly by the aspect of acid hydrolysis processes. Books or archival material stored in buildings in polluted areas could be characterized by increased acidity due to absorption of air contaminants (Daniel et al., 1990; Daniel, 1996; De Feber et al., 1998; Havermans and Steemers, 2005).For instance, according to ASHRAE 2015, "*Heating, Ventilating, and Air-Conditioning APPLICATIONS*", as far as sulfur dioxide is concerned, on cellulosic materials, such as paper, including historic wallpaper and textiles, where it catalytically hydrolyzes to $H_2SO_4$. $H_2SO_3$ and $H_2SO_4$ or absorbed directly onto these materials (the acid depolymerizes the cellulosic structure, and though damage is invisible, affected materials are embrittled and weakened). Moreover, it breaks down the molecular structure of leather weakening the material as the surface becomes powdery and is easily abraded (red rot).

In the case of nitric oxides, nitrous and nitric acids can damage the same acid-sensitive materials attacked by sulfuric or sulfurous acids. $NO_2$ enhances deterioration effects of $SO_2$ on leather. Nitrogen pollutants fade certain inks as well as organic pigments in illuminated manuscripts.

Furthermore, ozone embrittles fabrics, textiles, and cellulosic materials. Affects, also, leather, parchment, and animal skins. It also causes discoloration of photographic prints. Nitrogen oxides ($NO_x$) and ozone ($O_3$) in high relative humidity environments enhance the $SO_2$ uptake (Johansson et al., 2000; Johansson and Lennholm, 2000), catalyzing therefore the hydrolysis reactions. For such cases the storage of paper material under dry humidity is usually recommended targeting to elimination of the gaseous uptake. Finally, as far as the Particulate Matter is concerned, it is able to abase the surfaces and cause disfiguration to books.

### 3.2.2 Temperature and Relative Humidity control in Libraries

Temperature and relative humidity are of major importance for the preservation of library and archival collections. Extreme values of these are able to lead to the damage of the materials. Heat accelerates deterioration. The rate of most chemical reactions, including deterioration, is approximately doubled with each increase in temperature of 18°F (10°C) (Ogden, 2007). As for the relative humidity, in high levels creates a moisture environment which is capable to promote adverse chemical reactions in materials. The combination of these high levels with high temperature leads to mold growth and insect activity. On the other hand, very low relative humidity, for instance in heating buildings may cause desiccation and embrittlement of some materials.

Variances in temperature and relative humidity are also damaging. Library and archival materials are hygroscopic, readily absorbing and releasing moisture. They respond to diurnal and seasonal changes in temperature and relative humidity by expanding and contracting. Dimensional changes accelerate deterioration and lead to such visible damage as cockling paper, flaking ink, warped covers on books, and cracked emulsion on photographs. Mild changes appear to be buffered by certain types of storage enclosures and by books being packed closely together (Ogden, 2007).

# 4. EXPERIMENTAL

In this chapter the summer campaign performed for IAQ monitoring in the library of the National Observatory of Athens and all air monitoring equipment used for indoor and outdoor monitoring will be presented, in relevance to their operation principal and the main parameters have been measured.

## 4.1 Description of the library

This experiment concerns the measurement of air pollution inside the building of the Library of the Museum of Geoastrophysics of the National Observatory of Athens and the parallel comparison and correlation of the data to those extracted outdoor. The interest was focused on that specific area, as it hosts numerous scientific journals and books from the 16th century (Fig. 4.1). The main characteristics of the library are provided in Table 4-1.

**Table 4-1.** Main characteristics of the monitoring area and building.

| **Characteristics** | **Description** |
|---|---|
| Area | Urban background, historical center of Athens, away from main avenues, close to road |
| Age of building / floor | Approximately 170y / ground floor |
| Staff / visitors /smoking | 1-5, not permanently in the area / occasionally / no |
| Ventilation / usual condition | no (natural or air condition for short periods) / without HVAC, closed windows and door |
| Covering materials | None |
| Main materials | Books: paper, parchment, leather |
| Other materials | Furniture: wood<br>Roof: metallic remaining<br>Walls: paint |

**Fig.4.1** Interior of the Library of National Observatory of Athens.

## 4.2 General description of the monitoring procedure

The measurement of atmospheric pollution inside the building of the museum is a major issue for the preservation and conservation of historical materials hosted in the library. The most common indoor gases that pose a risk to cultural property, are gases such as sulfur dioxide, nitrogen oxides, ozone and carbon monoxide influenced by the exterior environment, acids such as acetic acid, formic acid which gained from boards, carpets, and cleaners, as well as many other materials and products that can also be generated by processes such as ventilation, cleaning, and heating or cooling or from activities of people and staff.

The amount of a given pollutant that is generated depends on the nature of the source materials (Andersen et al., 1975), the kinds and intensity of indoor activities (Chuang et al., 1992), and the efficiency of air-exchange and ventilation systems. The instrumentation used for monitoring of the indoor air quality inside the museum environment, is described in details in this chapter. The term "monitoring" refers to the determination of the presence of gaseous compounds and particles in air, that may cause damages to collections either directly or through conversion into secondary products (Grzywacz, 2006).

As far as the experimental procedure is concerned, equipment for monitoring gaseous and particulate species (with regard to their chemical composition) and temperature and relative humidity as well was placed in the study area. The series 360 of Horiba Analyzers used to monitor the gaseous species: CO was determined by means of the APMA-360 Carbon Monoxide Analyzer, APNA-360 Nitrogen Oxide Analyzer used for $NO_x$, APSA-360 Sulfur Dioxide Analyzer for $SO_2$ and APOA-360 Ozone Analyzer for $O_3$. PM10 aerosol samples

were collected on Quartz filters. The filters weighed in the weighing room of the Atmospheric Chemistry Laboratory of NOA with a 6-digits Mettler Toledo MX-5 balance operating in controlled conditions of temperature and humidity. A Rotronic MP101A-T7-W4W thermo hydrometer and a Tiny Tag TGP-4500 logger were operated for the monitoring of the relative humidity and temperature. The set up of the equipment inside the library is presented in Figure 4.2.

**Fig.4.2** Experiment equipment for gaseous species, particulates, temperature and relative humidity.

The experimental period lasted 26 days from 4/8/2016 up to the 31/08/2016. During the first five days the equipment operated in indoor conditions without interventions in order to study the pollutants variability under the regular conditions encountered in the library (‘*background’*, closed windows, natural lightning, no heating or air condition system). On 10/8, 12/8, 16/8 and 18/8 an intervention took place by the operation of air-conditioning equipment for a period of 12 hours (air-*‘conditioned period’*). Subsequently, during 22/8, 24/8 and 26/8 ventilation took place by opening the windows from 9.00-10.00 a.m. and 13.00-14.00 p.m. (‘*natural ventilation period*’), periods considered representative concerning the working hours of the library staff and the presence of visitors also in the area. Before and after the measurements the microenvironment parameters were cross checked for a few days by simultaneous operation in the weighing room of the ACL. Finally, the equipment was removed from the museum on 31/8 and then CO and $O_3$ analyzers were placed in the Thissio Air Pollution Station, sampling ambient air in parallel with the corresponding fixed equipment of the station, in order to inter calibrate them. It should be mentioned that during

the indoor measurements the Thissio Air Pollution Station was also operating providing the levels of pollution in the area out of the library.

### 4.3 Indoor pollution monitoring equipment

***Gaseous species***

For measuring the gaseous species, automatic analyzers taking advantage of ultraviolet absorption, chemiluminescence, non-dispersive infrared analysis and flame ionization detection have been used. All analyzers are able to provide one minute resolution results, but in the present work 30 min averages were available. Table 4-2 summarizes the models of gas measurements used in the experiment as well as their operation principles. All these systems apply unique cross-flow and multi-flow modulation methods. The first is an analytical technique based on the difference between the sample gas and a zero gas, identical to the sample. Specifically, it measures certain components from the sample gas comparing it with the zero which does not contain them. This comparison creates an alternating signal which provides stable and accurate measurements.

**Table 4-2.** AP-360 Horiba series specifications (Kato and Yoneda, 1997)

| **Pollutant** | **CO** | **$SO_2$** | **$O_3$** | **NO, $NO_2$, $NO_X$** |
|---|---|---|---|---|
| **Model** | APMA-360 | APSA-360 | APOA-360 | APNA-360 |
| **Principle** | Cross-flow modulation, infrared absorption technology (NDIR) | UV Fluorescence (UNF) | Cross-flow modulation, Ultra-violet absorption method (NDUV) | Cross-flow modulation, reduced pressure chemiluminescence (CLD) |

Details for each are provided below:

- **APMA-360 Carbon Monoxide Analyzer:** The analyzer of CO elements is based on infrared light absorption at specific frequencies. Figure 4.3 shows the parts of APMA-360 Carbon Monoxide Analyzer which contain a light source, a cell, a detector, an optical filter and a flow modulator (Kato and Yoneda, 1997). Fixed amounts of sample gas and zero gas in succession entered into the measurement cell and an alternating current is produced as a signal from the different absorption strengths. The oxidation catalysts, used by the system, remove only the carbon monoxide from the sample gas

so that it can be used as a zero gas. As a consequence, if there are any interventions in the sample gas, this does not cause any problem as they exist also in the zero gas.

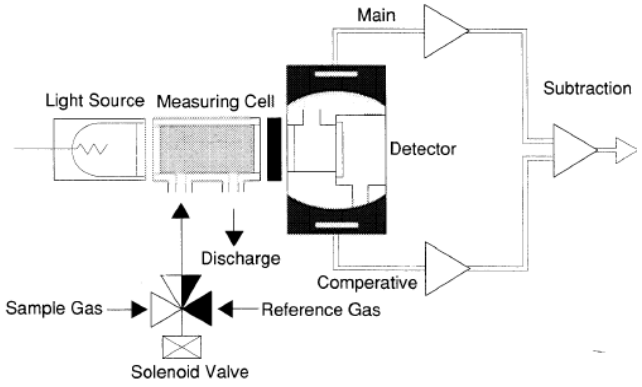



**Fig. 4.3** CO analyzer:Cross-flow Modulation Principle.
Non-dispersive Infrared Absorption (NDIR) Technology (Kato and Yoneda, 1997))

- **APOA-360 Ozone Analyzer:** This method is based only on absorption of specific wavelenghts of ultraviolent light. It provides accurate and stable measurements applying the cross-flow modulation method described above. Figure 4.4 shows the main principles of the ultraviolent light absorption using cross-flow modulation.

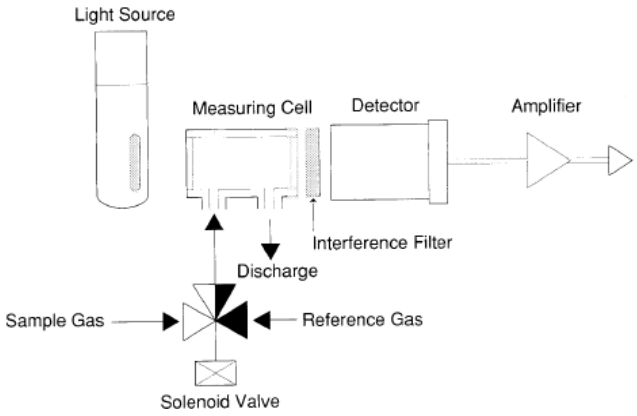



**Fig.4.4** O3 analyzer: Cross-flow Modulation Principle.
Ultra-violet Absorption (NDUV) Technology (Kato and Yoneda, 1997)

- **APNA-360 Nitrogen Oxide Analyzer:** The APNA-360 monitors atmospheric NO, $NO_2$ and $NO_x$ concentrations using a multi-flow modulated semi decompression chemiluminescence method. Specifically, there is a chemical reaction when nitrogen oxide comes into contact with $O_3$, producing $NO_2$. Chemiluminescence is produced by a part of generated $NO_2$ molecules which are in excited state in the 600 to 3000nm wavelength region as they return to the ground state. The strength of the light gives

information about the concentration of nitrogen oxides through the detection of a semiconductor photo-sensor. NO concentration is measured by the concentration of nitrogen oxides in the air, converted by a pre-processing device and measured by CLD method.

In Figure 4.5 the main principles of the nitrogen oxide analyzer are presented using multi-flow modulation method. It is assumed, that A is the sample gas, B is the sample gas processed by the NOx converter and C is the zero gas. When the introduction of these gases take place in the sample cell in a fixed cycle, signals are generated from the detector in the order A,B,C. However, component A is not read in the NO signal processing and in the NOx is neglected. To sum up, The APNA-360 employs an independent, internal method sampling device providing continuous monitoring and instantaneous gas analysis for monitoring the atmospheric pollution.

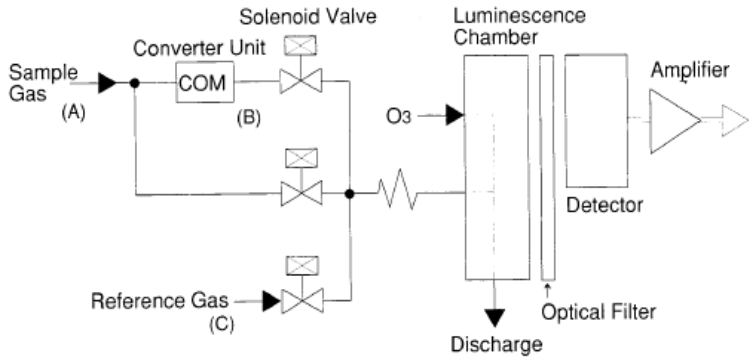



**Fig. 4.5** NOx analyzer: Multi-flow Modulation Principle.
Reduced Pressure Chemiluminescence (CLD) Technology (Kato and Yoneda, 1997)

- **APSA-360 Sulfur Dioxide:** The APSA-360 measures the concentration of sulfur dioxide ($SO_2$) using ultraviolet luminescence as the measurement principle. It is an independent detection device construction with an optical system which provides high levels of sensitivity and stability using a low background. A fluorescent light chamber minimizes of moisture influence. An aromatic HC cutter using a changeable permeable membrane system is built in (www.horiba.com). AP-360 series pollution monitors are easily upgraded due to their multi component configurations, installed in a compact, light-weight 19-inch frame. APSA-360 provides precise atmospheric pollution monitoring data.

***Particulate species***

**Partisol-FRM Model 2000 (PM10 Sampler)**

The Partisol Model 2000 Air Sampler is a flexible, cost-effective means of sampling particulate matter with filters using a PM10, PM2.5 or PM1 inlets. The apparatus has set the standard for high-quality low volume particulate matter sampling. The Partisol-FRM Air Sampler has USEPA PM-10 reference designation (RFPS-1298-126) containing a modified R&P PM10 inlet used at the entrance to the sampler providing a pre-cut at a 10 μm particle size. Moreover, it is used to protect the sample path against precipitation phenomena.

**Fig. 4.6** Partisol-FRM 2000. (www.thermo.com)

The main parts of Partisol-FRM Air Sampler are a filter exchange mechanism, a microprocessor with battery-backed internal data storage, an active volumetric flow control system and a pump (Fig. 4.6). A fan located in the filter compartment keeps the temperature of the sample filter not deviating by more than 5 °C from the ambient air temperature. Menu-driven software provides easy access to sampler functions.

The Partisol-FRM Sampler contains a filter exchange mechanism by pulling the mechanism's handle forward. The filters used must be remained in standard conditions of temperature and pressure and weighed before exposure and the same procedure must be followed and after use to determine the mass of the particulate matter collected during the 24-hour or other exposure time. The Partisol hardware stores the data to each collection period in its internal data logger for viewing and/or retrieval after the measurement. The information extracted include the total volume sampled ($m^3$), total collection time, and the average ambient temperature and pressure during the collection period. In addition, the device stores interval data records every five minutes to keep a record of the temperature of the ambient air and sample filter (www.thermo.com/air).

As for the operation principles are concerned, ambient air carrying particles passes through a single or multiple stage inlet system in order the desired size fraction to be achieved (Fig. 4.7). Consequently, the sample stream passes through a 47 mm diameter sample filter contained in the filter cassette. The flow rate remains constant due to a mass flow controller

downstream of the filter selected by the user (16.7 l/min by default). The sampler's microprocessor constantly alters the set point of the mass flow controller correspondingly with the latest measurements from ambient temperature and pressure sensors. The use of a flow controller minimizes pressure pulsations and provides a very constant flow rate result for proper size selection, fast flow audit and calibration processes. Furthermore, a field-proven AC-powered pump provides the vacuum necessary to draw the sample stream through the system, and operates with minimal maintenance requirements.

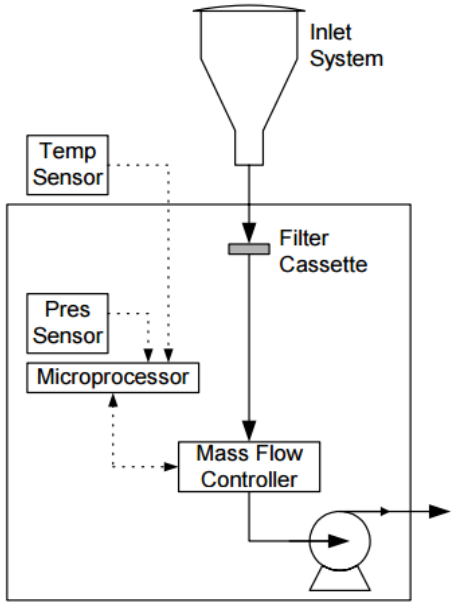



**Fig.4.7** Operation Principles of Partisol-FRM 2000.

The filters must be conditioned and weighed before and after the air sampling prion the chemical analysis.. The PALLFLEX Tissuquartz Filters 2500QAT-UP 47mm filters, used for the experiment, weighed in a specially designed room at the Atmosperic Chemistry Laboratory at Penteli with a 6-digits Mettler Toledo MX-5 Balance operating in constant conditions of temperature and humidity (20±3$^{o}$C and 40±5% RH respectively. During pre and post-sampling weighing the temperature was at 19-20$^{o}$C while the relative humidity was at the range of 40%.

### 4.4 Thermo hydrometric parameters: Temperature and Relative Humidity

Microclimate plays a significant role in the deterioration process of cultural heritage materials. These could be differently affected by the values of microclimatic parameters in time. Temperature and relative humidity in the environment are one of the most important causes of deterioration. Abrupt time changes and intense space variations of air temperature

and relative humidity assumed to induce stresses to several materials: this in turn creates cumulative and irreversible alterations of the physical and chemical properties which could accelerate the deterioration process (Corgnati et al., 2008).

***Tiny Tag TGP-4500***

The Tiny Tag TGP-4500 (Fig.4.8) is a waterproof logger which monitors temperatures from -25 to +85°C, and relative humidity from 0 to 100% using built-in sensors. It is designed for use in a wide range of indoor and outdoor or industrial applications. The coated RH sensor provides good resistance to moisture and condensation providing reliable and accurate measurements. Moreover, it has the capacity of saving data from 32.000 records and a low battery monitor. The logger requires Tinytag Explorer software and a USB cable (CAB-0007-USB). It is popular for applications, such as environmental monitoring, pharmaceutical manufacture, food processing and storage and conservation projects.

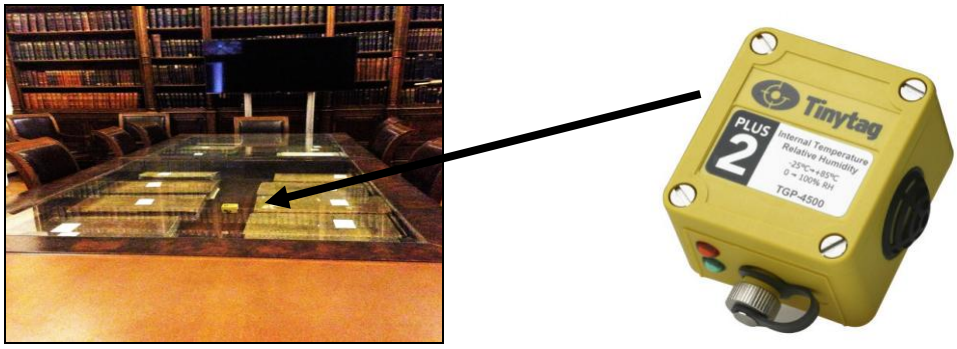



**Fig.4.8** Tiny Tag TGP-4500 and aspect from table book case in the Library.

***Rotronic MP101A-T7-W4W thermo hydrometer***

The MP101A-T7-W4W thermo hydrometer is manufactured by Rotronic. It is a probe that is ideal for measuring the humidity and temperature in air with the use of data loggers and transmitters. The probe used in meteorology and other applications, such as tunnels, airports, motorways. The unit can calculate humidity that ranges from 0% RH up to 100% RH. It also has the capacity to calculate temperatures ranging from -40 °C up

**Fig.4.9** MP101A-T7-W4W thermo hydrometer.

to +60 °C. The body of the unit is made of black polycarbonate, and it measures 15 mm in diameter, and 85 mm in length. It is connected with a datalogger in order to obtain automatically the values.

### 4.5 Outdoor atmospheric measurements

The external environment usually affects the interior space. Taking into account that parameters such as the relative humidity and temperature and the concentrations of particulate matter and various gaseous pollutants of building indoor could be affected by the external environment, along with the measurements performed inside the library, the same ambient measurements took place in the area surrounding the building of the museum.

Ventilation and meteorological conditions are the most important influencing factors affecting the concentration of pollutants. Outdoor pollutants can enter a building and pose a risk to collections. Naturally ventilated buildings have indoor concentrations of pollutants that could be nearly equal to the outdoor levels (Grzywacz, 2006). In particular, ventilation regulates the air entering and exiting a room. The major outdoor pollutants that are found inside museums and that pose a risk to cultural property are sulfur dioxide, nitrogen dioxide, nitrogen oxide, ozone and carbon monoxide. The equipment used for outdoor measurements was:

- Derenda low volume PM10 sampler with add-on sequential sampler. The operation principle is similar to Partisol sampler used indoor.
- CO Analyzer by Horiba. It was the same with the one used indoor.
- The Thermo 49i for $O_3$ monitoring: .The Model 49i UV Photometric Ozone Analyzer is a flexible, reliable device combining detection technology and easy to use menu software. The operation principle of that model is based on the fact that ozone ($O_3$) molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the ozone concentration, described by the Beer-Lambert Law.

$$\frac{I}{I_o} = e^{-KLC}$$

Where:

K = molecular absorption coefficient, 308 $cm^{-1}$ (at 0°C and 1 atmosphere)

L = length of cell, 38 cm C = ozone concentration in parts per million (ppm)

I = UV light intensity of sample with ozone (sample gas)

Io = UV light intensity of sample without ozone (reference gas)

Figure 4.10 shows the basic operation principle of the Model 49i UV Photometric Ozone Analyzer. The sample is drawn into the device through the sample bulkhead and is separated into two gas streams. One gas stream flows through an ozone scrubber to become the reference gas (Io) which then flows to the reference solenoid valve. The sample gas (I) flows straight to the sample solenoid valve. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A has the reference gas, cell B contains sample gas and the opposite. The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for many seconds to allow the cells to be empty. The Model 49i calculates the ozone concentration for each cell and gives the information about the average concentration to the front panel display, the analog outputs, and also makes the data available over the serial connection.

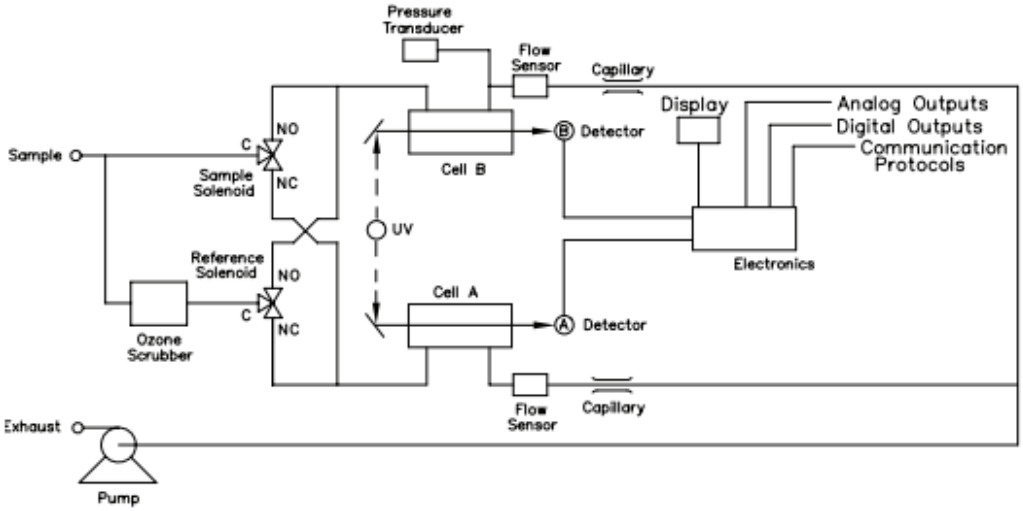



**Fig.4.10** Operation Principle of Thermo 49i UV Photometric Ozone Analyzer (www.thermo.com).

## 4.6 Chemical analyses of PM10 filter samples

Indoor and outdoor PM10 filter samples after sampling are treated as follows:

- **Calculation of mass concentration:** The mass concentration expressed in $\mu g/m^3$ is calculated by the equation $C = (m_f - m_i)/V$. C is the concentration, $m_f$ and $m_i$ the final and initial mass of the filter representing the aerosol collected on the filters versus the mass of the unused filter before use and V is the total volume of air collected for the selected period.

- **Determination of ionic composition:** Punches of 2 $cm^2$ from the quartz filters were extracted in an ultrasonic bath with 10mL of nanopure water for 45 min and were then filtered using syringe filters (PALL IC Acrodisc (PES), 0.45 μm, 13 mm) to remove any insoluble species. The acquired filtered solutions were analyzed by ion chromatography for the determination of the main ionic species concentrations (anions: $Cl^-$, $Br^-$, $NO^{-3}$, $SO_4^{-2}$ , $PO_4^{-3}$, $C_2O_4^{-2}$ ; cations: $NH^{+4}$ , $K^+$, $Na^+$, $Mg^{+2}$, $Ca^{+2}$). The analytical procedure is provided in details in Paraskevopoulou et al., 2014. The detection limit of the analysis was 20, 12, 40, 12 and 40 ppb for $NH^{+4}$ , $K^+$, $Na^+$, $Mg^{+2}$ and $Ca^{+2}$, respectively, while the corresponding detection limit for all anions ($Cl^-$, $Br^-$, $NO^{-3}$, $SO_4^{-2}$ , $PO_4^{-3}$, $C_2O_4^{-2}$) was 20 ppb. The reported concentrations were corrected for blanks.

- **Determination of OC and EC content:** The quartz filters (samples and blanks) were analyzed by a thermal optical transmission technique, using a Sunset Laboratory Inc. (Oregon) carbon analyzer according to Paraskevopoulou et al., 2014. A punch of 1 $cm^2$ was removed from the filter and loaded into the analyzer. OC and EC were determined using the EUSAAR-2 (European Supersites for Atmospheric Aerosol Research) protocol. Briefly, the first phase subsumes four stages of heating to 200, 300, 450 and 650$^oC$ in He atmosphere, while, during the second four-step temperature program, the sample is heated to 500, 550, 700 and 850$^oC$ in $He/O_2$ atmosphere. The detection limit of the analysis was 0.26 and 0.05 μgC $cm^{-2}$ for OC and EC, respectively. The reported results were blank-corrected.

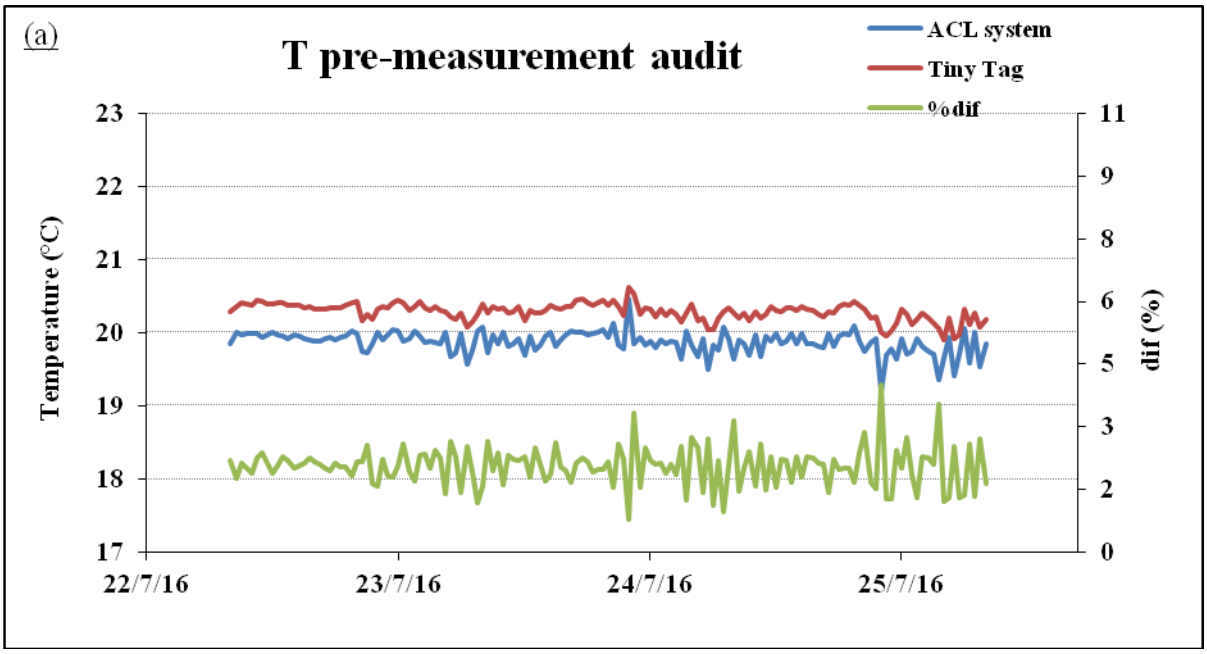
# 5. RESULTS OF THERMO HYDROMETRIC PARAMETERS (TEMPERATURE AND RELATIVE HUMIDITY DATA)

In this chapter indoor macro (library room) and microclimate (show case) conditions are analyzed and discussed. Moreover, there will be a comparison with simultaneous ambient (outdoor) measurements. The possible impacts on the materials met in the library will be assessed in Chapter 6 in total with the findings of indoor pollution.

## 5.1 Pre and post measurements audit of temperature and relative humidity

Before and after the experiment in the library of the Museum of Geoastrophysics of the National observatory of Athens (MG/NOA), parallel measurements of temperature (T) and relative humidity (RH) were conducted, in order to quantify the deviation of the two different systems used in the study: the ACL system and the Tiny Tag. The simultaneous monitoring took place in the weighting room of the Atmospheric Chemistry Laboratory of the National Observatory of Athens (ACL/NOA), under specific and regulated conditions. In the weighting room the temperature is adjusted at 20±3ºC and the relative humidity at 40±5%.

In Figure 5.1(a) the temperature pre measurement audit of the ACL and Tiny Tag apparatus is presented. Five minutes values for the period 22/7/2016 at 20:00 to 25/7/2016 at 20:00 were obtained. The two systems have the same variability and according to the findings the temperature range from 18.7ºC to 20.7 ºC and from 19.5 ºC to 20.9 ºC for the ACL system an Tiny Tag respectively with a mean of 19.9ºC and 20.3ºC for each case. The deviation between them was estimated at 1 to 4%.



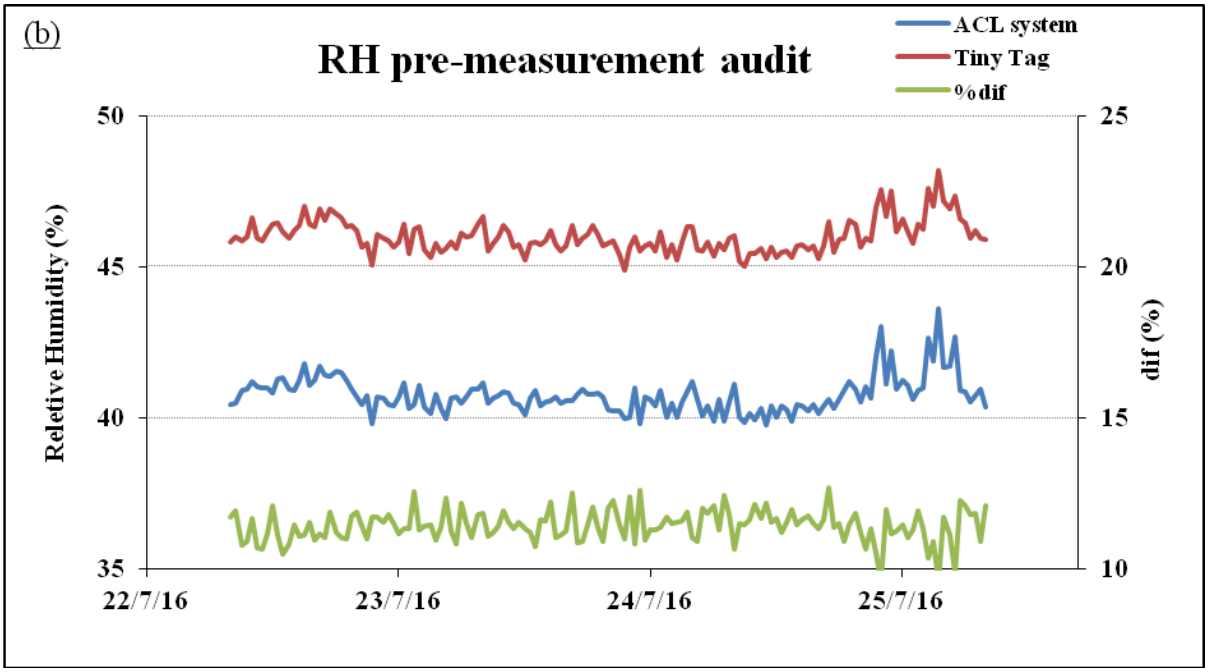



**Fig. 5.1** (a)Temperature and (b) Relative humidity pre-measurement audit with ACL system and Tiny Tag (5 minute intervals).

Likewise, for RH the pre measurements results are presented in the Figure 5.1(b). Relative Humidity has also the same variability for both systems with the values ranging from 38 % to 49 % and 44 % to 54 % for the ACL system and Tiny Tag respectively with a mean of 41 % and 46 %. The difference between the two systems was 10 to 13%.

Audit measurements were also carried out after the end of the experiment under the same conditions in order to identify the validity of the results through the consistency of the deviations. It is set hereby, first in order, the plot including temperature post measurements during the period of 10/9/2016 10.00 to 14/9/2016 10.30 a.m. (Fig. 5.2(a)). The two systems had again (as for the pre audit) the same variability and according to the findings the temperature range from 19.2ºC to 20.7ºC and from 20.3 C to 21.1ºC for the ACL system and Tiny Tag with a mean of 19.8ºC and 20.5ºC for each case. Finally, 3-4 % deviation was calculated for the T post audit, which is of the same order with the pre audit.

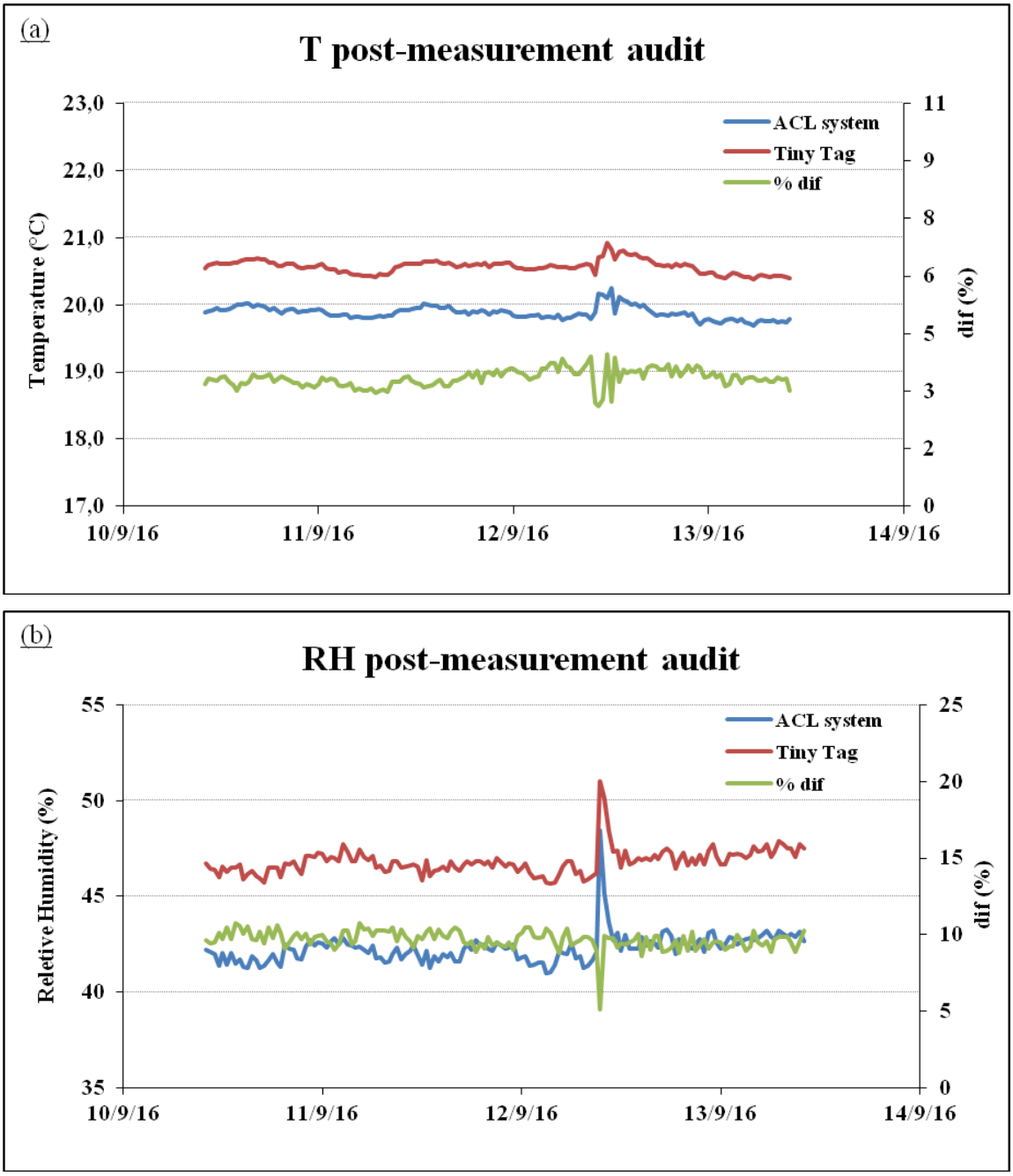



**Fig. 5.2** (a)Temperature and (b) Relative humidity post-measurement audit with ACL system and Tiny Tag (5 minute intervals).

Concerning the relative humidity, the difference between the two methods ranges at 5-11%, again in the same order with the pre audit. Relative Humidity was ranging from 40 % to 51 % and 45 % to 55 % for the ACL system and Tiny Tag respectively with a mean of 42 % and 47% (Fig.5.2(b)).

The two systems provide mean measurements within the limits have been set for the room with the exception of the tiny tag RH which is slightly increased above the upper threshold of 45% by about 5%. According to the findings and based on the stability of the

deviation between the two systems for both parameters (Table 5-1) we can be confident about the performance of the equipment during the measurements in the library. Also, it can be used the maximum divergence for the evaluation of the measurements within the museum which is 4% and 13% for temperature and relative humidity respectively.

**Table 5-1.** Presentation of the pre and post measurements deviation calculations for temperature (T) and relative humidity (RH).

| Parameter\Deviation | Pre meas. audit | Post meas. audit | Max % dif |
|---|---|---|---|
| **Temperature** | 1-4 % | 3-4% | 4% |
| **Rel. Humidity** | 10-13 % | 5-11 % | 13% |

### 5.2 Indoor temperature and relative humidity data and investigation of I/O relations

This subchapter refers to the measurements of the Library Museum of Geoastrophysics indoor environment (macroenvironment) and the comparison with the external measurements (outdoor or ambient) carried out simultaneously. The ambient conditions were provided by the Meteorological Station of the National Observatory of Athens operated in short distance from the museum. Scope of the parallel study is the investigation of the indoor to outdoor relation of the macroenvironmental thermo hydrometric parameters.

As it is already mentioned, the regular conditions in the museum do not support HVAC system (Heating, Ventilation and Air Conditioning). Hence, forward these regular conditions will be referred as '*background measurements*'. Nevertheless, throughout August three distinct periods were selected and two domestic air condition systems (available in the library and operated selectively only for short periods when visitors are present in the room) were operated for a few hours in order to investigate the cooling capability and the potential changes on T and RH, and the indoor air quality (IAQ) as a result. These intervals will be referred as '*air conditioned periods'*. Also, three additional periods were defined as '*natural ventilation periods*', followed by opening the windows of the library for certain time periods. They were selected based on the working hours of the staff as more realistic according to the day period that someone could be in the area and open the windows.

The Indoor-Outdoor measurements started at 14:00 p.m. on the 4$^{th}$ of August 2016 and ended at 10:20 a.m. on the 31$^{th}$ of the same month. Usually, during August the atmospheric temperatures are still increased and north-north eastern winds prevail this period of the year.

So, the impact of T and RH under summer extreme climatic conditions (heat) could be investigated during August. In the plot that lies hereby (Fig 5.3) the outdoor and indoor

measurements of temperature as well as of relative humidity are presented in time base of 5 minute intervals. The five minutes averages were selected as the optimum case for the investigation of the changes mainly during the short natural ventilation periods. By using 30-min or hourly data the resolution would be poor. The anti correlated behavior of T relatively to the RH in diurnal basis can be figured out for both indoor and outdoor measurements. Under increased temperature the relative humidity decreases and vice versa. Temperature maximum and humidity minimum is located at midday, whereas during night or early in the morning RH and T are maximized.

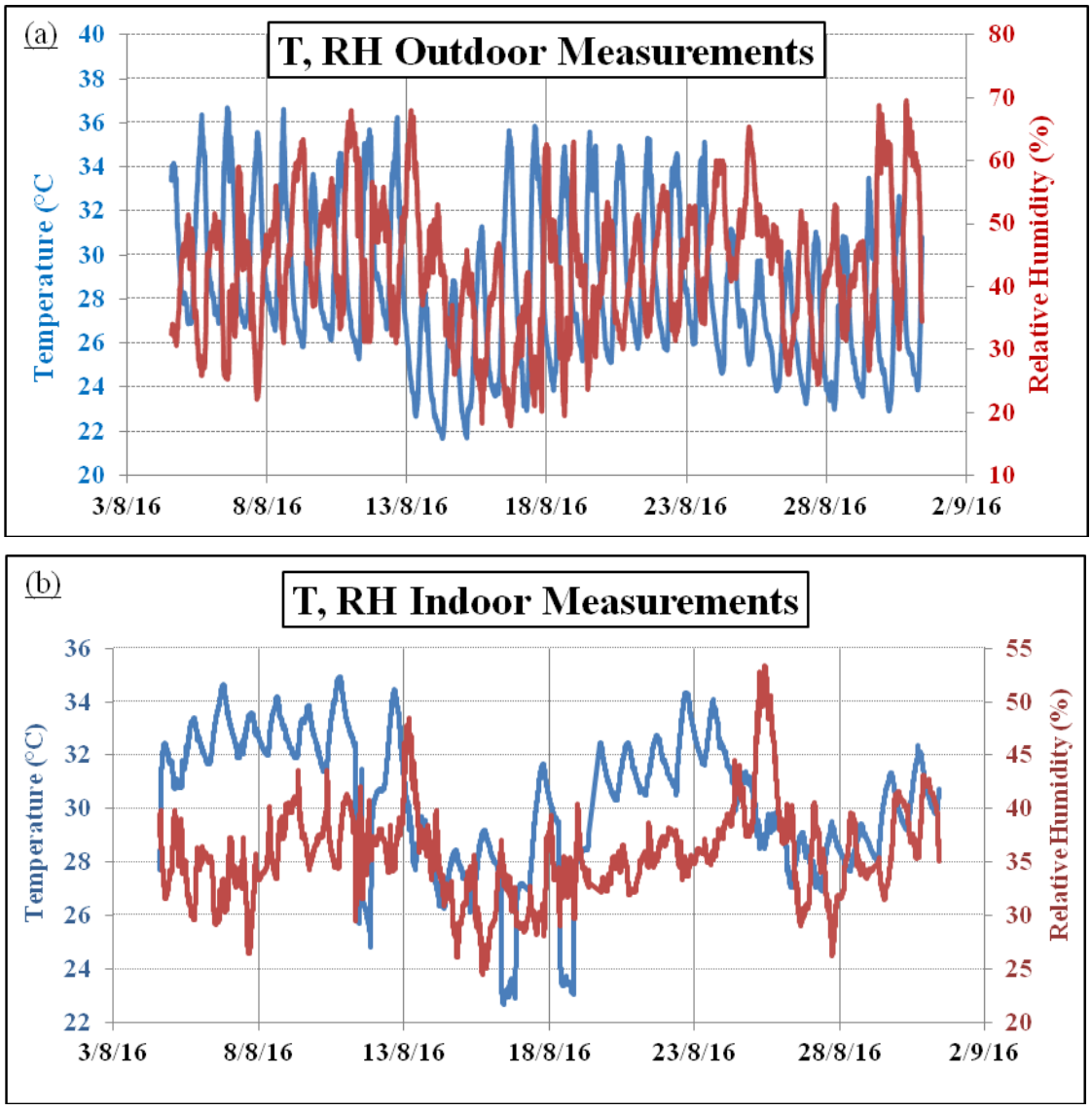



**Fig.5.3** (a) Outdoor and (b) Indoor data of temperature and relative humidity for the period of 4-31/8/2016 (5 minute intervals).

Concerning the indoor data, the *air conditioned periods* were set on 11/8, 16/8 and 18/8 from 8:00 a.m. to 20:00 p.m. and the *natural ventilation* was tested on 22/8, 24/8 and

26/8 for a period of two hours, one hour in the morning from 9:00 to10:00 a.m. and during 13:00-14:00 p.m. in the noon. In Figure 5.4 the temporal variability of both indoor and outdoor temperatures is presented. The *air conditioned periods* are marked with red frames and the *natural ventilation periods* with green vertical lines. It should be mentioned that during the experiment there were no visitors and apart from the operator, only a person was present for short time occasionally for cleaning purposes. Each of these periods, and the *background period* also, were studied separately and the results of the basic statistical analysis are provided in Tables 5-2, 5-3 and 5-4. The range (minimum up to maximum) as well as the mean and the standard deviation of the measurements are provided below.

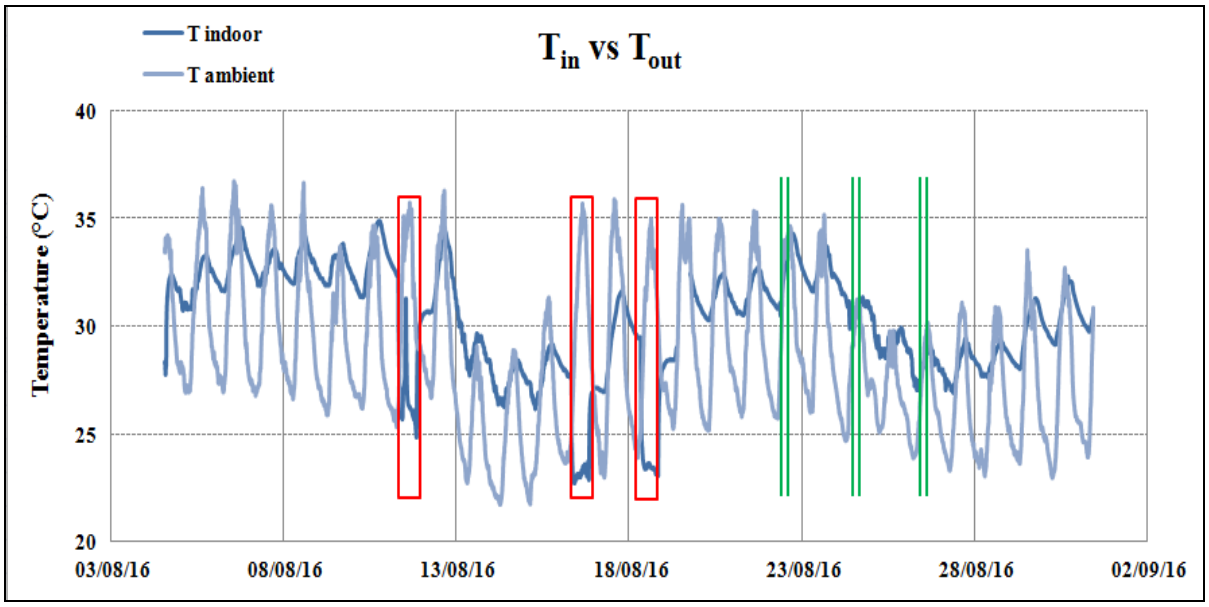



**Fig.5.4** Temporal indoor and outdoor variability of temperature during the experimental period. Red frames represent the air condition periods and green vertical lines the ventilation periods.

In any distinct background period the mean indoor temperature is always higher that the ambient (Fig.5.4 and Table 5-2) which is reflected to an average of 2.2ºC. According to Figure 5.4 in diurnal basis the ambient temperature (maximized at noon) is almost always higher in the ambient environment relatively to the indoor. It is also obvious that the minimum is more pronounced for ambient conditions. Nevertheless, the lower diurnal temperature gradient in the library leads to higher mean level comparatively to the outdoor.

**Table 5-2**. Statistics of the temperature (T) results for the background measurements in the library.

| Background | T indoor (°C) | T outdoor (°C) | Dif (°C) |
|---|---|---|---|
| **1st period** | 27.8-34.9 | 25.9-36.7 | |
| | 32.7±1.01 | 30.2±2.93 | 2.5 |
| **2nd period** | 26.2-34.4 | 21.7-36.3 | |
| | 29.2±2.11 | 26.5±3.37 | 2.7 |
| **3rd period** | 27.0-31.7 | 23.0-35.9 | |
| | 29.2±1.83 | 29.0±4.31 | 0.2 |
| **4th period** | 28.1-32.7 | 25.1-35.6 | |
| | 31.1±1.91 | 29.3±3.23 | 1.8 |
| **5th period** | 30.9-34.3 | 24.7-35.2 | |
| | 32.7±0.94 | 29.2±3.10 | 3.5 |
| **6th period** | 27.1-31.4 | 23.9-31.2 | |
| | 29.6±1.09 | 27.0±1.88 | 2.6 |
| **7th period** | 26.9-32.4 | 22.9-26.7 | |
| | 29.3±1.26 | 26.7±2.74 | 2.6 |
| **Average background period** | **26.2-34.9** | **21.7-36.7** | |
| | **30.5 ± 0.45** | **28.3±0.73** | **2.2** |

**Table 5-3**. Statistics of the temperature (T) results during air condition operation in the library.

| Air conditioned | T indoor (°C) | T outdoor (°C) | Dif (°C) |
|---|---|---|---|
| 1st period | 25.5-32.4 | 26.2-35.7 | |
| | 26.9±1.5 | 32.7±2.6 | 5.8 |
| 2nd period | 22.7-27.7 | 24.9-35.7 | |
| | 23.3±0.6 | 32.1±3.0 | 8.8 |
| 3rd period | 23.1-27.2 | 25.3-35.0 | |
| | 23.6±0.6 | 31.8±2.4 | 8.2 |
| **Average air condition period** | **27.2-32.5** | **24.9-35.7** | |
| | **24.6±0.51** | **32.2±0.30** | **7.6** |

**Table 5-4**. Statistics of the temperature (T) results during natural ventilation of the library.

| Natural ventilation | 1st period | | 2nd period | | 3rd period | | Average ventilation period | |
|---|---|---|---|---|---|---|---|---|
| | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 |
| T indoor (ºC) | 30.5-31.0 | 33.1-33.5 | 29.9-30.8 | 30.5-30.8 | 27.0-27.7 | 28.4-28.6 | **27.0-31.0** | **28.4-33.5** |
| | 30.7±0.15 | 33.3±0.15 | 30.1±0.24 | 30.6±0.10 | 27.2±0.13 | 28.5±0.1 | **29.3±0.06** | **30.8±0.03** |
| T outdoor (ºC) | 28.0-29.9 | 33.2-34.1 | 27.3-28.0 | 29.9-30.9 | 25.3-26.3 | 28.9-29.5 | **25.3-29.4** | **28.9-34.1** |
| | 28.9±0.54 | 33.7±0.26 | 27.6±0.26 | 30.6±0.33 | 25.7±0.26 | 29.2±0.14 | **27.4±0.16** | **31.2±0.10** |
| Dif (ºC) | 1.8 | 0.4 | 2.5 | 0.0 | 1.5 | 0.7 | **1.9** | **0.4** |

On the Figures 5.5 that follow each of the air conditioned and natural ventilation period is presented magnified and the findings are presented on Tables 5-3 and 5-4. It is clearly seen that during the air conditioned periods the temperature in the library decreases rapidly and is maintained at around 24ºC. It takes less than an hour to reach the optimum temperature. The difference of initial to optimum level was at the range of 5.4, 4.7 and 2.9ºC for each period respectively. It has to be mentioned that on 11$^{th}$ of August the sudden increase around noon is attributed to a short interruption of the air condition system, which is reflected to lower gradient during the air condition operation for the specific day. The mean level is lower by almost 8ºC relatively to the outdoor and during noon the maximum deviation of indoor to outdoor can be even more than 10ºC. After the end of cooling the temperature elevates to ambient conditions at about one hour again. This means that the domestic air condition systems of the library efficiently and relatively quick cool the library but after the operation period the temperature is elevated and driven by the ambient conditions and the structural features of the building demonstrating its inertia since the cool environment is not maintained.

The variability of the temperature inside and outside the library is similar for the ventilation period but under different rate. For the morning ventilation, indoor is always warmer by even 2.5ºC. It is observed that for all three cases the ambient temperature tends to decrease at the beginning of the ventilation, heat from the library is transferred out of the window, but afterwards is increased following the ambient trend with 30% lower rate.

Midday levels are almost equal with less than 0.5ºC difference. The midday increase rate of ambient and indoor environment ranges at 0.4ºC/h. and 0.3ºC/h respectively. Taken into account that during noon the ambient temperature is always increased, we can firstly

suggest avoiding natural ventilation those hours. Taking into consideration the temperature variability we could propose to prefer the morning natural ventilation relatively to the midday, if this is the only choice for ventilation.

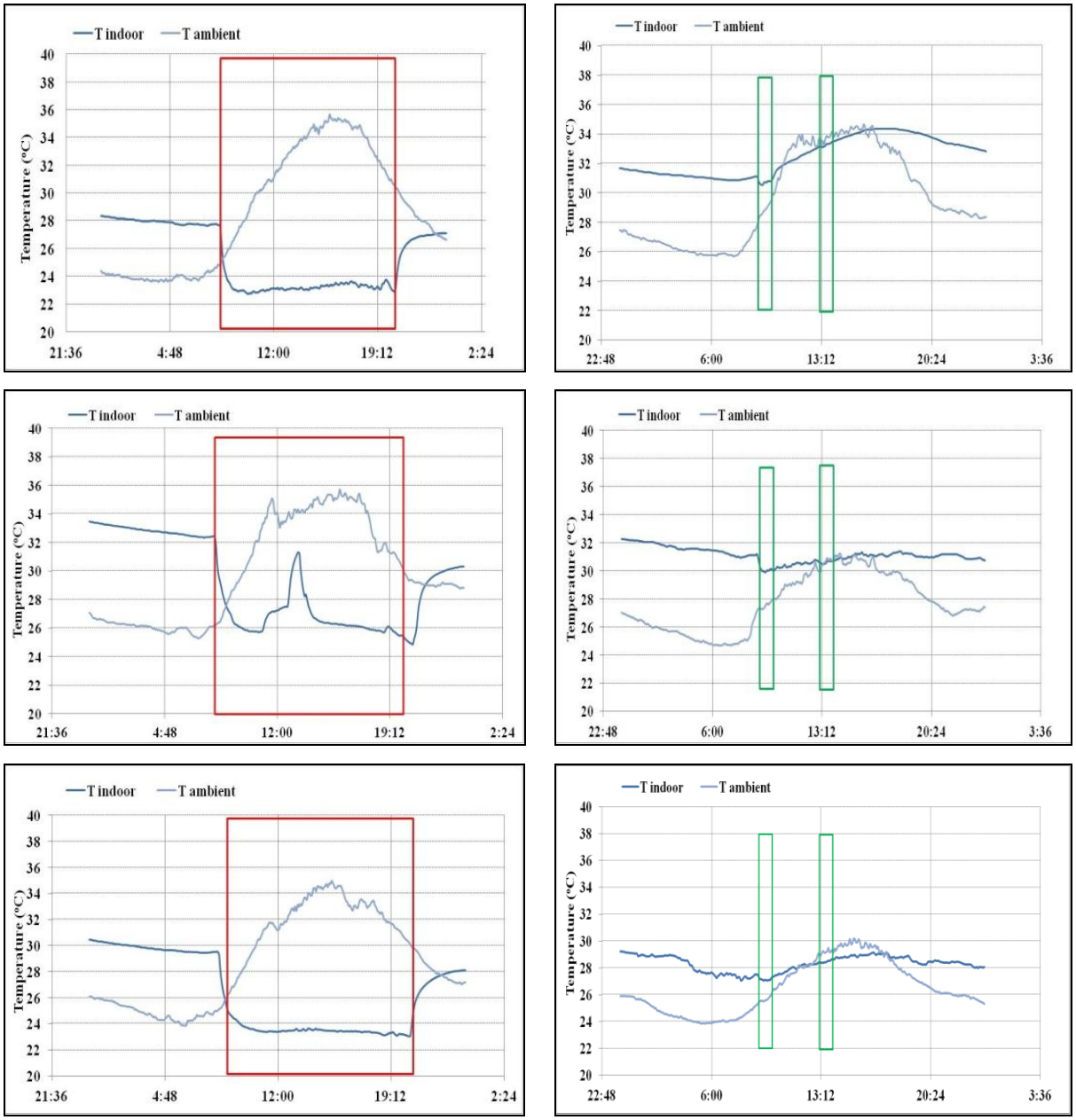



**Fig.5.5** Maximized plots of temperature during (left column) the air conditioned periods (red frames on 11/8, 16/8, 18/8 from 8:00-20:00) and (right column) the ventilation period (green frames on 22/8, 24/8, 26/8 from 9:00-10:00 and 13:00-14:00).

As for the relative humidity is concerned the I/O dataset trend is presented in Figure 5.6 and the same approach is followed as for the case of temperature and the statistics for each period are presented in Tables 5-5, 5-6 and 5-7. The temporal variability of both datasets is similar. The mean indoor relative humidity is always lower that the ambient (Fig.5.6 and

Table 5-5) which is reflected to an average of 7.3% difference in absolute level (36% RH average background indoor relatively to 43% ambient). The minimum to maximum variability is more pronounced for ambient conditions.

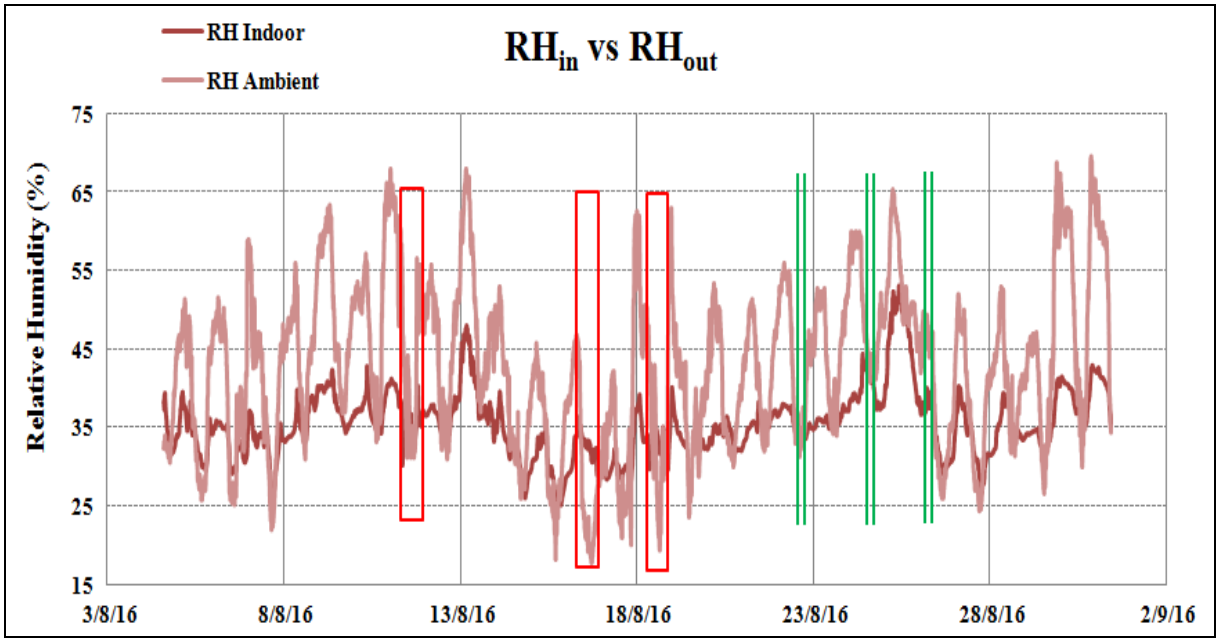



**Fig.5.6** Temporal indoor and outdoor variability of relative humidity during the experimental period. Red frames represent the air condition and green the ventilation periods.

**Table 5-5**. Statistics of the relative humidity (RH) results for the background measurements in the library.

| Background | RH indoor | RH outdoor | Dif (%) |
|---|---|---|---|
| 1st period | 26.5-42.9 | 22.0-66.2 | |
| | 35.2±3.12 | 43.5±9.74 | 8.3 |
| 2nd period | 24.7-48.2 | 18.2-68.0 | |
| | 34.8±5.12 | 41.6±10.63 | 6.8 |
| 3rd period | 28.2-37.5 | 20.2-62.6 | |
| | 30.5±2.23 | 34.1±9.80 | 3.6 |
| 4th period | 31.9-39.9 | 23.6-56.0 | |
| | 35.0±1.81 | 41.6±7.52 | 6.6 |
| 5th period | 33.7-40.5 | 31.4-60.0 | |
| | 36.3±1.67 | 46.8±8.23 | 10.5 |
| 6th period | 36.8-53.2 | 40.8-65.4 | |
| | 43.1±5.28 | 50.2±6.07 | 7.1 |
| 7th period | 26.6-43.1 | 24.4-69.6 | |
| | 35.7±3.88 | 44.0±11.56 | 8.3 |
| **Average background period** | **24.7-53.2** | **18.2-69.6** | |
| | **35.8±1.51** | **43.1±1.90** | **7.3** |

**Table 5-6**. Statistics of the relative humidity (RH) results during air condition operation in the library.

| Air conditioned | RH indoor | RH outdoor | Dif (%) |
|---|---|---|---|
| 1st period | 30.3-41.8 | 31.2-57,4 | |
| | 35.4±2.54 | 39.5±7.65 | 4.1 |
| 2nd period | 30.7-36.6 | 17.8-45.4 | |
| | 32.9±1.32 | 24.6±7.17 | 8.3 |
| 3rd period | 29.8-35.3 | 19.4-43.2 | |
| | 33.3±1.14 | 30.9±6.04 | 2.4 |
| **Average air condition period** | **29.8-41.8** | **17.8-57.4** | |
| | **33.9±0.76** | **31.7±0.82** | **2.2** |

**Table 5-7.** Statistics of the relative humidity (RH) results during natural ventilation of the library.

| Natural ventilation | 1st period | | 2nd period | | 3rd period | | Average ventilation period | |
|---|---|---|---|---|---|---|---|---|
| | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 |
| RH indoor | 36.8-37.9 | 33.5-36.8 | 41.8-44.5 | 41.4-44.0 | 37.9-39.1 | 31.3-32.0 | **36.7-44.5** | **31.2-44.0** |
| | 37.3±0.34 | 35.0±1.24 | 43.7±0.69 | 42.6±1.06 | 38.6±0.48 | 31.6±0.22 | **39.9±0.18** | **36.4±0.54** |
| RH outdoor | 41.2-47.8 | 32.2-37.0 | 48.4-52.8 | 41.2-45.0 | 40.0-47.2 | 28.6-29.8 | **40.0-52.8** | **28.6-45.0** |
| | 43.8±1.79 | 34.3±1.78 | 50.9±1.25 | 43.2±1.49 | 41.5±1.93 | 29.2±0.39 | **45.2±0.36** | **35.6±0.73** |
| Dif (%) | 6.5 | 0.7 | 7.2 | 0.6 | 2.9 | 2.4 | **5.3** | **0.8** |

On the Figures 5.7 each of the air conditioned and natural ventilation period is presented magnified and the findings are presented on Tables 5-6 and 5-7. Indoor RH follows the ambient trend but less pronounced. During the air conditioned periods the total mean relative humidity in the library is almost unaffected relatively to the former and later levels. Out of the cooling period RH does not exceed the ambient conditions since the temperature indoor is increased relatively to the ambient. This means that the impact of the domestic air condition systems of the library is low.

The variability of the relative humidity inside and outside the library is similar for the ventilation period. For the morning ventilation periods indoor RH is always lower by even of about 7%. Midday levels are equal with less than 1% difference. The variability for midday

I/O change is insignificant. For the morning ventilation we observe that for all three cases the indoor relative humidity tends to change of about 1%/h relatively to 3%/h for ambient conditions.

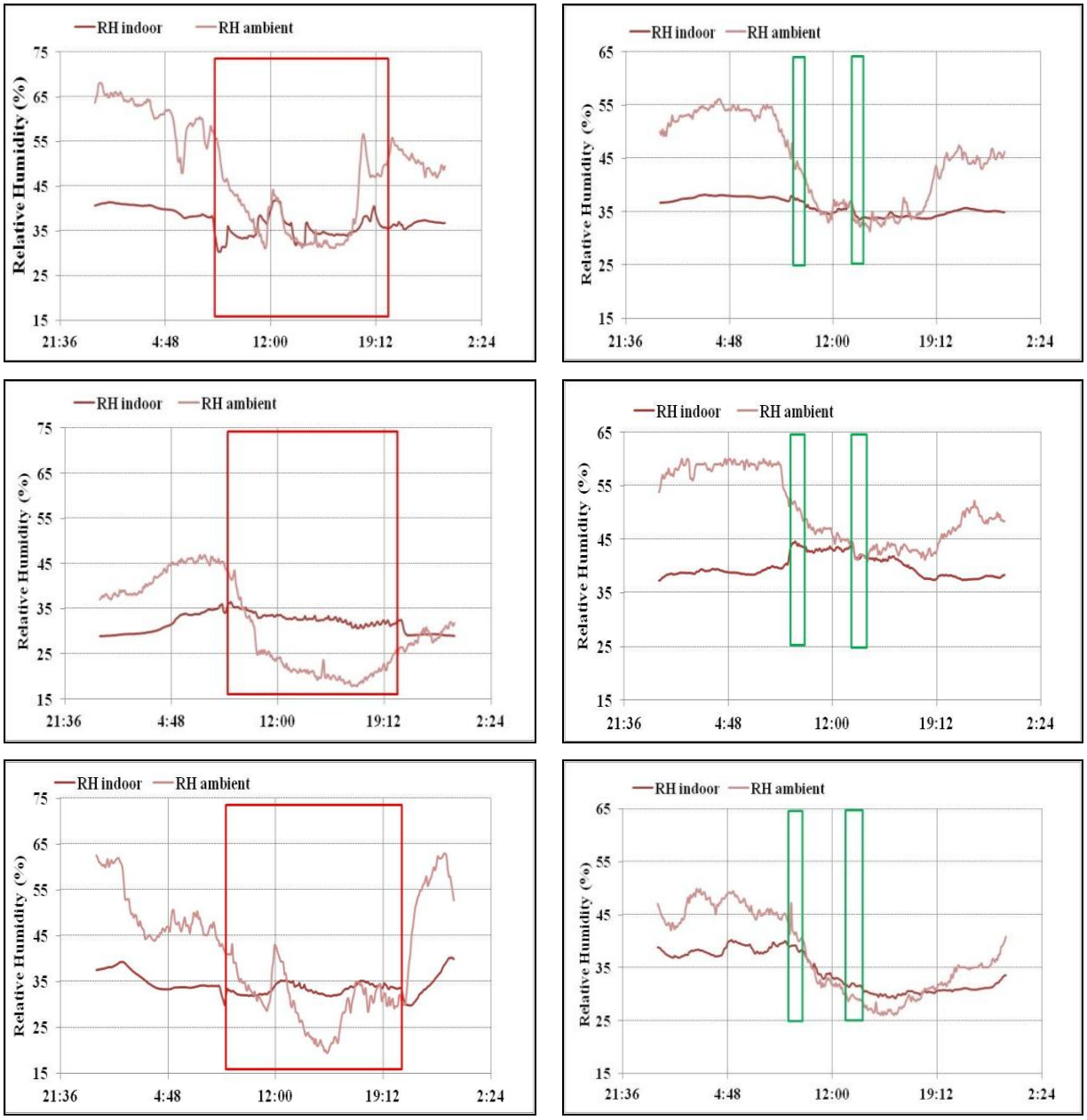



**Fig.5.7** Maximized plots of temperature during (left column) the air conditioned periods (red frames on 11/8, 16/8, 18/8 from 8:00-20:00) and (right column) the ventilation period (green frames on 22/8, 24/8, 26/8 from 9:00-10:00 and 13:00-14:00).

### 5.3 Show case temperature and relative humidity data and investigation of the interaction with the library room

The device TGP-4500 Tiny Tag was used along with the ACL system of measuring both temperature and humidity aiming at the identification of differences on micro environmental parameters between the library room and a show case. This device was situated in a closed table book case (show case) without access to anyone, providing an isolated environment for the enclosed books. The measurements were carried out from 31/7/2016 9:00 a.m. until 6/9/16 at 13:00 p.m. Actually, it was placed in the area for approximately a week before and after the main measurements (period A and B respectively). Figure 5.8 depicts the temporal variability of T and RH measured by Tiny Tag during that specific time span and the Tables 5-8, 5-9 and 5-10 summarize the statistics of the T, RH results measured by ACL system and Tiny Tag respectively. Aiming to the comparison of the library macroenvironment with the book case microenvironment the temperature and relative humidity are presented in parallel in Figure 5.9. The same encoding as previously is used for the presentation of the air conditioned and natural ventilation periods.

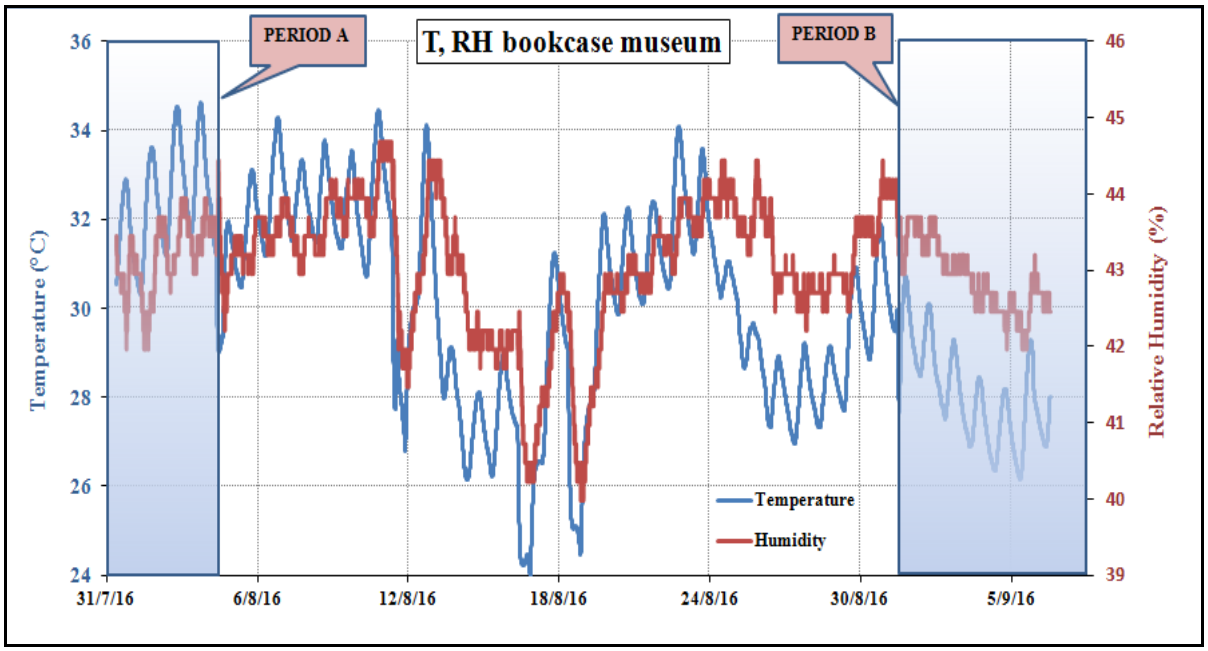



**Fig.5.8** Temporal variability for indoor table book case temperature and relative humidity measured by Tiny Tag in 5 minutes base. The space between period A and period B is the experimental period

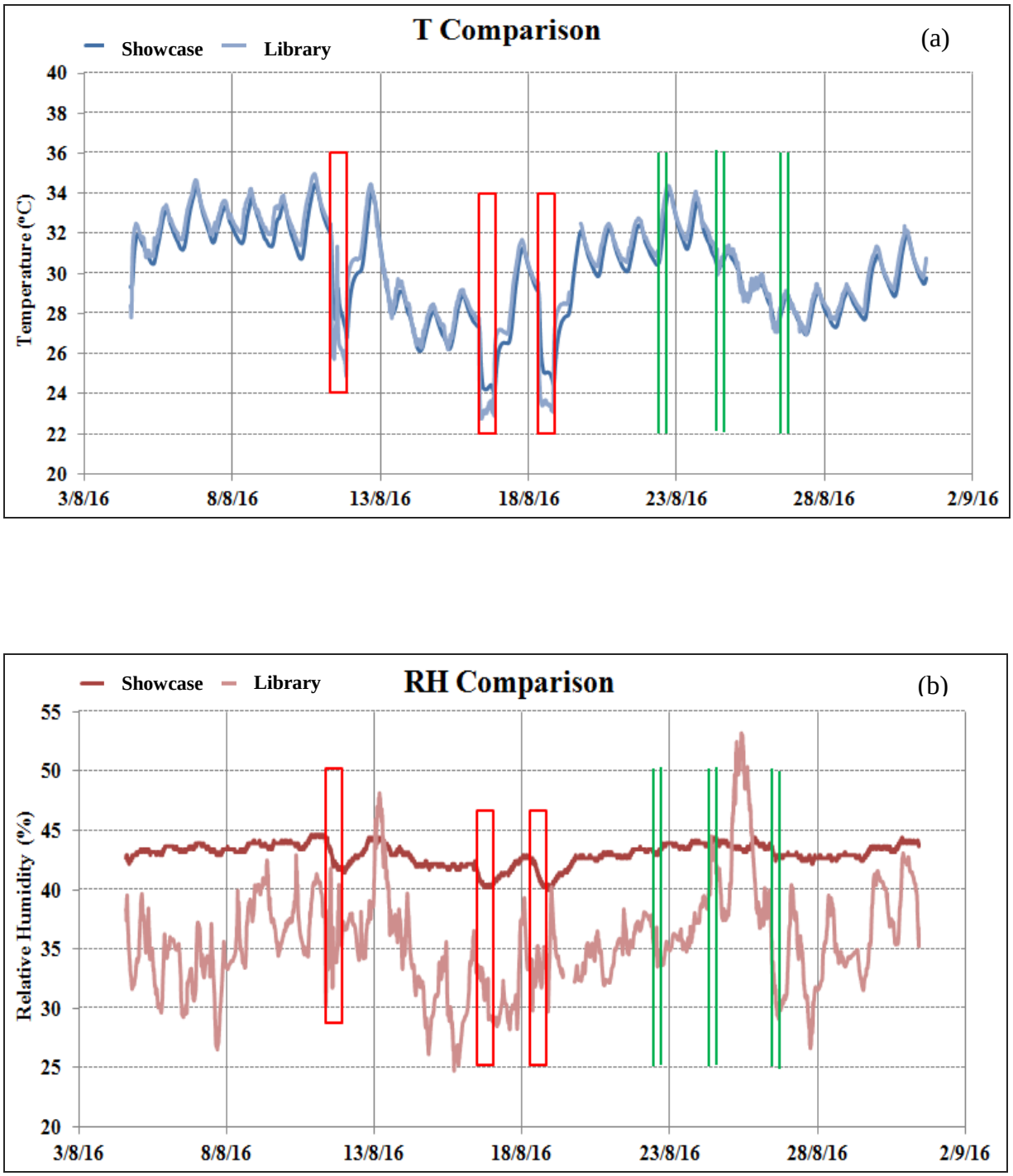



**Fig.5.9** Variability of temperature and relative humidity in (a) the library and (b) the show case. Red frames represent the air condition and green the ventilation periods.

**Table 5-8.** Statistics of the T, RH results for the background measurements in the library room measured by ACL system and the show case measured by the Tiny Tag.

| Background | Library, ACL (T) | Show case, Tiny Tag (T) | Library, ACL (RH) | Show case, Tiny Tag (RH) |
|---|---|---|---|---|
| **1st period** | 27.8-34.9 | 29.3-34.5 | 26.5-42.9 | 42.2-447 |
| | 32.7±1.01 | 32.3±1.02 | 35.2±3.12 | 43.6±0.40 |
| **2nd period** | 26.2-34.4 | 26.1-34.1 | 24.7-48.2 | 41.5-44.4 |
| | 29.2±2.11 | 28.8±20.3 | 34.8±5.12 | 42.8±0.82 |
| **3rd period** | 27.0-31.7 | 26.1-31.3 | 28.2-37.5 | 40.5-42.7 |
| | 29.2±1.83 | 28.5±1.98 | 30.5±2.23 | 41.6±0.63 |
| **4th period** | 28.1-32.7 | 26.8-32.4 | 31.9-39.9 | 40.2-43.7 |
| | 31.1±1.91 | 30.6±1.37 | 35.0±1.81 | 42.6±0.74 |
| **5th period** | 30.9-34.3 | 30.5-34.1 | 33.7-40.5 | 43.0-44.2 |
| | 32.7±0.94 | 32.2±1.00 | 36.3±1.67 | 43.8±0.23 |
| **6th period** | 27.1-31.4 | 27.4-31.1 | 36.8-53.2 | 43.2-44.4 |
| | 29.6±1.09 | 29.5±0.97 | 43.1±5.28 | 43.8±0.29 |
| **7th period** | 26.9-32.4 | 27.0-31.9 | 26.6-43.1 | 42.2-44.4 |
| | 29.3±1.26 | 29.0±1.24 | 35.7±3.88 | 43.1±0.51 |
| **Average background period** | **26.2-34.9** | **26.1-34.5** | **24.7-53.2** | **40.2-44.7** |
| | **30.5 ± 0.45** | **30.6±0.45** | **35.8±1.51** | **43.04±0.22** |

**Table 5-9.** Statistics of the T, RH results during air condition operation in the library room measured by ACL system and the show case measured by the Tiny Tag.

| Air conditioned | Library, ACL (T) | Show case, Tiny Tag (T) | Library, ACL (RH) | Show case, Tiny Tag (RH) |
|---|---|---|---|---|
| 1st period | 25.5-32.4 | 27.3-32.0 | 30.3-41.8 | 41.7-44.4 |
| | 26.9±1.5 | 28.5±1.13 | 35.4±2.54 | 42.9±0.87 |
| 2nd period | 22.7-27.7 | 24.0-27.3 | 30.7-36.6 | 40.2-42.5 |
| | 23.3±0.6 | 24.7±0.80 | 32.9±1.32 | 41.0±0.71 |
| 3rd period | 23.1-27.2 | 24.5-29.1 | 29.8-35.3 | 40.0-42.7 |
| | 23.6±0.6 | 25.5±1.06 | 33.3±1.14 | 41.1±0.80 |
| **Average air condition period** | **27.2-32.5** | **24.1-32.0** | **29.8-41.8** | **32.0-44.5** |
| | **24.6±0.51** | **26.3±0.17** | **33.9±0.76** | **41.7±0.08** |

**Table 5-10**. Statistics of the T, RH results during natural ventilation in the library room measured by ACL system and the show case measured by the Tiny Tag.

| Natural ventilation | 1st period | | 2nd period | | 3rd period | | Average ventilation period | |
|---|---|---|---|---|---|---|---|---|
| | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 |
| Library, ACL (T) | 30.5-31.0 | 33.1-33.5 | 29.9-30.8 | 30.5-30.8 | 27.0-27.7 | 28.4-28.6 | **27.0-31.0** | **28.4-33.5** |
| | 30.7±0.15 | 33.3±0.15 | 30.1±0.24 | 30.6±0.10 | 27.2±0.13 | 28.5±0.1 | **29.3±0.06** | **30.8±0.03** |
| Show case, Tiny Tag (T) | 30.5-30.6 | 32.1-32.7 | 30.3-30.5 | 30.6-30.6 | 27.3-27.4 | 28.1-28.3 | **27.4-30.6** | **28.1-32.7** |
| | 30.5±0.03 | 32.4±0.20 | 30.4±0.07 | 30.6±0.02 | 27.4±0.02 | 28.2±0.07 | **29.4±0.03** | **30.4±0.10** |
| Library, ACL (RH) | 36.8-37.9 | 33.5-36.8 | 41.8-44.5 | 41.4-44.0 | 37.9-39.1 | 31.3-32.0 | **36.7-44.5** | **31.2-44.0** |
| | 37.3±0.34 | 35.0±1.24 | 43.7±0.69 | 42.6±1.06 | 38.6±0.48 | 31.6±0.22 | **39.9±0.18** | **36.4±0.54** |
| Show case, Tiny Tag (RH) | 43.5-43.5 | 43.0-43.2 | 43.7-44.2 | 44.0-44.4 | 43.7-44.0 | 42.5-43.0 | **43.5-44.2** | **42.5-44.5** |
| | 43.5±7.39 E-15 | 43.1±0.13 | 44.0±0.20 | 44.2±0.17 | 43.9±0.11 | 42.9±0.14 | **43.7±0.10** | **43.4±0.02** |

According to the diagrams above, there is absolute correlation of the temperature in the library and the showcase regardless the conditions. In case of air condition use the temperature in the showcase decreases also significantly relatively to the ambient conditions, but remains at level of about 1.5°C higher than the library. Considering the 3% overestimation

of tiny tag over the ACL system we conclude that actually there is no difference in the temperature between the library and the showcase, as the difference falls finally within 1.0ºC.

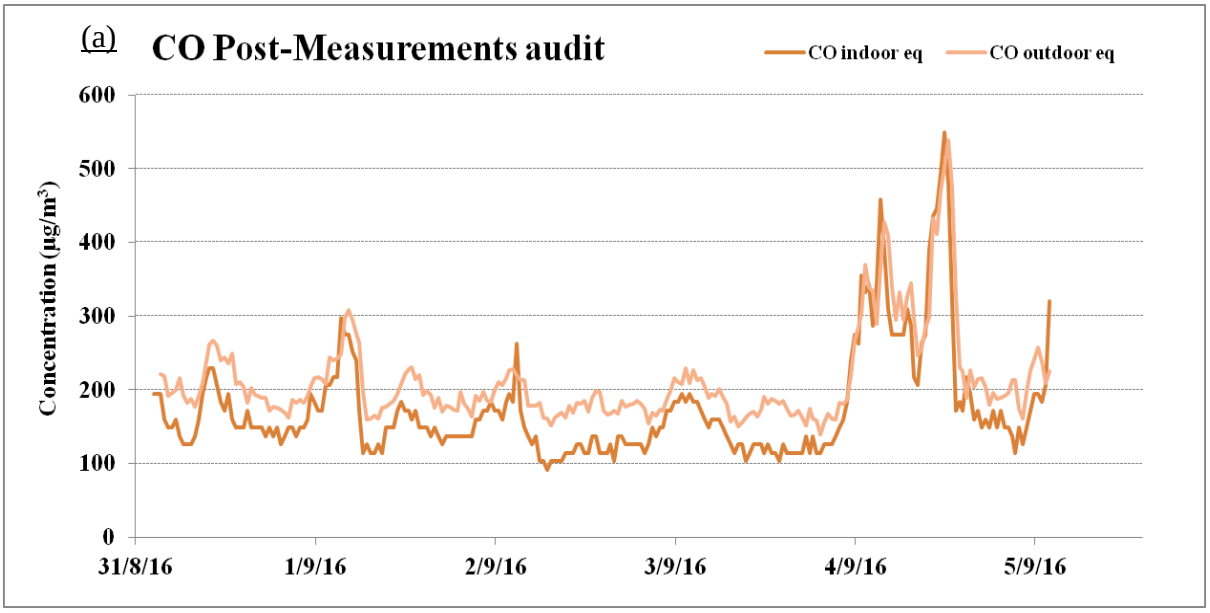
On the other hand, the relative humidity presents less variability and significant difference by the library macroenvironment and seems to be independent to the ambient changes. The level of the tiny tag RH is higher than the library with mean background values at 43% and 36% respectively. The difference between the macro and micro environment is at the order of 20%. According to the pre and post measurements audit there was a discrepancy of 14% for RH. Therefore the actual increase of the showcase is estimated at 6%.

# 6. RESULTS OF POLLUTION MEASUREMENTS

The synergy of thermo and hydrometric parameters and air pollution usually drives the acceleration of the decay and eventually the damage of Cultural Heritage objects. The most common of gaseous pollutants, which their concentrations are analyzed and assessed in this chapter, are nitrogen oxides (NOx, NO, $NO_2$), sulfur dioxide ($SO_2$), ozone ($O_3$), carbon monoxide (CO) used here as an indicator of outdoor anthropogenic sources) and suspended particulate matter (PM10).

## 6.1 Inter calibration of automatic analyzers

After the end of the measurements in the library, intercalibration (parallel measurements in ambient environment) of the common equipment used indoor and outdoor took place in order to quantify the deviation of the different systems used in the study. The simultaneous measurements were conducted in the Air Pollution Monitoring Station of NOA located next to the building of the library for a period of five days (1/9/2016 00.00 to 5/9/2016 23.59 p.m) and concerns the CO and $O_3$ analyzers. In Figures 6.1(a) and (b) the results of the audit are presented for CO and $O_3$ respectively.



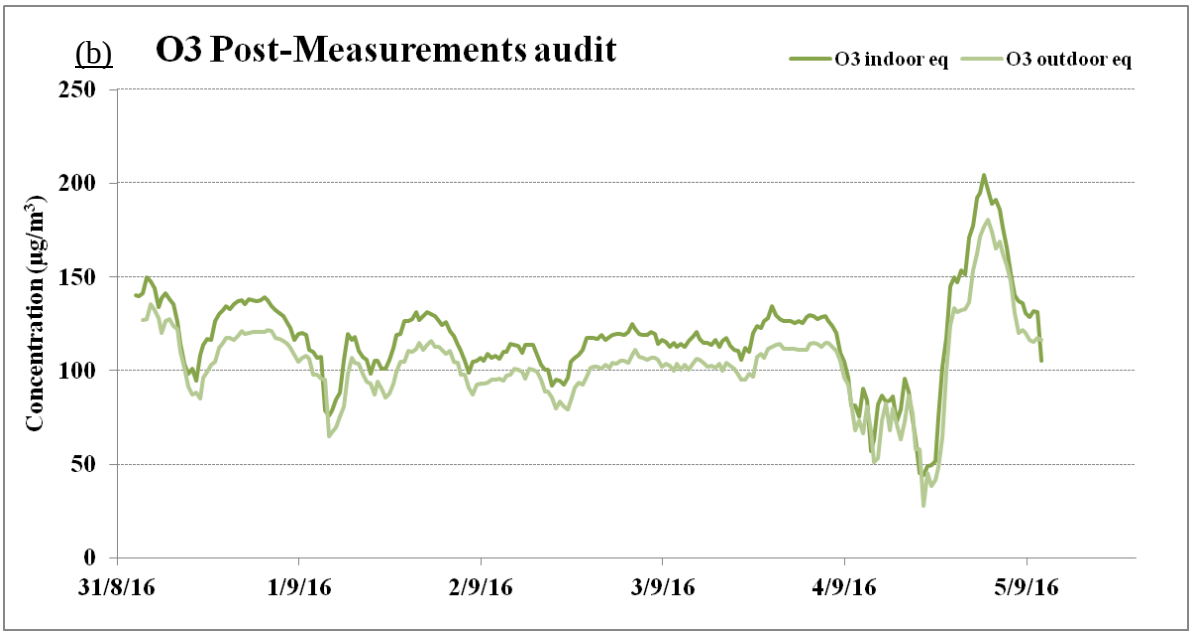
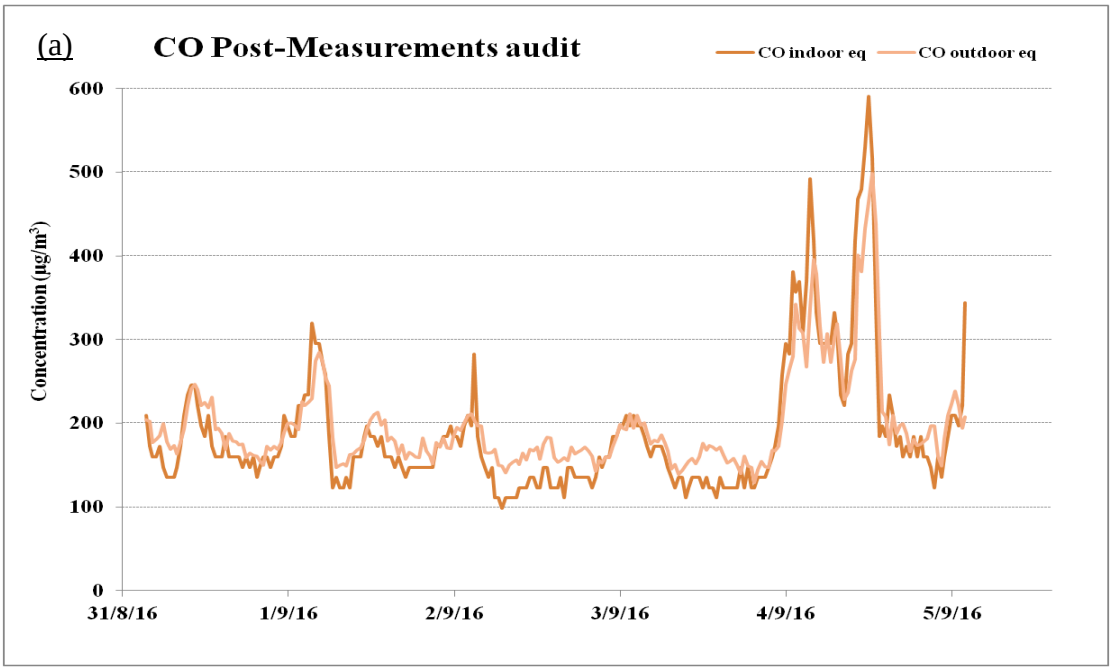



**Fig. 6.1** Post-measurement audit under ambient conditions for (a) CO and (b) $O_3$.

The analyzers used in the library monitoring are marked as 'indoor' relatively to the 'outdoor' which operate permanently in the Air Pollution Monitoring Station and they were used for the I/O investigation. In both cases the systems have the same variability. The discrepancies vary at 15% and 12% for CO and $O_3$ respectively. The difference is accepted since is slightly above the generally accepted deviation of 10% for such analyzers. Nevertheless, each set of collocated analyzers are calibrated and should provide the same levels of pollutants. The optimum solution is to use a mean error and calibrate indoor and outdoor datasets by 7.5% and 6% in order to provide similar levels. The results are presented in Figures 6.2 (a) and (b) and prove the appropriateness of the correction procedure. The datasets for indoor and outdoor measurements are respectively corrected in order to provide quality assurance and comparable data.



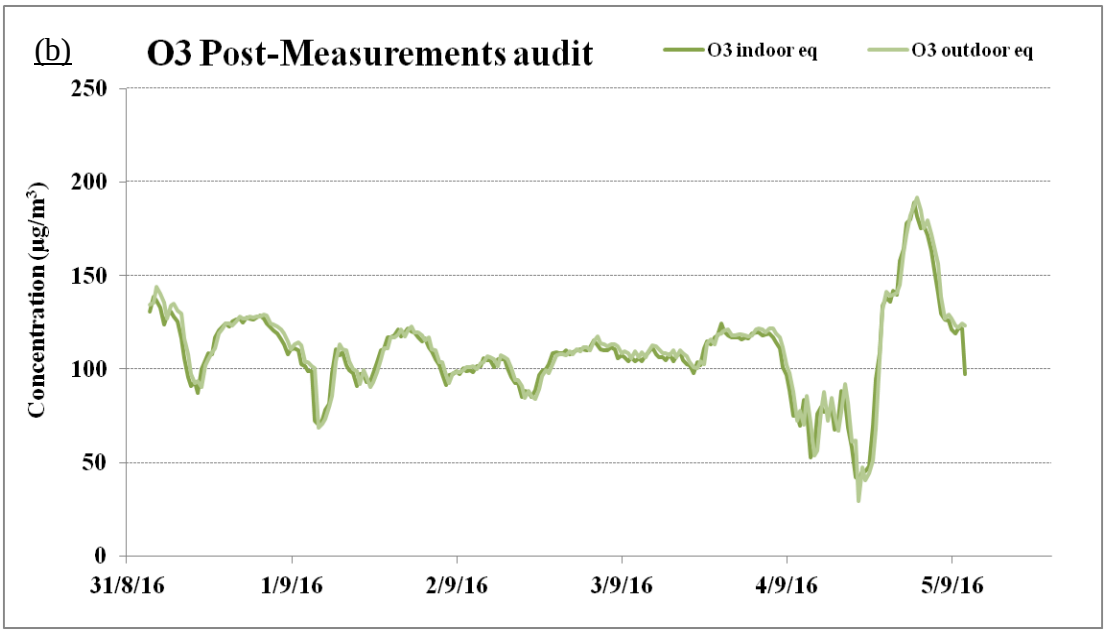




**Fig.6.2** Corrected post-measurement audit under ambient conditions for (a) CO and (b) $O_3$.

## 6.2 Gaseous pollution data and investigation of I/O relations

This subchapter refers to the measurements of the library indoor environment concerning major gaseous pollutants: CO, $SO_2$, NO, $NO_2$ (sum as NOx) and $O_3$ and the evaluation of these results. Furthermore, there were parallel ambient measurements (outdoor), which were carried out by means of CO and $O_3$ analyzers. Due to the lack of equipment, the parallel measurements conducted only for the CO and $O_3$ The ambient conditions were provided by the Meteorological Station of the National Observatory of Athens operated in short distance

from the museum. Scope of the parallel study is the investigation of the indoor to outdoor relation of these gaseous parameters. As it is already mentioned, the regular conditions in the museum do not support HVAC system (Heating, Ventilation and Air Conditioning). Here, again we consider the *background measurements,* the *air conditioned periods* where library was conditioned for a few hours and the *natural ventilation periods* which were followed by opening the windows of the library for certain time periods.

The Indoor measurements started at 14:00 p.m. on the 4$^{th}$ of August 2016 and ended at 10:00 a.m. on the 31$^{th}$ of the same month. In the plot that lies hereby (Fig 6.3), the indoor measurements of, NO, $NO_2$ and $SO_2$ and the indoor versus outdoor measurements of CO and $O_3$ as well, are presented in time base of 30 minute intervals. For $O_3$ and CO the I/O ratios are also depicted in Figure 6.3. The air *conditioned periods* are marked with red frames and the *natural ventilation periods* with green lines. Concerning the indoor data, the *air conditioned periods* were set on 11/8, 16/8 and 18/8 from 8:00 a.m. to 20:00 p.m. and the *natural ventilation* was tested on 22/8, 24/8 and 26/8 for a period of two hours, one in the morning from 9:00 to10:00 a.m. and 13:00-14:00 p.m. in the noon. Each of these periods, and the *background period* also, were studied separately and the results of the basic statistical analysis are provided in Tables 6-1, 6-2 and 6-3. The range (minimum up to maximum) as well as the mean and the standard deviation of the measurements are provided.

For the ambient measurements it was generally observed an increase early in the morning and late in the night after midnight. The morning peak (7:00-9:00) was attributed to traffic rush hours and the second (2:00-3:00) coincides with the end of the summer night-time entertainment and return to home. Increased level of pollution was also observed before and after the holiday of 15 of August due to increase traffic (departure and return of Athens citizens). The strong (>5m/sec) wind of north origin during periods of 13-15 and 24-28 of August also contributed to decreased pollution levels (cleaner air was transferred in the center of the city).

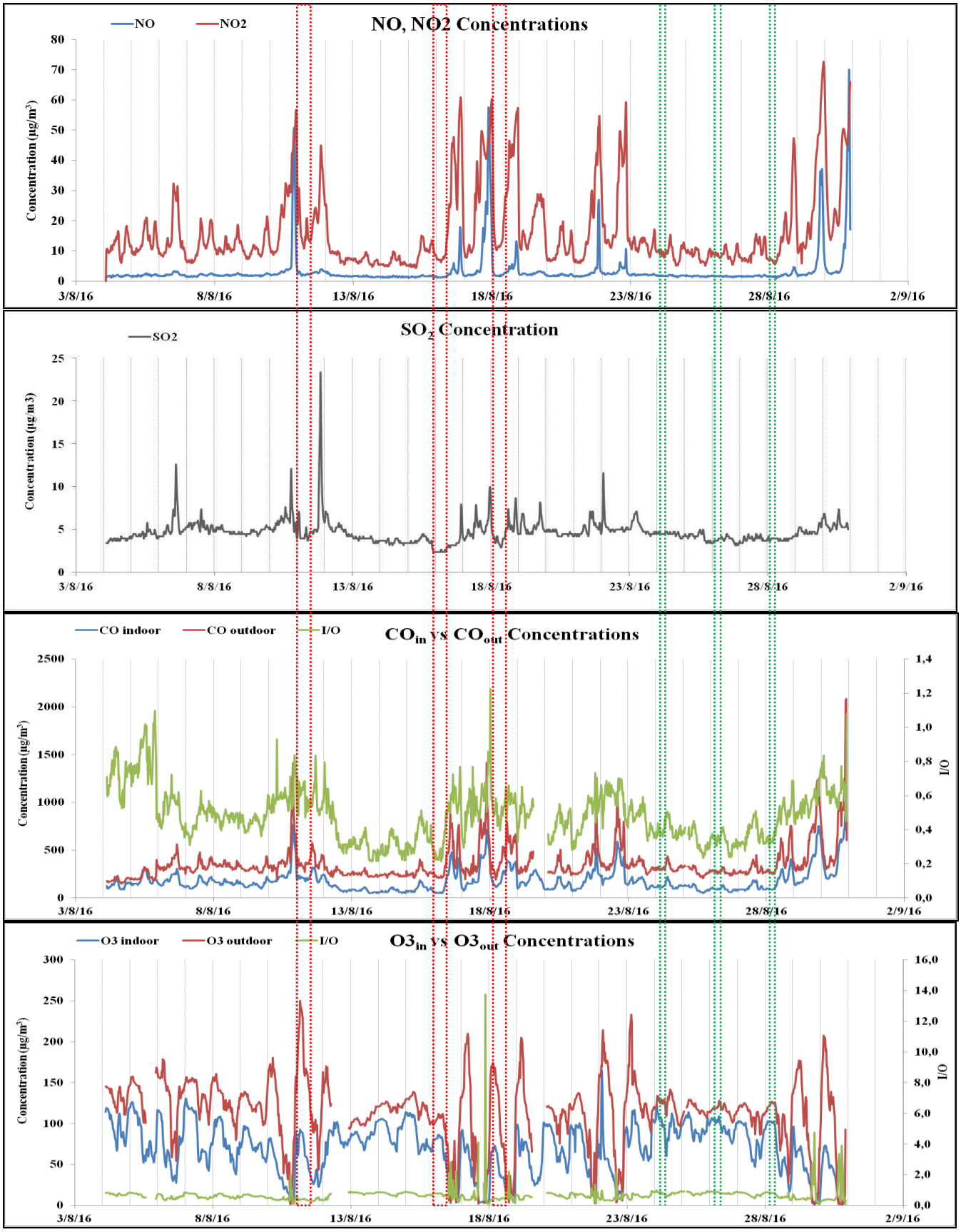



**Fig. 6.3** Indoor and outdoor temporal variability of gaseous species. Air conditioned and ventilation periods are denoted by red frames and green lines respectively.

**Table 6-1**. Statistics of the gaseous concentration (μg/m$^3$) results (CO, NO, $NO_2$, $O_3$, $SO_2$) during background days in the library.

| Background | NO | $NO_2$ | $SO_2$ | CO | $O_3$ |
|---|---|---|---|---|---|
| 1st period | 1.1-3.3 | 6.0-32.2 | 3.4-12.6 | 138-356 | 27.7-130.8 |
| | 1.9±0.38 | 12.6±4.80 | 4.9±0.95 | 209±99 | 80.2±25.2 |
| 2nd period | 1.1-3.9 | 4.3-44.8 | 3.2-23.3 | 111-382 | 22.7-113.9 |
| | 1.8±0.62 | 9.9±7.62 | 4.6±2.27 | 168±124 | 81.5±22.6 |
| 3rd period | 1.6-17.9 | 7.7-60.8 | 2.9-7.9 | 135-542 | 3.9-92.3 |
| | 3.76±3.45 | 27.5±16.85 | 4.3±1.26 | 291±178 | 42.9±27.5 |
| 4th period | 1.5-26.9 | 6.0-57.2 | 3.9-8.7 | 135-579 | 3.5-101.3 |
| | 3.0±3.10 | 19.5±13.39 | 5.1±0.90 | 249±154 | 58.2±30.4 |
| 5th period | 1.8-10.7 | 7.9-59.1 | 4.2-7.1 | 148-652 | 5.5-144.1 |
| | 2.8±1.36 | 18.8±12.83 | 5.2±0.66 | 290±180 | 62.5±31.1 |
| 6th period | 1.2-2.1 | 5.1-15.2 | 3.4-5.0 | 111-283 | 60.0-114.0 |
| | 1.7±0.18 | 8.9±2.21 | 4.3±0.33 | 176±95 | 94.2±11.7 |
| 7th period | 0.9-70.2 | 5.5-72.6 | 3.1-7.3 | 123-1071 | 2.6-109.2 |
| | 4.9±9.39 | 19.5±16.32 | 4.4±0.81 | 288±247 | 62.6±32.8 |
| Average background period | 0.9-70.2 | 4.3-72.6 | 2.9-23.3 | 111-1071 | 2.6-144.1 |
| | 2.8±3.3 | 16.7±5.7 | 4.7±0.6 | 239±54 | 68.7±7.2 |

**Table 6-2**. Statistics of the gaseous concentration (μg/m$^3$) results (CO, NO, $NO_2$, $O_3$, $SO_2$) during air condition operation in the library.

| Air conditioned | 1st period | 2nd period | 3rd period | Average air condition period |
|---|---|---|---|---|
| NO | 1.7-50.8 | 1.1-2.5 | 1.6-57.4 | 1.1-57.4 |
| | 7.8±2.11 | 1.6±0.33 | 11.7±14.87 | 7.0±7.7 |
| $NO_2$ | 10.7-56.6 | 6.2-25.4 | 10.2-60.2 | 6.2-60.2 |
| | 26.6±12.72 | 10.9±4.27 | 30.9±16.2 | 22.8±6.1 |
| $SO_2$ | 3.7-12.1 | 2.4-4.5 | 2.9-10.0 | 2.4-12.1 |
| | 5.5±1.69 | 3.0±0.74 | 4.9±1.63 | 4.5±0.5 |
| CO | 172-756 | 111-295 | 234-825 | 111-825 |
| | 362±234 | 159±110 | 347±215 | 289±66 |
| $O_3$ | 2.6-93.0 | 43.6-86.4 | 3.7-73.3 | 2.6-93.0 |
| | 45.2±31.2 | 72.9±10.0 | 31.6±25.5 | 49.9±10.9 |

**Table 6-3.** Statistics of the gaseous concentration (μg/m$^3$) results (CO, NO, $NO_2$, $O_3$, $SO_2$) during natural ventilation of the library.

| Natural ventilation | 1st period | | 2nd period | | 3rd period | | Average ventilation period | |
|---|---|---|---|---|---|---|---|---|
| | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 |
| NO | 3.3-17.4 | 2.1-2.7 | 2.0-2.1 | 1.7-2.0 | 1.6-1.8 | 1.5-1.7 | 1.6-17.4 | 1.5-2.7 |
| | 8.6±7.70 | 2.37±0.31 | 2.0±0.07 | 1.8±0.12 | 1.8±0.14 | 1.6±0.14 | 4.1±4.3 | 1.9±0.1 |
| $NO_2$ | 39.7-54.6 | 12.8-18.8 | 10.0-16.2 | 8.8-10.5 | 8.1-10.5 | 8.7-9.6 | 8.1-54.6 | 8.7-18.8 |
| | 47.0±7.44 | 16.7±3.37 | 12.3±3.39 | 9.7±0.85 | 9.0±1.36 | 9.0±0.54 | 22.7±3.1 | 11.8±1.6 |
| $SO_2$ | 5.0-5.5 | 6.3-11.5 | 4.5-4.7 | 4.5-4.72 | 3.4-3.7 | 3.4-3.7 | 3.4-5.5 | 3.4-11.5 |
| | 5.2±0.30 | 8.9±2.62 | 4.5±0.15 | 4.6±0.15 | 3.6±0.15 | 3.6±0.15 | 4.4±0.1 | 5.7±1.4 |
| CO | 332-542 | 197-295 | 172-197 | 172-197 | 135-148 | 160-172 | 135-542 | 160-295 |
| | 427±168 | 238±113 | 184±74 | 180±76 | 139±68 | 164±68 | 250±56 | 194 ±24 |
| $O_3$ | 3.7-82.7 | 56.5-165.2 | 60.2-105.4 | 104.6-123.5 | 89.9-107.2 | 103.5-106.7 | 51.2-98.4 | 88.2-131.8 |
| | 45.5±39.7 | 116.7±55.3 | 88.2±24.5 | 115.7±9.8 | 99.9±9.0 | 105.1±1.6 | 77.9±24.4 | 112.5±22.2 |

The bottom plots of Figure 6.3 show the results of monitoring measurements of gaseous pollutants CO and $O_3$ in the museum compared with the external relevant measurements. The concentration values of the two gases seem to be higher outside the museum than inside. This is among to others (infiltration of pollutants into the building depending on insulation) due to the fact that parts of gaseous pollutants have the ability to react with objects located in the space of library, such as walls and furniture or aerosol particles which present with other gases. This contributes to limited air exchange (Krupinska et al., 2011).

The variability of levels both inside and outside the library is equivalent. Differences are observed during the dates 11/8, 14/8 and 18/8 due to the fact that in those days and hours, the air conditioning systems of the library were on. For the ventilation periods seems that the factors driving the ambient level (sources and processes determine the production or depletion) also influence the internal. Tables 6-4 to 6-9 summarize the findings of parallel indoor-outdoor measurements with the ratio I/O for each period.

**Table 6-4**. Statistics of the gaseous indoor and outdoor concentration (μg/m$^3$) results of CO for the background measurements in the library.

| Backgound | CO indoor | CO outdoor | CO I/O |
|---|---|---|---|
| 1st period | 138-356 | 116-328 | 1.06 |
| | 209±99 | 197±33 | |
| 2nd period | 111-382 | 120-315 | 1.06 |
| | 168±124 | 159±19 | |
| 3rd period | 135-542 | 114-454 | 1.27 |
| | 291±178 | 229±98 | |
| 4th period | 135-579 | 112-785 | 0.98 |
| | 249±154 | 252±116 | |
| 5th period | 148-652 | 148-371 | 1.45 |
| | 290±180 | 200±35 | |
| 6th period | 111-283 | 159-476 | 0.72 |
| | 176±95 | 244±72 | |
| 7th period | 123-1071 | 147-1508 | 0.84 |
| | 288±247 | 341±253 | |
| Average background period | 111-1071 | 112-1508 | 1.03 |
| | 239±54 | 232±78 | |

**Table 6-5**. Statistics of the gaseous indoor and outdoor concentration (μg/m$^3$) results of $O_3$ for the background measurements in the library.

| Background | $O_3$ indoor | $O_3$ outdoor | $O_3$ I/O |
|---|---|---|---|
| 1st period | 27.7-130.8 | 53.8-180.7 | 0.61 |
| | 80.2±25.2 | 131.9±22.5 | |
| 2nd period | 22.7-113.9 | 43.5-169.9 | 0.70 |
| | 81.5±22.6 | 109.31±17.71 | |
| 3rd period | 3.9-92.3 | 2.7-209.7 | 0.45 |
| | 42.9±27.5 | 94.9±64.6 | |
| 4th period | 3.5-101.3 | 0.8-124.3 | 0.99 |
| | 58.2±30.4 | 58.7±36.7 | |
| 5th period | 5.5-144.1 | 72.0-93.4 | 0.77 |
| | 62.5±31.1 | 80.9±6.7 | |
| 6th period | 60.0-114.0 | 13.3-123.8 | 1.09 |
| | 94.2±11.7 | 86.3±30.2 | |
| 7th period | 2.6-109.2 | 1.1-192.7 | 0.72 |
| | 62.6±32.8 | 86.2±46.7 | |
| Average background period | 2.6-144.1 | 0.9-209.7 | 0.76 |
| | 68.7±7.2 | 93.5±19.1 | |

**Table 6-6**. Statistics of the gaseous indoor and outdoor concentration (μg/m$^3$) results of CO and O during air condition operation in the library.

| Air conditioned | 1st period | 2nd period | 3rd period | Average air condition period |
|---|---|---|---|---|
| **CO indoor** | 172-756 | 111-295 | 234-825 | 111-825 |
| | 362±234 | 159±110 | 347±215 | 289±66 |
| **CO outdoor** | 157-824 | 120-322 | 111-826 | 111-826 |
| | 275±140 | 163 ±43 | 301±148 | 247±56 |
| **CO I/O** | 1.20 | 0.97 | 1.26 | 1.17 |

**Table 6-7**. Statistics of the gaseous indoor and outdoor concentration (μg/m$^3$) results of $O_3$ during air condition operation in the library.

| Air conditioned | 1st period | 2nd period | 3rd period | Average air condition period |
|---|---|---|---|---|
| **$O_3$ indoor** | 2.6-93.0 | 43.6-86.4 | 3.7-73.3 | 2.6-93.0 |
| | 45.2±31.2 | 72.9±10.0 | 31.6±25.5 | 49.9±10.9 |
| **$O_3$ outdoor** | 1.3-250.0 | 64.2-125.8 | 1.7-174.4 | 1.3-250.0 |
| | 119.3±76.3 | 105.1±13.6 | 93.3±59.4 | 105.9±32.4 |
| **$O_3$ I/O** | 0.4 | 0.7 | 0.4 | 0.5 |

**Table 6-8**. Statistics of the gaseous indoor and outdoor concentration (μg/m$^3$) results of CO during natural ventilation of the library.

| Natural ventilation | 1st period | | 2nd period | | 3rd period | | Average ventilation period | |
|---|---|---|---|---|---|---|---|---|
| | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 |
| **CO indoor** | 332-542 | 197-295 | 172-197 | 172-197 | 135-148 | 160-172 | 135-542 | 160-295 |
| | 427±168 | 238±113 | 184±74 | 180±76 | 139±68 | 164±68 | 250±56 | 194±24 |
| **CO outdoor** | 264-317 | 193-210 | 171-185 | 173-132 | 151-171 | 158-166 | 195-224 | 175-189 |
| | 288±27 | 199±9 | 176±8 | 182±10 | 161±10 | 163±5 | 208±15 | 181±8 |
| **CO I/O** | 1.3 | 0.9 | 0.7 | 07 | 0.5 | 0.6 | 0.8 | 0.7 |

**Table 6-9**. Statistics of the gaseous indoor and outdoor concentration (μg/m$^3$ results and $O_3$ during natural ventilation of the library.

| Natural ventilation | 1st period | | 2nd period | | 3rd period | | Average ventilation period | |
|---|---|---|---|---|---|---|---|---|
| | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 | 9.00-10.00 | 13.00-14.00 |
| **$O_3$ indoor** | 3.7-82.7 | 56.5-165.2 | 60.2-105.4 | 104.6-123.5 | 89.9-107.2 | 103.5-106.7 | 51.2-98.4 | 88.2-131.8 |
| | 45.5±39.7 | 116.7±55.3 | 88.2±24.5 | 115.7±9.8 | 99.9±9.0 | 105.1±1.6 | 77.9±24.4 | 112.5±22.2 |
| **$O_3$ outdoor** | 91.5-115.4 | 169.3-214.2 | 115.6119.8 | 126.8-134.0 | 114.0114.6 | 116.5-119.0 | 107.0-116.6 | 137.6-155.7 |
| | 103.8±11.9 | 195.0±23.1 | 117.3±2.2 | 130.9±3.7 | 114.2±0.3 | 118.0±1.3 | 111.8±4.8 | 148.0±9.4 |
| **$O_3$ I/O** | 0.4 | 0.6 | 0.8 | 0.9 | 0.9 | 0.9 | 0.7 | 0.8 |

Between the two gaseous pollutants and their comparison between indoor and outdoor concentrations, the most remarkable difference is noticed in the case of $O_3$, with higher I/O relatively to CO. This happens due the higher reactivity of this compound compared to others. In both cases, the I/O ratio peak seems to be in 18/8/16, where the air condition was on.

### 6.3 Particulate pollution data and investigation of I/O relations

As it is already mentioned, particles are classified into primary and secondary. Primary are emitted directly in the atmosphere, while secondary are formed by transformations of gases excisting in the air. Natural sources of PM include volcanic eruptions, fires, biological costituents such as pollen and bacteria and anthropogenic ones are mainly attributed to industries, transportation and argriculture (Krupinska et al., 2013). Indoor pollutants in libraries originate by structural or decorative materials, activities of visitors and staff and by the intrusion of outdoor pollutants. In some cases, the artifacts themselves may emit gases as well (Baer and Banks, 2009).

Airborne particulate sampling was conducted specific days and hours during the experimental period. Table 6-10 summarises the days where the filter sampling was carried out with comments about the day and the conditions. BC corresponds to background measurements, AC samples were collected during air condition operation, whereas AV conditions is for sampling after natural ventilation. Figure 6.4 presents the temporal duirnal varriability of PM10 data collected indoors and outdoors of the museum. Average mass concentration values were 26.3 $\mu g/m^3$ for outdoor measurements and 19.9 $\mu g/m^3$ for indoor with an average I/O ration equal to 0.8. The indoor and outdoor mass concentration values seem to covary (Figure 6.4), which indicates that the main factor determining the indoor PM10 concentration could be the outdoor conditions. The I/O ratios for the whole experimental period for PM10 were lower than 1, ranging from 0.6 to 0.9. I/O ratio higher to unity (>1) reflects into high inflow of the outdoor air towards the inside of the museum or additional sources indoor, while low I/O ratio means low inflow (Krupińska et al., 2013). The I/O ratio presents hereby fluctuations with the minimum value 0.6 the day 25/8 and maximum in the day 23/8 with ratio equal to 0.9. This indicates that the outdoor-indoor flow of air is not fixed with time, and may depend on many other factors such as ambient air wind speed or structular characteristics of the building.

**Table 6-10.** Details about the PM10 filters sampling.

| Start | End | Comments |
|---|---|---|
| **10/8/2016 9:00** | 11/8/2016 8:00 | BC (Wed) |
| **11/8/2016 8:20** | 11/8/2016 20:20 | AC (Thu) |
| **12/8/2016 8:00** | 13/8/2016 8:00 | BC (Fri) |
| **15/8/2016 8:00** | 16/8/2016 8:00 | BC (Mon) |
| **16/8/2016 8:15** | 16/8/2016 20:15 | AC (Tue) |
| **17/8/2016 8:21** | 18/8/2016 8:21 | BC (Wed) |
| **18/8/2016 8:25** | 18/8/2016 20:25 | AC (Thu) |
| **19/8/2016 8:25** | 20/8/2016 8:25 | BC (Fri) |
| **23/8/2016 8:15** | 24/8/2016 8:15 | BC (AV) (Tue) |
| **25/8/2016 8:20** | 26/8/2016 8:20 | BC (AV) (Thu) |
| **29/8/2016 8:20** | 30/8/2016 8:20 | BC (AV) (Mon) |

The presence of targeted chemical compounds in high concentrations can be considered as a threaten to the preservation of paper and books, thus a detailed chemical characterisation of atmospheric aerosols collected in the library was necessitated. Figure 6.5 presents the indoor and outdoor variability and the I/O relations as well for every chemical compound measured in the filters collected in and out of the library. In general, the indoor levels folow the same trend as the outdoor, possibly implying that the air quality of the library is driven by th ambient conditions. The elements that seem to be in similar levels indoor and outdoor are the $SO_4^{2-}$ whith the exception of one sample, and $NO_3^-$ ions. EC, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ and $Ox^-$ were met in higher levels outside relatively to the indoor library area. The rest of compounds was lower indoors.

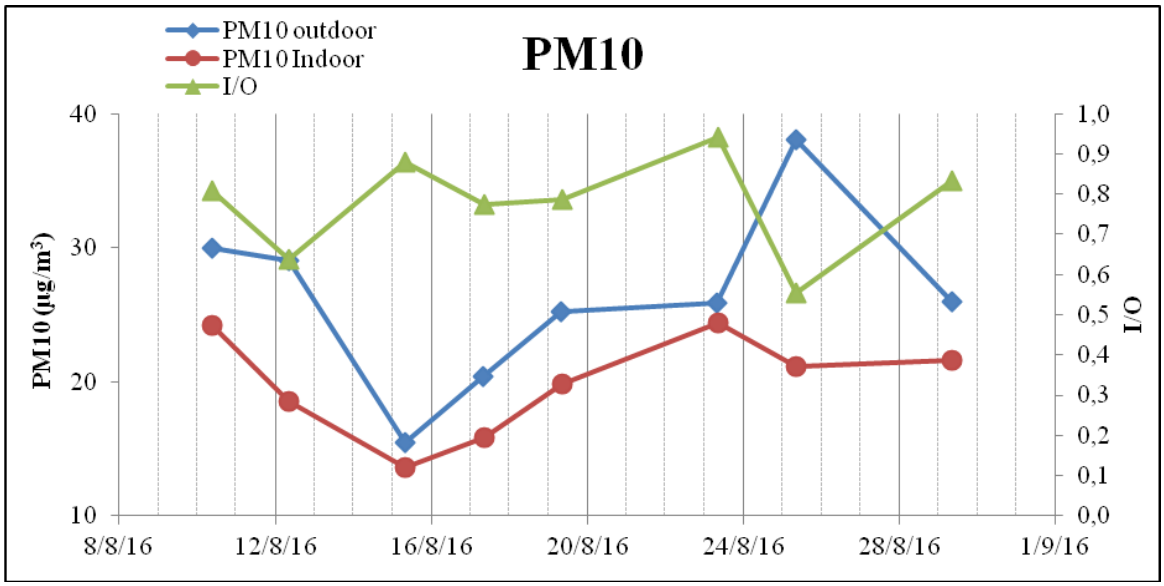
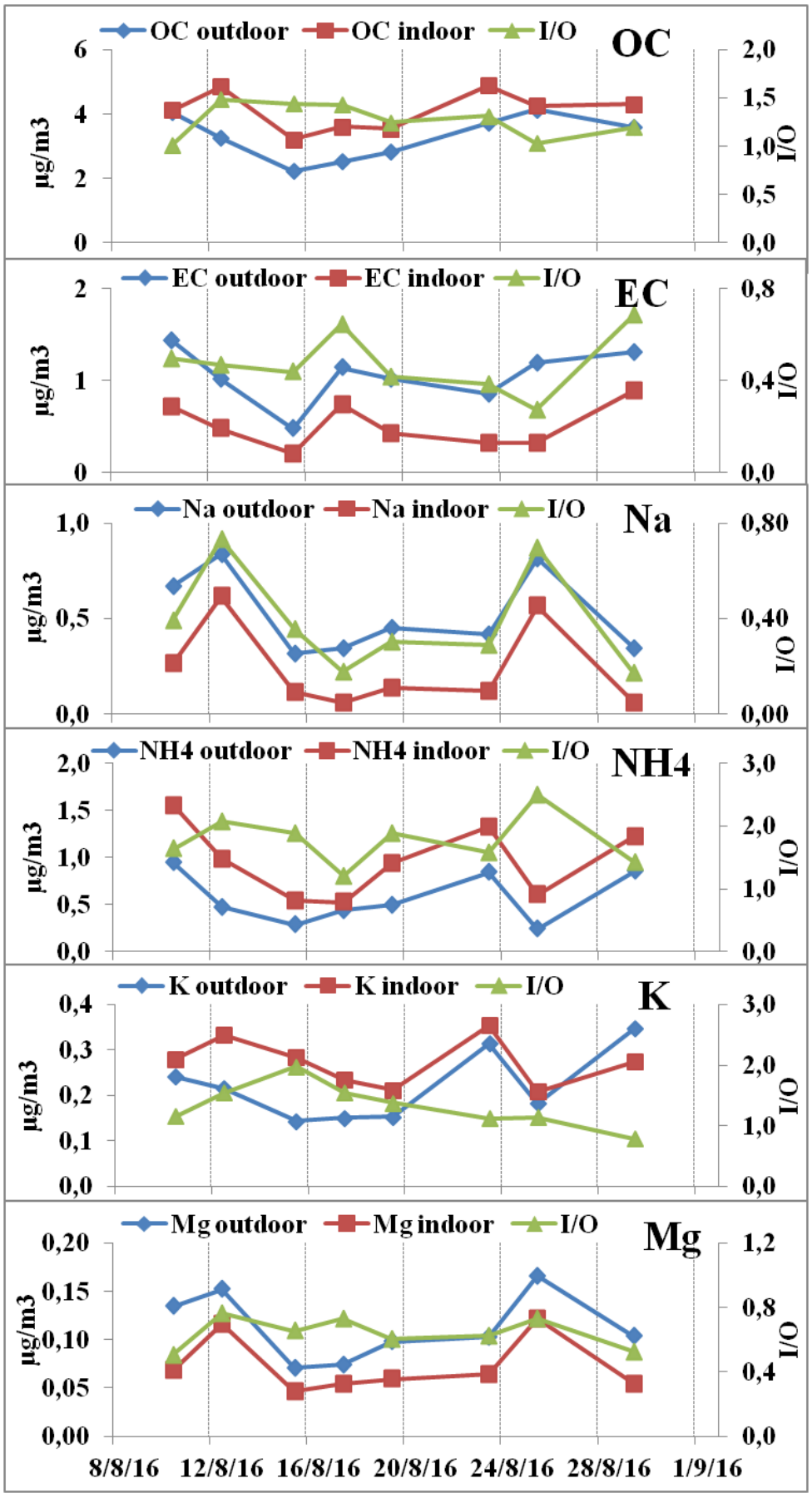



**Fig.6.4** Temporal variability of indoor, outdoor PM10 mass cocnentration and I/O ratio.


OC outdoor
OC indoor
I/O
OC
µg/m3
I/O
EC outdoor
EC indoor
I/O
EC
Na outdoor
Na indoor
I/O
Na
NH4 outdoor
NH4 indoor
I/O
NH4
K outdoor
K indoor
I/O
K
Mg outdoor
Mg indoor
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28/8/16
1/9/16

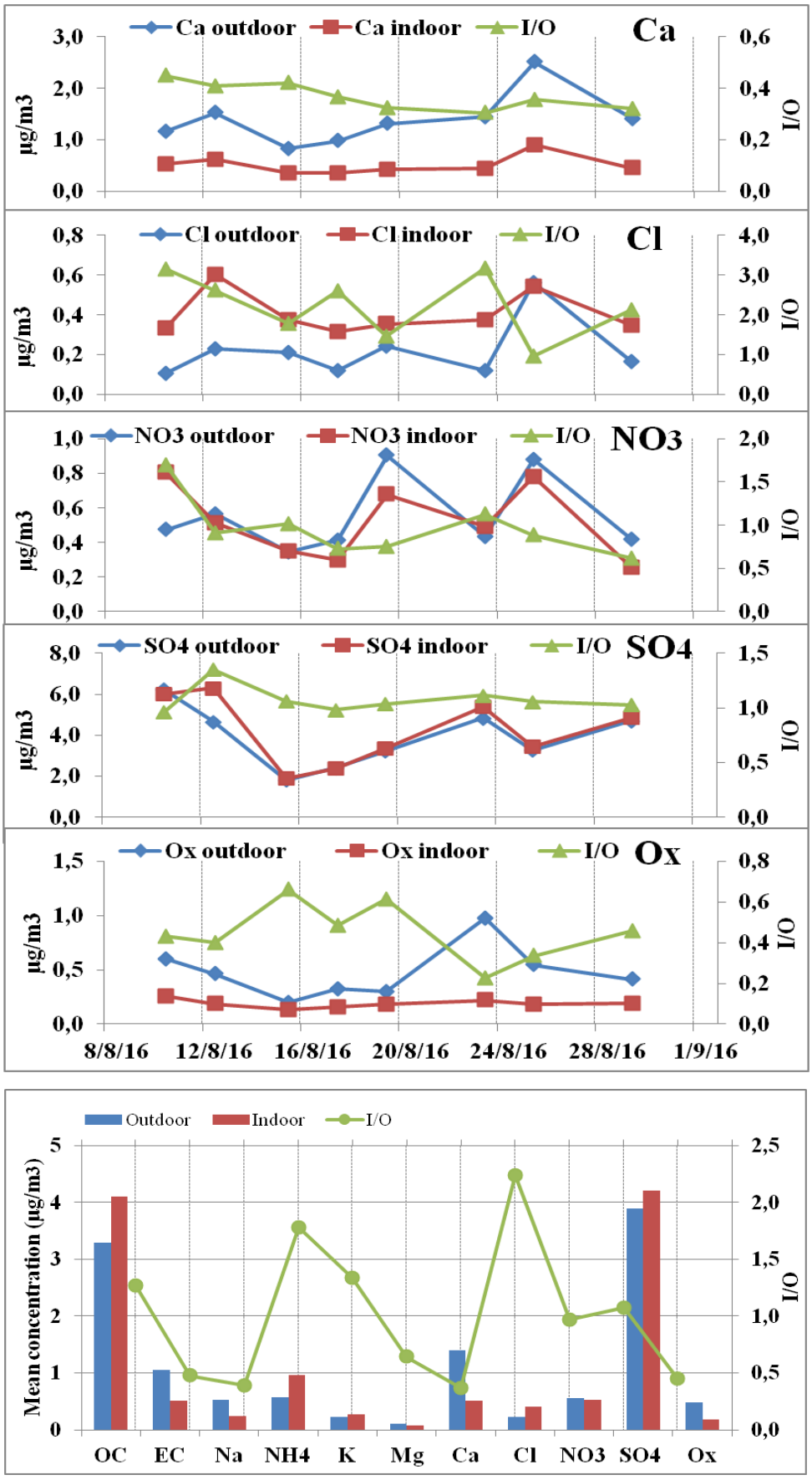


**Fig.6.5** Variability of indoor, outdoor concentration and the I/O ratios of the species determined on the PM10 filters. The plot in the bottom coresponds to the mean levels of the aforementioned chemicals.

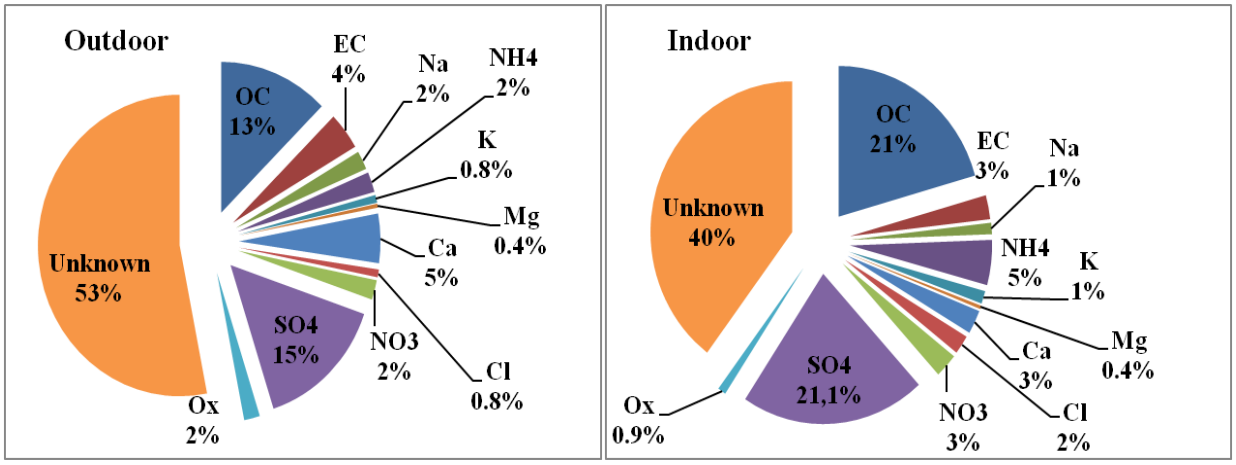


**Fig. 6.6** Mass closure on indoor and outdoor filter samples.

Figure 6.6 presents the mass closure based on the chemical analysis have been done relatively to the total mass concentration of the filter samples indoor and outdoor. The mass closure was up to almost 60% for indoor and 47% for outdoor measurements. The most abundant species inside the space of museum were the sulfate ions $SO_4^{2-}$ and the organic carbon (OC) by approximately 21% each. Moreover, ammonium ($NH_4^+$) concentration was found in significant amounts of 5% and the rest of species were almost equally distributed. Outdoor OC and $SO_4^{2-}$ also were the most abundant species but in lower percentages (12 and 15%, $Ca^{2+}$ was ranging at 5% and EC at 4%. The species determined both indoor and outdoor were correlated to each other trying to identify common origin. Taking into account the limited number of samples and based on the findings of the Tables 6-11 and 6-12 it was quite difficult to extract safe conclusions about the sources. The correlations were weak with the exception of Na and Mg in both environments. Additionally, salts such as NaCl and $MgCl_2$ (Anaf et al, 2014) could be present indoor denoting impact of sea salt or buildings materials (mortars according to Krupińska et al., 2013).

**Table 6-11.** Correlation coefficients of the particulate scpecies determined outdoor.

| **OUTDOOR** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***$R^2$*** | ***OC*** | ***EC*** | ***Na*** | ***NH4*** | ***K*** | ***Mg*** | ***Ca*** | ***Cl*** | ***NO3*** | ***SO4*** | ***Ox*** |
| **OC** | 1.00 | | | | | | | | | | |
| **EC** | 0.43 | 1.00 | | | | | | | | | |
| **Na** | 0.36 | 0.14 | 1.00 | | | | | | | | |
| **NH4** | 0.24 | 0.24 | 0.02 | 1.00 | | | | | | | |
| **K** | 0.36 | 0.12 | 0.01 | 0.64 | 1.00 | | | | | | |
| **Mg** | 0.60 | 0.24 | 0.91 | 0.00 | 0.03 | 1.00 | | | | | |
| **Ca** | 0.48 | 0.11 | 0.45 | 0.06 | 0.02 | 0.64 | 1.00 | | | | |
| **Cl** | 0.09 | 0.00 | 0.31 | 0.43 | 0.10 | 0.35 | 0.72 | 1.00 | | | |
| **NO3** | 0.07 | 0.05 | 0.25 | 0.14 | 0.11 | 0.27 | 0.46 | 0.53 | 1.00 | | |
| **SO4** | 0.58 | 0.39 | 0.17 | 0.71 | 0.51 | 0.27 | 0.02 | 0.09 | 0.01 | 1.00 | |
| **Ox** | 0.50 | 0.03 | 0.06 | 0.31 | 0.40 | 0.14 | 0.13 | 0.01 | 0.00 | 0.41 | 1.00 |

**Table 6-12.** Correlation coefficients of the particulate scpecies determined indoor.

| **INDOOR** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **$R^2$** | **OC** | **EC** | **Na** | **NH4** | **K** | **Mg** | **Ca** | **Cl** | **NO3** | **SO4** | **Ox** |
| **OC** | 1.00 | | | | | | | | | | |
| **EC** | 0.01 | 1.00 | | | | | | | | | |
| **Na** | 0.23 | 0.08 | 1.00 | | | | | | | | |
| **NH4** | 0.31 | 0.15 | 0.01 | 1.00 | | | | | | | |
| **K** | 0.40 | 0.01 | 0.00 | 0.25 | 1.00 | | | | | | |
| **Mg** | 0.32 | 0.06 | 0.94 | 0.01 | 0.00 | 1.00 | | | | | |
| **Ca** | 0.20 | 0.04 | 0.74 | 0.00 | 0.05 | 0.84 | 1.00 | | | | |
| **Cl** | 0.27 | 0.16 | 0.88 | 0.04 | 0.03 | 0.86 | 0.59 | 1.00 | | | |
| **NO3** | 0.02 | 0.08 | 0.30 | 0.08 | 0.07 | 0.26 | 0.39 | 0.08 | 1.00 | | |
| **SO4** | 0.71 | 0.09 | 0.15 | 0.70 | 0.39 | 0.14 | 0.07 | 0.09 | 0.09 | 1.00 | |
| **Ox** | 0.32 | 0.10 | 0.02 | 0.80 | 0.08 | 0.02 | 0.05 | 0.01 | 0.33 | 0.64 | 1.00 |

# 7. IMPACT OF INDOOR AIR QUALITY ON THE BOOK COLLECTION

The collection in the library of the Library of the Museum of Geoastrophysics of the National Observatory of Athens (MG/NOA) can be considered as uniform, consisted by books. Paper is the main material and we will focus on that, whereas leather or parchment for covers or bindings could also be met. Other materials such as wooden furniture (bookcases and desks) and the materials of the roof (paint and metal) are of secondary importance for this study and the possible implications will not be investigated thoroughly. Nevertheless possible implications attributed to those factors will be assessed if needed. Comparison with standards and literature references will be held in combination with available tools for the estimation of the threats for the collection of the MG/NOA, taking also into account the urban environment of the area.

The natural aging of paper is attributed to both endogenous and exogenous factors (Area and Cheradame, 2011). The cellulose macromolecules' properties and the industrial processes of paper production belong to the endogenous parameters. The conservation conditions (temperature, humidity, illumination), the contamination of the air with pollutants and the use of books consist the exogenous contributors. The degradation of the paper could be chemical (acid or enzymatic hydrolysis, alkaline degradation and oxidative degradation), thermal (due to temperature levels and variations) and radiation induced decay (exposure to UV/Vis radiation). The role of air pollution is crucial. The presence of air pollutants could be critical for the fate of the book collection, especially in exhibition areas or storage rooms with uncontrolled micro-environment parameters, mainly by the aspect of acid hydrolysis processes. Books or archival material stored in buildings in polluted areas could be characterized by increased acidity due to absorption of air contaminants (Daniel et al., 1990; Daniel, 1996; De Feber et al., 1998; Havermans and Steemers, 2005). For instance, sulphur dioxide ($SO_2$) could be oxidized into sulphuric acid ($H_2SO_4$) synergistically with the humidity of the paper or the air and other atmospheric chemicals. Nitrogen oxides ($NO_x$) and ozone ($O_3$) in high relative humidity environments enhance the $SO_2$ uptake (Johansson et al., 2000; Johansson and Lennholm, 2000), catalyzing therefore the hydrolysis reactions. For such cases the storage of paper material under dry humidity is usually recommended targeting to elimination of the gaseous uptake. On this view r we will try to assess the possible risk for the books taking into account the findings for T, RH and pollutants presented in previous chapters.

### 7.1 Risk assessment of the temperature and relative humidity in the library collection

Temperature and relative humidity are the most crucial factors for libraries and archival collections. Relative humidity and temperature are related in reverse order. When the temperature increases, the warm air can hold more moisture, so the relative humidity drops. On the contrary, when the temperature decreases, the cooler air hold less moisture and the relative humidity increases (Canadian Council of Archives, 2003). Generally, there is a rule that supports that the change of temperature drives the aging reaction rates. The rate of chemical reactions can be changed and even to double with an increase in temperature of 10$^{o}$C and for some unstable materials by only 5$^{o}$C (Henderson, 2013). Archival collections consisted of organic materials such as paper, leather (book bindings), and parchment are hygroscopic. That means that they can readily absorb and release moisture from the environment resulting in expansion of the material. In contrast, when the levels of relative humidity decreases, organic materials lose moisture content and tend to shrink. High relative humidity levels can create growth of mold and mildew, cockling of paper and parchment, flanking ink, warping of the covers of books and leads to biological damages by organisms. Low relative humidity makes the archival collection brittle and susceptible to cracking.

Table 7-1 summarizes some of the accepted relative humidity and temperature suggested levels. The limit values of 21±1ºC and 50±3%RH introduced in 1979 (LaFontaine) are still very often the basis for the deterioration of material. The classic reference conservation conditions according to Thomson (1994) are set at 50%RH and 20ºC. A slight change to 45%RH and 18ºC (currently recommended by Davis, 2006) can significantly increase the lifetime of certain types of objects. Moreover, for Museum environment the lower limit is set by possible cracking, breaking of fibers, and damage by embrittlement (Thomson,1986).This becomes a danger for wood, bone, ivory, basketry, parchment and heavy leather book bindings at about 40 %. Paper in use in libraries also becomes more liable to break at these levels. Therefore RH should preferably be above 45 % and should not be allowed to fall below 40%.

Based on the best current knowledge and referring to the Temperature and Relative Humidity specifications for collections, included on the 2015 ASHRAE Handbook (American Society of Heating Refrigeration and Air-Conditioning Engineers handbook), the limit values of 50%RH and temperature range of 15-25ºC can be used for sensitive material. The tolerance is a bit higher for general collections ranging at 60%RH and temperatures of 20-30ºC. In general and taking into consideration different standards (Wilson, 1995; Australian Standard

AS 4390, 1996; Ogden, 1999b; BSI [British Standards Institution] BS 5454, 2000; ISO 11799, 2003; BSI [British Standards Institution] PD 5454, 2012; State Records Authority of New South Wales, 2012) the suggested temperature for books and archival material storage varies from 14 to 21ºC. Each norm nominates an optimum level or range, which depicts the compromise between the optimum for conservation purposes and affordable. As it concerns the relative humidity 30-55% is usually suggested. For lower level paper which is already subjected to decay will lose its flexibility and become brittle. It has to be mentioned that these limits require the minimum fluctuations within their range, otherwise warping and cracking would be occurred.

**Table 7-1.** Summary of relative humidity and temperature standards used for conservation of books and archival material.

| Standard/Refference | Conditions/Material | Temperature | Relative Humidity |
|---|---|---|---|
| **LaFontaine 1979** | Limits for deterioration of materials | 21±1ºC | 50±3%RH |
| **Thomson 1994** | classic reference conservation conditions | 20ºC | 50%RH |
| **WILSON (1995:2)** | Paper | | 30-50 % |
| | Parchment | | 30-50 % |
| **ISO 11799: 2003** | Archival book material | 2-18±1ºC | 30-60±3%RH |
| **Davis 2006** | Updated recommended parameters | 18ºC | 45%RH |
| **Sterflinger 2010** | | | Fungi development>55% |
| **PAS 198:2012** | Paper, prints, watercolors, drawings, manuscripts, textiles | $5^{o}C$ – $25\ ^{o}C$ | 30-60 % |
| | Leather, horn, bone, wood, ivory | $5^{o}C$ – $20\ ^{o}C$ | 30-60 % |
| **ASHRAE 2015** | Sensitive materials | 15-25 ºC | <50% |
| | General collections | 20-30 ºC | <60% |
| **UNI 10586, Andretta et al 2016** | Librarian artifacts | $14^{o}C$ – $20\ ^{o}C$ $\Delta T_{24} < 2\ ^{o}C$ | 50-60 % $\Delta RH_{24} < 5\%$ |

Except from the absolute levels of T and RH the sudden changes and the duration of the fluctuation are also significant. The fluctuations can lead to mechanical damage of the objects, due to expansion and contraction of hydroscopic materials. These concerns introduced restrictions and set the limits of 50±3%RH and 21±1ºC in 1979 by LaFontaine, which are still

applicable in many cases with respect to the materials of the objects that may introduce further restrictions. 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 points out that repositories for archive and library materials should be kept at a cool temperature and at a relative humidity below the point where microbiological activity occurs. According to the present state of knowledge, there is an increasing risk of microbiological activity above 60 % relative humidity and increased brittleness at very low relative humidity. The lowest acceptable humidity for long-term storage of archive and library materials is under discussion and the kind of materials should be the key factor for application of limit levels of T and RH. Generally speaking efficient conservation, depicting to longer life time, is achieved at lower temperatures and at lower relative humidity. As guidance, the data of Table 7-2 recommended by the International Standard ISO 11799:2003 may be used. The best practice is to achieve as much as possible stable temperature and relative humidity without sharp fluctuations that put stress on library materials and should therefore be avoided.

**Table 7-2.** Recommended temperature and hydrometric conditions for the long-term storage of archive and library materials according to the International Standard ISO 11799:2003 'Information and documentation – Document storage requirements for archive and library materials.

| Type of materials | Temperature $^{o}$C | | | Relative Humidity (%) | | |
|---|---|---|---|---|---|---|
| | Min | Max | Tolerable daily changes within the limits | Min | Max | Tolerable daily changes within the limits |
| Paper, optimum preservation | 2 | 18 | ±1 | 30 | 45 | ±3 |
| Paper, staffed stack areas, items in regular use | 14 | 18 | ±1 | 35 | 50 | ±3 |
| Parchment, leather | 2 | 18 | ±1 | 50 | 60 | ±3 |

The mean T and RH levels encountered in our case at MG during August 2016 for each period are presented in Table 7-3 along with the reference values for comparison purposes. The mean temperature exceeds the recommended values in the library and the showcase even for the air conditioned period. The mean relative humidity falls within the limits. Talking about the absolute values of the library macro and micro environment according to Figure 5.9

a and b, temperature is always above the limits. Relative humidity for the micro environment (show case) is within the limits and the macroenvironment also with a few exceptions.

**Table 7-3**. Mean temperature and relatively humidity met in the library and in the show case. The reference values are also presented.

| Background | Ambient | Library | Showcase |
|---|---|---|---|
| **Average background period** | **28.3 ± 0.73ºC** | **30.5 ± 0.45ºC** | **30.6 ± 0.45ºC** |
| | **43.1 ± 1.90%** | **35.8 ± 1.51%** | **43.0 ± 0.22%** |
| **Air conditioned** | **32.2 ± 0.3ºC** | **24.6 ± 0.51ºC** | **26.3 ± 0.17ºC** |
| | **31.7 ± 0.82%** | **33.9 ± 0.76%** | **41.7 ± 0.08%** |
| **Natural ventilation** | **31.2 ± 0.10ºC** | **30.8 ± 0.03ºC** | **30.4 ± 0.10ºC** |
| | **35.6 ± 0.73%** | **36.4 ± 0.54%** | **43.4 ± 0.02%** |
| ***ISO 11799:2003*** | - | ***2-18ºC*** | |
| | - | ***30-60%*** | |
| ***UNI 10586, Andretta et al 2016*** | - | ***14-20ºC*** | |
| | - | ***50-60%*** | |

The deviations within the day are crucial significant and their role should be investigated. Figures 7.1 (a) and (b) present the 24 hours (daily) differences between minimum and maximum of the temperature and relative humidity measured in the library (indoor with the ACL system and with the Tiny Tag in the showcase) and they are also compared with the outdoor ones. The air condition use and natural ventilation period are depicted within the frames. For these periods the test hours have been excluded. We use the tolerance daily changes of 1$^{o}$C and 3% of the ISO 11799:2003. According to Andretta et al. (2015) and, based on the UNI 10586 standards the acceptable values of daily thermal gradient for libraries are extended to 2$^{o}$C and 5% for relative humidity respectively. Regardless the norms in any case the gradient met for temperature was out of the limits for most of the cases. The RH gradient for the showcase was within the limits but for the library macroenvironment exceedances were encountered almost every day. It is clear that within the 24hour, during the experiment period there are significant exceedances in relevance to the threshold values specified by the norms and guidelines, introducing issue of risk for the objects. The library thermo hydrometric parameters vary in accordance with the ambient meteorological conditions and they are met at lower levels, implying poor inertia of the building.

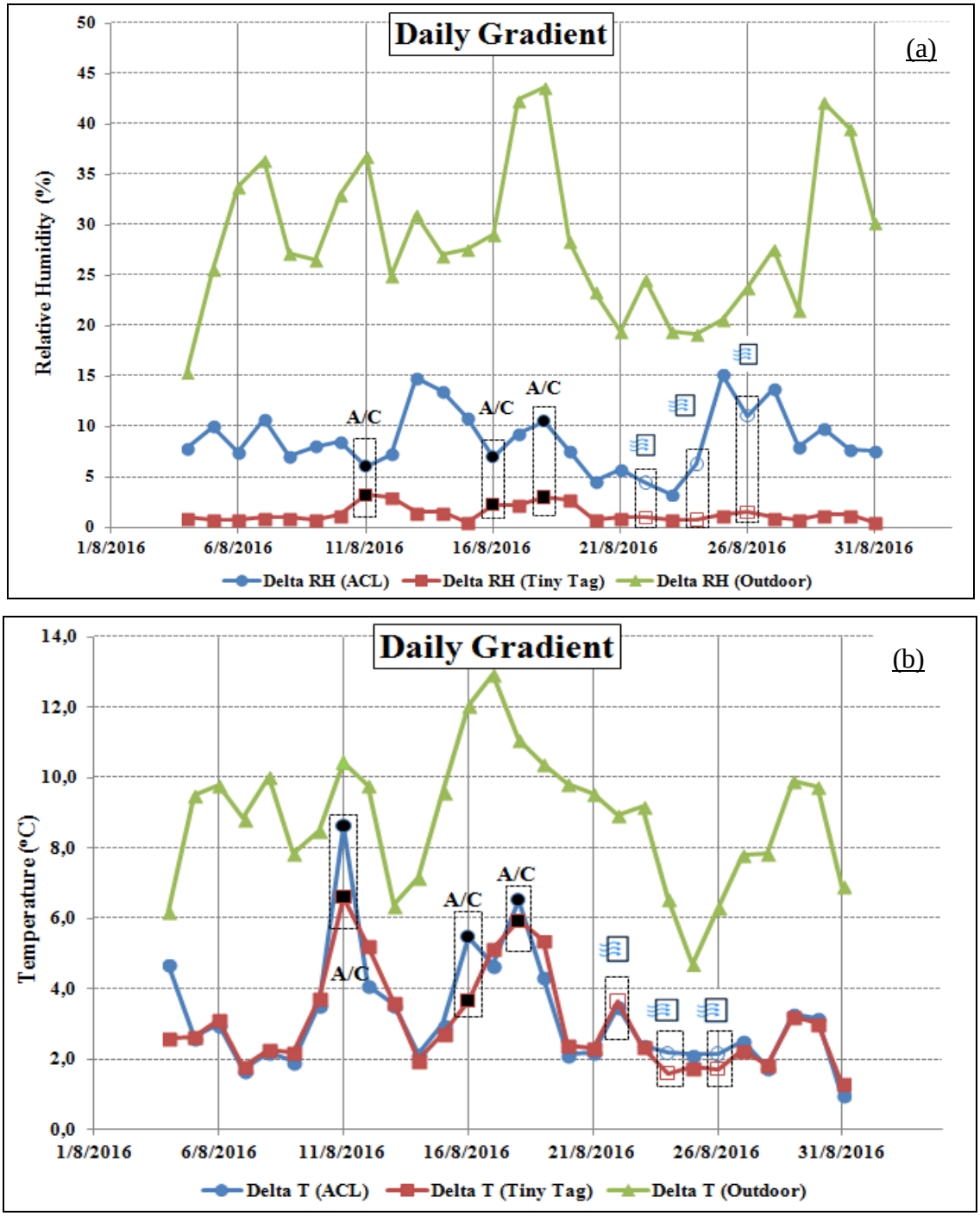


**Fig.7.1** Daily excursions for (a) temperature and (b) relative humidity during the experimental period within the Library. The black frames present the days that the air library was both either air conditioned and or naturally ventilated. ACL system represents the measurements in the space of library, while Tiny Tag represents the measurements in the Showcase.

An approach of the combined effect of T and RH in the library collection is the evaluation of the combined conditions regarding the acceptable conditions. By means of that technique, the Performance Index (PI) of the building is calculated in order to evaluate the Indoor Microclimatic Quality (IMQ). PI expresses the percentage of time in which the

microclimatic parameters of the library do not match to the recommended values. We prepare the figures 7.2 (a) and (b) for the library and the glass fronted showcase respectively, where the hourly mean values of our measurements are presented. The axis x represents the relative humidity and the axis y the temperature. The red lines are the acceptable limits for storage according to ISO 11799:2003 (2-18ºC and 30-60%) and Andretta et al. 2015 (14-20ºC and 50-60%). In the optimum case the pairs of T, RH should be within the areas defined by these limits. According to the findings the conditions of the library and the showcase are not the preferable, posing risk for the collection of books. Even if we use more general guidelines of 20-20ºC and 45-55% the conditions are out of the limits.

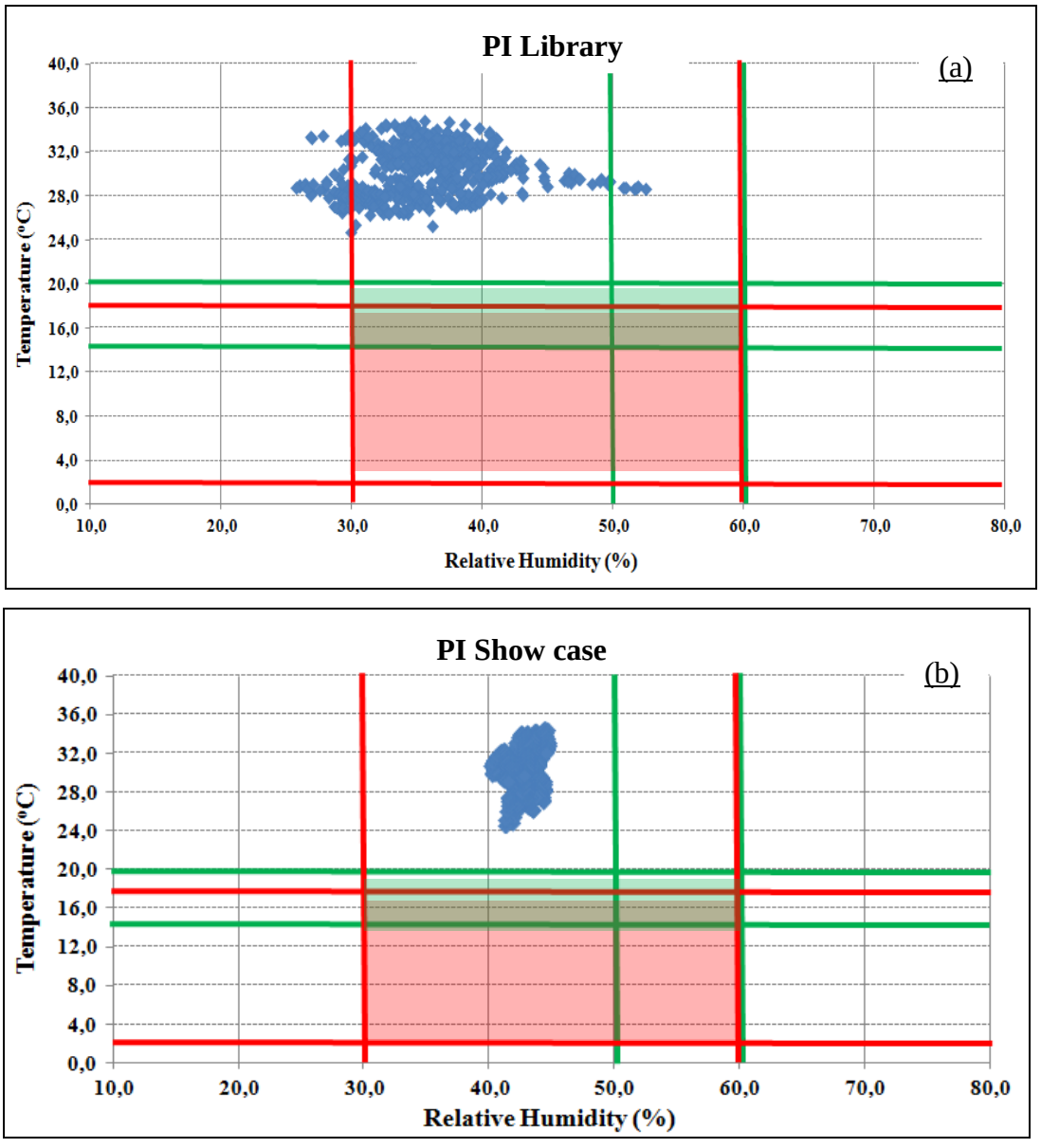


**Fig.7.2** Performance Index (PI) for the experiment period according to Temperature and Relative Humidity measured (a) in the Library by ACL system and (b) the show case by means of the Tiny Tag.

Very generally speaking, lowering the temperature and/or lowering the relative humidity will lengthen the life of the documents. However, other effects may run counter to this, notably condensation if the temperature sinks below the dew point and substrate brittleness when the relative humidity becomes low. According to the 2015 ASHRAE Handbook, relative humidity and temperature belong to the most important types of threats to collections. For each material there is a level of environmental moisture content (EMC), a threshold value for maximum chemical, physical or biological resistance. For very low or high EMC the risk factor is increased. Also, unstable relative humidity with large level variations could also deteriorate sensitive objects. The temperature is strongly anti-correlated with relative humidity and can also drive aging processes, especially for cases of elevated levels. At the same time can also magnify the effect of incorrect RH. Consequently, T and RH should be taken into consideration together for conservation issues related to material such as paper.

A useful tool to measure aging rates or deterioration rates is the Preservation Calculator created by the Image Permanence Institute (IPI 2006), which can be accessed for free from the IPI Web site at http:// www.dpcalc.org. This software calculates the preservation index (PI), which expresses the preservation quality of a storage environment for organic materials. It is a useful tool to understand the effects of temperature and relative humidity on natural aging of organic collections made from organic materials. Every environment has exactly one combination of temperature (T), relative humidity (RH) and dew point (DP). The DP is a measure of the absolute amount of water in the air and is determined as the temperature at which the air cannot hold all the moisture in it and water condenses. We determine our Dew Point by using the mean levels of temperature and relative humidity for each case described in Table 7-4. The results are presented on Table 7-4 along with the EMC and the estimated risk. The interpretation of the possible risk is based on the evaluation of PI and EMC according to Figure 7.3. The mean conditions met in the library could cause natural aging since according to PI<45. The % EMC ranges at 6.7-7.9, which means that there is no risk for mechanical damage or metal corrosion. Also there is no danger for mold growth for the specific conditions.

**Table 7-4**. Impact of environmental conditions with respect to Natural Aging, Mechanical Damage, Mold Growth and Metal Corrosion.

| library | T | RH | DP | PI | Days to Mold | EMC |
|---|---|---|---|---|---|---|
| **background** | 31°C | 36% | 14°C | 17 | No Risk | 6.9% |
| **air condition** | 25°C | 34% | 8°C | 36 | No Risk | 6.7% |
| **natural ventilation** | 31°C | 36% | 14°C | 17 | No Risk | 6.9% |
| | | | | | | |
| **showcase** | **T** | **RH** | **DP** | **PI** | **Days to Mold** | **EMC** |
| **background** | 31°C | 43% | 17°C | 14 | No Risk | 7.9% |
| **air condition** | 26°C | 42% | 12°C | 26 | No Risk | 7.9% |
| **natural ventilation** | 30°C | 43% | 16°C | 16 | No Risk | 7.9% |

The findings and the risk assessment concern only the study period during August for an average level of T and RH. The fluctuation within the day and their frequency should also be considered. Taking into account that during winter the ambient conditions that influence the indoor environment are different the risk should be evaluated. During winter lower temperatures and higher relative humidity could be met in the area. For those cases the risk could be different and should be evaluated by long term monitoring of T and RH.

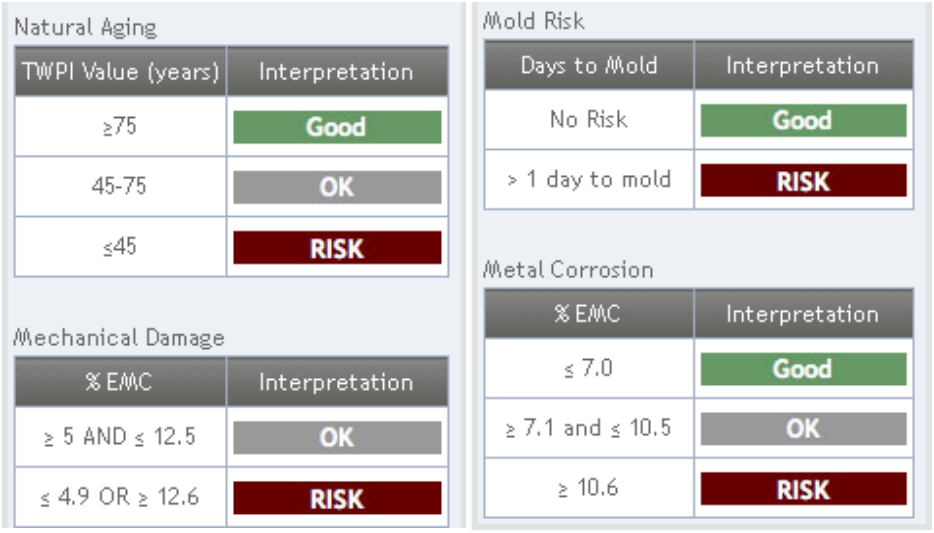


**Fig.7.3** Interpretation of PI and %EMC for risk assessment of the climatic parameters

### 7.2 Risk assessment of the pollution in the library collection

Along with the climatic parameters (T and RH) the level of pollutants should be considered due to the impact on the aging reaction rates. Air pollutants have severe impacts not only to human health and to the environment but also to many materials. The direct effects are limited but in the long term irreversible effects such as color change, surface deterioration and weaking of the material may occur especially to sensitive ones like paper, leather and parchment. In this subchapter, the threshold concentration limits of the gaseous pollutants, which analyzed above, will be assessed. Moreover, the major impacts on the materials that hosted in library will be discussed.

Based on the best current knowledge and referring to the current recommended levels of key gaseous pollutants for collections, included on the 2015 ASHRAE Handbook (American Society of Heating Refrigeration and Air-Conditioning Engineers handbook), the limit values of nitrogen dioxide ($NO_2$) range from 0.05 to 2.6, of ozone ($O_3$) range below 0.05 and for sulfur dioxide ($SO_2$) from 0.04 to 0.4 which can be used for sensitive material. Furthermore, taking into consideration a different standard (ISO 11799, 2003) the suggested concentrations in ppb for books and archival material storage varies from 5-10 ppb for Nitrogen Oxides (NOx), sulfur dioxide ($SO_2$) and Ozone ($O_3$). Each norm nominates an optimum level or range, which depicts the compromise between the optimum for conservation purposes and affordable. The concentration levels encountered in this specific case at library during August 2016 for the whole experiment period as a reference are presented in Table 7-5.

**Table 7-5**. Mean pollutants concentrations (ppb) met in the library during background, air conditioned and natural ventilation periods. The reference values are also presented.

| Pollutants | Background period | Air conditioned period | Natural Ventilation period | *ISO 11799:2003* | *ASHRAE 2015* |
|---|---|---|---|---|---|
| **NO** | **2.3 ± 2.7** | **5.7 ± 6.3** | **2.4 ± 2.4** | **-** | ***<0.05*** |
| **$NO_2$** | **8.9 ± 3.0** | **12.1 ± 3.2** | **9.2 ± 0.6** | **-** | ***<0.05 to 2.6*** |
| **NOx** | **11.3 ± 5.2** | **17.8 ± 8.6** | **12.6 ± 3.7** | ***5 - 10*** | **-** |
| **$SO_2$** | **1.8 ± 2.3** | **1.7 ± 0.2** | **1.9 ± 0.4** | ***5 - 10*** | ***<0.04 to 0.4*** |
| **$O_3$** | **60.0 ± 3.7** | **25.4 ± 5.6** | **83.1 ± 0.8** | ***5 - 10*** | ***<0.05*** |
| **PM10 (μg/m$^3$)** | **19.9 ± 3.8** | **-** | **-** | ***50*** | **-** |

As it is shown in the Table 7-5, particulate matter is under the limit set by the ISO 11799:2003, the concentrations for nitrogen oxides and ozone are above the limit values, while as far as sulfur dioxide is concerned the values are between the limits, only in case of ISO 11799:2003 standards. Nitrogen dioxide, sulfur dioxide, ozone are the main damage-causing gases present outdoors. They come mainly from fuel burning in transport, buildings and industry. Much of the nitrogen dioxide and ozone is not formed directly, but in secondary reactions involving the action of sunlight on pollutants emitted largely from motor vehicles.

Blades et al. in *Guidelines on pollution control in heritage buildings* in 2000, have summarized the effects of pollutants in different cultural heritage materials. Specifically, they refer that sulfur dioxide can cause embrittlement and discolorance of the paper and weakening or powdered surface of the leather covers of books. Specifically, it can be absorbed onto cellulosic materials such as paper, where it catalytically hydrolyzes to $H_2SO_4.H_2SO_3$ and $H_2SO_4$ can also be absorbed directly onto this (ASHRAE, 2015). Moreover, could $SO_2$ react with leather and parchment, breaking down their molecular structure and weaking the materials. As a result, it contributes to powdery surface which is easily abraded. Additionally, apart from $SO_2$, ozone as well can damage books affecting leather and parchment. Ozone, as a strong oxidant, causes fading of dyes and pigments and induces attack on organic materials (Morten, 2006). As far as $NO_2$ is concerned, the presence of humidity, could be converted into nitric acid ($HNO_3$) and $SO_2$, if also oxidants are available, into sulfuric acid ($H_2SO_4$). Acidic air pollution usually leads to the hydrolytic degradation of leather, parchment and paper materials causing significant damage of the artifacts (Pavlogeorgatos, 2003)

# 8. CONCLUSIONS

An exhibition area, a Library in our case which hosts books of a great cultural value, should be protected from extreme climatic conditions and air pollution. Materials and artworks, exposed to non-controlled environmental conditions or to gaseous pollutants, airborne particles emitted indoors or penetrating from the outdoor environment, could be imposed on accelerated natural decay.

The present study focuses on the of airborne particulates (PM10 and determination of their content in OC, EC and ions) and gaseous pollutants (NO, $NO_2$, $SO_2$, CO, $O_3$), as well as the thermo hydrometric conditions indoors and outdoors of the Library of the Museum of the Geoastrophysics of the National Observatory of Athens which hosts books and archival materials from the $16^{th}$ century. During the present study, it was found that the library of the National Observatory of Athens is exposed to risk mainly due to temperature and relative humidity levels, during the measurements campaign. Especially, concerning to temperature and relative humidity, the results showed that both T and RH indoor (library and showcase) are driven by the ambient meteorological conditions, with the exception of the showcase RH which demonstrates stability in the levels and the variability. The use of air condition adjusts the temperature of library according to the set levels and maintains the humidity in the levels of the pre air conditioned period. The natural ventilation for short periods contributes almost insignificantly to the indoor T and RH tendency. Moreover, despite the fact that RH complies with the norms, T is always out of the limits of the regulations, whereas both present a wide range of fluctuations ($\Delta T_{24}>2^oC$ and $\Delta RH_{24}>5\%$) that could potentially contribute to books decay. The combined T and RH findings are totally (PI=0%) out of the acceptable limits posing risk for the materials. Under the conditions determined during the study, natural aging seems to be the potential risk for the materials in the library.

As far as the air pollution in the space of library is concerned, the Indoor Air Quality is induced by ambient pollution and the fate of the contaminants in the library which could be justified by their reactivity (I/O of 0.6 and 1.1 for $O_3$ and CO respectively). Indoor $O_3$ and NOx could contribute to the decay reactions due to increased levels. Furthermore, particles infiltrate by 80% in the building. Their composition should be further investigated in order to provide accurate information about the impact of different ambient sources and implications on the material in correlation with the T and RH conditions.

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