EFFECTS OF TRAFFIC RELATED AIR POLLUTANTS ON DOLMABAHÇE PALACE INDOOR AIR QUALITY

by

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APPROVAL PAGE

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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ABSTRACT

In this study, traffic related pollutants were investigated in Dolmabahçe Palace. For this purpose, indoor and outdoor air samples were collected with winter and summer campaign at 65 different places that included Dolmabahçe Palace. Nitrogen oxide (NO_2), sulphur dioxide (SO_2), Aldehydes, Particulate Matter (PM) Black Carbon (BC) and heavy metals such as Chromium (Cr), Copper (Cu), Manganese (Mn), Nickel (Ni), Cadmium (Cd), and Lead (Pb) parameters were monitored. NO_2, SO_2 were analysed with Ion Chromatography (IC). Aldehydes were analysed with High-Pressure Liquid Chromatography (HPLC). PM was sampled with by Cascade Impactor and heavy metals were measured by Graphite Furnace Atomic Absorption (GFAAS) and also BC was sampled with Aethalometer. We determined distribution of air pollution inside the palace. Two different model used for evaluated result and we defined the associated highest corrosion risks for the rooms of the palace.

In summer season almost air pollution parameters measured highest in Dolmabahçe Palace.

Keywords: Dolmabahçe Palace, Indoor air quality, Traffic related pollutants

TRAFİK KAYNAKLI KİRLETİCİLERİN DOLMABAHÇE SARAYI İÇ ORTAM HAVA KALİTESİNE ETKİSİ

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ÖZ

Bu çalışmada, trafik kaynaklı kirleticilerin Dolmabahçe Sarayı iç ortam hava kalitesine etkileri araştırılmıştır. Bu amaçla yaz ve kış aylarında saray içinde ve saray dış ortamı temsil edecek toplam 65 örnekleme noktasında örnekleme yapılmıştır. Azot oksit (NO_2), Sülfür dioksit (SO_2), Aldehitler, Partikül Madde (PM) Black karbon (BC) ve ağır metaller Krom(Cr), Bakır(Cu), Mangan(Mn), Nikel(Ni), Kadmiyum(Cd), Kurşun(Pb) gibi parametreler izlenmiştir. NO_2, SO_2 analizleri İyon Kromatogrofi (IC) cihazında, yapılmıştır. Aldehit analizleri ise High-Pressure Liquid Kromatogrofi (HPLC) cihazında yapılmıştır. PM örneklemesi ise Kaskat İmpactör ile yapılmış, metal tayini Grafit Fırınlı Atomik Absorpsiyon (GFAAS) cihazı ile yapılmış, ayrıca elementel karbon örneklemesi Aethalometre ile yapılmıştır. Saray içindeki hava kirliliğinin dağılımı belirlenmiştir. İki farklı model kullanılarak korozyon acısından yüksek risk altındaki odalar belirlenmiştir.

Dolmabahçe Sarayında birçok parametreye ait kirlilik değerlerinin yaz mevsiminde daha yüksek olduğu tespit edilmiştir.

Anahtar Kelimeler: Dolmabahçe Sarayı, iç ortam hava kalitesi, trafik kaynaklı kirletiçiler

DEDICATION

To my lovely family

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LIST OF SYMBOLS AND ABBREVATIONS

SYMBOLS/ABBREVATIONS

2,4-DNPH	2,4-dinitrophenylhydrazine
AA	Acetaldehyde
ARB	California Environmental Protection Agency Air Resources Board
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
BC	Black Carbon
BTX	Benzene, Toluene, Xylene
$CaC0_3$	Calcium Carbonate
$CaSO_4H_2O$	Hydrate of Calcium Sulphate
Cd	Cadmium
Cl	Chlorine
CO_2	Carbon dioxide
EC	Elemental Carbon
EPA	U.S. Environmental Protection Agency
EU5FP	European Union Fifth Frame Work Programme
EWO	Early Warning dosimeter for Organic materials
FA	Formaldehyde
FAAS	Flame Atomic Absorption Spectrometry
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
IAQ	Indoor Air Quality
H_2O	Water
H_2SO_4	Hydrogen Sulphide
HCHO	Formaldehyde
HKDYY	Air Quality Assessment and Management Regulations
HNO_3	Nitric acid

HPLC	High-Performance Liquid Chromatography
HVAC	Heating Ventilating and Air Conditioning
Multi Assess	Model for Multi-Pollutant Impact and Assessment of Threshold Levels for Cultural Heritage
N_2O_2	Dinitrogen pentoxide
Na	Sodium
NAAQS	U.S. National Ambient Quality Standards
Ni	Nickel
NO	Nitrogen Oxide
NO_2	Nitrogen Dioxide
NOx	Nitrogen Dioxides
O_2	Oxygen
O_3	Ozone
OH•	Hydroxyl Radical
PAN	Peroxycarboxylic nitric anhydrides
Pb	Lead
PF	Phenol-Formaldehyde
PM	Particulate Matter
$PM_{2.5}$	Coarse Particulate Matter
PM_{10}	Fine Particulate Matter
RH	Relative Humidity
SO_2	Sulphur Dioxide
SO_3	Sulphur Tridioxide
SO_4	Sulphate
SPSS	Statistical Package for the Social Sciences
SPM	Suspended Particulate Matter
STEL	Short Term Exposure Limit
Q	Sampling Rate
T	Temperature
TEA	Triethanolamine
TUBİTAK	The Scientific and Technological Research Council of Turkey
TWA	Time-weighted average

USA-NIOSH	National Institute for Occupational Safety and Health
UV	Ultraviolet
VOC	Volatile Organic Carbon
WHO	World Health Organization

CHAPTER 1

BACKGROUND

1.1 INDOOR AIR QUALITY (IAQ) IN MUSEUMS

Museum and conversation staffs have paid great attention to the indoor environment in museum objects during the 20th century. Temperature effect, light exposure and the effect of air humidity have been analysed and explained for the last hundred years or maybe more than that. On the other hand the problem is that the contaminants in the indoor museum setting have not been given enough attention. It is very interesting because the pollutants in the area can be as destructive to the objects in the museum as high light exposition can be. This ignorance may be result from the invisible effect of pollutants; because some of the destructions can be easily seen and soiling is one of them. However, some other deteriorations cannot be easily recognized, they are invisible; the decrease in material's fiber strength can be an example for this. The issue becomes more complicated because the contamination is not the only element in the decay process; it is combined with humidity, temperature and other factors (Ryhl-Svendsen, 2006). In recent researches, it has found out that temperature, humidity, particulate matter, and gaseous pollution effect indoor museum objects.

Great importance has been attached to air contamination impact on the objects in the past two decades. Air pollution is thought to be a modern issue; however, it has been depicted that it has a long historical background going back to the ancient times. The relation between air contamination and the destruction of the stone is not simplistic. Many reports showed the raising deterioration of buildings and stone works during the last few decades (Grieken et al., 2001).

The history of air pollution and climate is essence in order to understand the degradation of the built heritage. Buildings may be old, accumulate damage, and located in cities confronting urban pollution and climate. Therefore, it is important to

understand both the factors that damage building stones today, and those processes that contribute to building stone decay over the entire lifetime of the structure. This usually involves considering the historical changes in fuels, urban pollution and climate Because of the climate which changes and affects both the amount and distribution of damage to historic buildings, the future has to be considered from the perspective of planning and conservation (Grossi et al., 2007)

For the conservation of materials in museums there are certain targets.

The *conservation* of works of art and antiquities is intended to: (a) the preservation of cultural heritage, (b) the deceleration of their deterioration processes and (c) the restoration, in some cases, of their form in order to be comprehensible from the public. All of these purposes can be achieved with: (i) control of the environment, (ii) saving static interferences on the heritage (i.e., structural conservation), which restore the static sufficiency of the heritage, so it does not fall down; (iii) saving interferences on the surface of the heritage, since all corrosion actions begin from the surface of the heritage (Metaxa, 2011).

In museums for the control of the environment some parameters are needed to be monitored and these parameters should have standard limits. They are divided into two sections: air pollutants and other environmental factors. There are no certain parameters for air pollutants. Environmental parameter effecting indoor air quality of museum and cultural heritage are temperature, humidity, and light.

1.1.1 Temperature

Temperature alone can damage the collections. An increase in temperature will cause an increase in chemical reaction rates, the general rule being that there will be a doubling of reaction rates for every 10ºC rise in temperature. Most of materials damage by high temperatures such as acidic paper, acetate and nitrate films, celluloid and rubber also objects which contain waxes or resins such as ethnographic collections and wax/resin lined paintings (Hamilton et al., 2009).

1.1.2 Relative Humidity

As with temperature, a high Relative Humidity (RH) increases decay rates of most materials by providing more water to take part in chemical reactions. The main

problems caused by relative humidity are that if too high, above an RH of about 70 percent, there is the probability of fungal growth, and also the corrosion of metals and glass objects. If RH amount is below approximately 40 per cent drying of organic materials will occur (Hamilton et al., 2009).

1.1.3 Light

Light has a more harmful effect on cultural collections than excessive temperature. Light is made up of energy collections that are called photons. They travel as flows and this is called electromagnetic radiation (Hamilton et al., 2009).

1.2 AIR POLLUTANTS IN MUSEUM

1.2.1 Gaseous air pollutants

Air pollution caused damage on cultural heritage (Blades et al., 2007). Gaseous pollutants are such chemicals that because they are reactive, they damage museum objects. The source of these pollutants can be external and internal. External pollutants can be caused by the building's HVAC system or by open windows, and they vary in three types:

- Sulphur dioxide (SO_2) and hydrogen sulphide (H_2SO) which are produced by fossil fuels that have been burnt, coal that consists of sulphur and other organic materials.
- Nitrogen dioxide (NO_2) which is gas mainly related to traffic, and its precursors that form smog (also including VOC) and ground level ozone. The nitrogen dioxide has two causes: either emission sources (main pollutants), or from the chemical reaction happening in the atmosphere (secondary pollutant). (Han et al., 2006)
- Ozone (O_3), which is produced by the reaction of sunlight and pollutants in the upper atmosphere, and also indoors by devices that produce light and electricity, and some other devices that filter air. Sulphuric acid and Nitric acid are produced by the combination of moisture and sulphur and nitrogen compounds. This acid, damages objects in a vast range. The ozone contacts the object and distorts it (NPS Museum Handbook, 1999)

1.3 AIR POLLUTION EFFECT OF MUSEUMS METARIALS

The air quality in museums will affect the objects in different ways. The solid content is abrasive and may damage the object permanently. They are also the right condition for developing meld. Solid content is discomforting for the user and it increases the cost for maintenance. Gaseous air pollutants, such as oxides of nitrogen and sulphur dioxide can affect organic materials by conversion to acids and ozone is a powerful oxidant, breaking apart every carbon double bond, severely damaging all organic material. Other gaseous pollutants, such as formaldehyde, may be off-gassing from storage cabinets or glues in the museum (Chicora Foundation Inc, 1994). During the 1990s synergistic corrosive effects of sulphur dioxide with nitrogen dioxide and also ozone were demonstrated (Ferm et al., 2006) The effect of a pollutant on the indoor surfaces depends on the material of the surfaces, in conjunction with the ascendant indoor temperature and relative humidity conditions, indoor air flow near the surfaces, the synergistic effects of other pollutants, as well as the mixing ratio of the various pollutants present indoors (Drakou et al., 2001).

In many studies indicate that pollutants effect of materials in two terms of “dry” and “wet” deposition. Wet deposition includes transport of pollutants by means of precipitation and is often affecting materials. Dry deposition includes transport by any other processes. The dry deposition term is effected by some parameters SO_2, NO_2 and O_3 which pollution sources in urban and industrial locations. (Kucera, 2005)

Air pollutants and air pollutants effect on materials given in Table 1.1.

Table 1.1 Air pollutants effects of Materials (Brimblecombe, 1994, Deutsch, 2007)

Object Materials	**Deterioration**	**Primary Air Pollutants**	**Environmental Factors**
			Accelerating Damage
Metals	corrosion/tarnishing	sulphur oxides and other acidic gases	water, oxygen, salts
Stone	surface erosion, discoloration	sulphur oxides and other acidic gases, particulates	water, temperature, fluctuations, salt, vibration, microorganisms, carbon dioxides
Paint	surface erosion, discoloration	sulphur oxides, hydrogen sulphide, ozone, particulates	water, sunlight, microorganisms
Textile dyes and pigments	fading, colour change	nitrogen oxides, ozone	sunlight
Textiles	weakened fibres, soiling	sulphur oxides, nitrogen oxides, particulates	water, sunlight, mechanical wear
Paper	embrittlement	sulphur oxides	moisture, mechanical wear
Leather	weakening, powdered surface	sulphur oxides	mechanical wear
Ceramics	damaged surface	acid gases	moisture

In the past ten years the corruptive effect of sulphur dioxide and nitrogen dioxide and later also of sulphur dioxide and ozone has been found out, and the decreasing levels of SO_2 is no longer considered the only reviver of corruption. On the other hand its combination with other pollutants such as NO_2, O_3 has to be taken into account. The new situation is a multi-pollutant one, where the other two pollutants nitric acid and particles need to be especially focused on. They are both harmful for museum objects and when it comes to the field of atmospheric erosion they are less focused upon. In addition HNO_3 a secondary pollutant formed by oxidation of NO_2 (Kucera, 2005).

Table 1.2 Deposition velocities of air pollutants on materials (Leygraf, 2002, Samie, 2006)

		Deposition velocity (cm s^{-1})	
Pollutant	**H***	**Outdoor**	**Indoor**
H_2S	0.1	0.38	0.03
SO_2	1.2	0.01-1.2	0.05
NO_2	0.007	0.02-0.8	0.006
O_3	0.012	0.05-1	0.036
HNO_3	2.1*105	0.1-30	0.07

- Unit is, mol L^{-1} atm^{-1}

The relative effects of other pollutants, especially nitric acid (HNO_3), nitrogen dioxide (NO_2), ozone (O_3) and on the corrosion of materials have increased because of the decreasing of SO_2 concentration. Table 1.2 shows the solubility, in terms of Henry´s laws constant, and the deposition velocity of important gaseous corrosion stimulators. There is an important point in Table 1.2 the pollutants effect materials in outdoor than indoor. HNO_3 is the most dangerous secondary pollutants for cultural heritage in outdoor and indoor (Samie, 2006). In addition to gases air pollutants, particulate matter also destroys cultural heritage and indoor museum materials. Airborne particulate matter and cultural heritage: Particulate matter can produce soiling of works and the deposited material can attack collections chemically. Possible artwork degradation depends on: a) Particle size, b) Number concentration, c) Chemical composition and d) Nature of Near- Surface Air flow

- The Surface material,
- Pollutant indoor concentration,
- The temperature of the space and the moist level,
- Lighting levels,
- Air flow near the surfaces,
- The synergistic effects of other indoor pollutants,
- Homogeneous and heterogeneous chemical reactions.
- Indoor air pollutant levels depend on:

- Outdoor pollutant concentrations
- Indoor sources of pollutants
- Building's design, use and operation.

Consequences of observations in museums reveal that "indoor concentrations of outdoor pollutants" is attached to the form of construction and use. To give an example, consequences of observations which are carried out both in the inner and outer part of the Historic Museum in Oslo, Norway, reveal that NO_X values were the same both inside and outside. However, the SO_2 concentration inside was decreased when it was compared to the values outside. The observations of ozone in museums Cracow showed that museums were quickly aired by opening doors and windows and through this they gained "indoor ozone concentrations of about 42–44 % of the outdoor values (Dahlin, 2004).

The main air pollutants effecting indoor museum material are sulphur dioxide, nitrogen dioxide, ozone, particulate air pollutants. The effects of these pollutants on materials are explained in detailed in the following sections.

1.3.1 Sulphur Dioxide

Fossil fuels which include sulphur, such as coal and petroleum, have been in use in several fields like industry, heating, transportation. So, SO_2 has been seen not only in developed but also in developing countries. As SO_2 includes water-soluble characteristics, sulphur trioxide (SO_3) reacts with water vapour in order to so corrosive form sulphuric acid (H_2SO_4) (Kim, 2010).

Sulphur dioxide is the main pollutant involved in stone decay. It produces outcomes of sulphate formation on stone Concentrations of SO_2 which have reduced significantly in the last years, however, despite that, there is still high economic distortion reported. The facet of stone which is porous might have been changed in a permanent way in walls which are not washed through past exposure to high pollutant levels and the present high degrees show that there is an influence of memory of the previous exposure. Sulphating includes the dry deposition reaction (1) between SO_2 gas and the limestone itself, when there is high relative humidity, an oxidant and a catalyst.

$$CaC0_3 + SO_2 + 2H_20 + 1/2\ 0\ 2 + CaS0_4.2H_20 + C0_2 \qquad (1)$$

The final product (gypsum) is known well, however, there is not much knowledge about the intermediate steps. Fly ash becomes a part of stone sulphur fixation, because it includes V, Fe, Cu, Cr and Mn, which catalyse the transformation of SO_2 into sulphate (Grieken et al., 1998).

1.3.2 Nitrogen Dioxide

The moment fossil fuels (coal, gasoline, diesel, and natural gas) are burned, nitrogen monoxide (NO) and nitrogen dioxide (NO_2) gases are dispersed into the atmosphere. Oxides of nitrogen (NO_x) are characterized as the accumulation of both NO and NO_2. Because of the increase of the use of fossil fuel, such as road transport, power plants, combustion in industrial and commercial uses, and residential heating, NO_x is a common pollutant (Kim, 2010).

The oxides of nitrogen supply an important degree of the total loading of air pollution and of acid rain. However, the products of reaction are not existent on carbonate stone as the same level of SO_2. The presence of biological sources of nitrate further makes the relation between atmospheric NO_X levels and the occurrence of nitrates on exposed stone surfaces complicated (Grieken et al., 2001).

$$NO_2 + OH\bullet + M \rightarrow HNO_3 + M \quad (2)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (3)$$

With the existence of humidity, the nitrogen dioxide can easily transform into the strong nitric acid with illustrate in (2) and (3). It is important to state that nitric acid is volatile. The secondary pollutant HNO_3 is mainly formed in the atmosphere through the reaction of NO_2 with the OH• (hydroxyl radical) during daytime (3) and hydrolysis of dinitrogen pent oxide (N_2O_5) at night-time (4). Here M is an O_2 or N_2 molecule (Samie, 2006).

1.3.3 Ozone

Ozone does not have a central function in the deterioration of limestone, but it is significant as it is a strong oxidizing agent. Ozone has been shown to speed the sulphate formation at a calcite surface in an SO_2 atmosphere, under both humid and dry

condition (Grieken et. al, 1998). In addition ozone is second important pollutant corrosion of copper after sulphur dioxide (Kucera, 2005).

The Early Warning dosimeter for Organic materials (EWO dosimeter) the impact on organic materials of pollutants that are usually generated outdoors (i.e. NO_2 and O_3) and act in synergy with climate parameters (i.e. temperature / RH and UV Light). The effect illustrated with equation (4) (Lopez-Aparicio et al., 2010).

$$\text{EWO-G effect} = 0.75(0.17)\ NO_2 + 1.34(0.3)\ O_3 + 0.51(0.088)\ T + 0.35(0.21)\ UV \qquad (4)$$

1.3.4 Particulate air pollutants

The sources of PM change greatly, from human activities to natural sources, including dusts from roads, construction sites, and agricultural land, combustion of fossil fuels, ammonia from agriculture, marine aerosols, pollen, biomass burning and secondary particles, such as ammonium sulphate and ammonium nitrate. A central source of fine PM emissions in urban regions is diesel vehicles. Directly emitted elemental carbon soot from diesel vehicles, re-suspended dust from roads, and secondary acidic particles are main contributors of PM at urban roadside areas (Kim, 2010).

It has been emphasized that in Multi Assess project, which searches for the pollutants that impact the historical works and corrosion that is formed in relation to that, Particulate matter has the characteristic of corrosive and soiling on cultural sites. (MULTI ASSESS, 2005).

Especially particulates are extremely dangerous because of their attacking possibility to moisture and gaseous pollutants (NPS Museum Handbook, 1999).

Particles increase the corrosion by supplying and clinging on the corrosion stimulators. If they are substantial, it is probable for particles to decrease the corrosion correlation in some situations by neutralization of the surface water form which is came in to existence on the corrupted material. Corroding material's surface can be decreased by inert particles and corrosion product’s nucleation may be initiated by individual particles (Kucera, 2005).

Particles are one of the significant contaminating solid objects in air. It is important to perceive the source distribution for enhancing the influential strategies to decrease PM10 and to increase air condition standards. Aggressively is another crucial difference

between fine and coarse particles. Particulate matter's the corrosion effect is quite complex. In general the higher the fraction of water soluble ions, the higher is the aggressive. The corrosion effect of particulate matter is very complex. In connection with its variable composition different steps in the initial or steady-state corrosion process can be affected by particles by providing (MULTI ASSESS, 2005).

i) Aggressive substances accelerating the corrosion
ii) Substances decreasing the corrosion by neutralization of gaseous pollutants
iii) Galvanic action
iv) Substances establishing a differential aeration cell
v) Substances decreasing the surface tension
vi) Substances attracting water (hygroscopic particles).

1.4 LITERATURE REVIEW

Several studies have been conducted on atmospheric particles and gasses can be considered harmful for cultural heritage in museum.
Gysels et al. (2002) investigated characterization of particulate matter in Royal Museum during two campaigns in winter and summer. They used to cascade impactor (cut off 20, 8, 4, 2, 1, and 0.5 µm) for collection of aerosol samples in indoor and parallel outdoor. They found correlation between wind speed and particulate matter. Additional fine particulate matter (2.5 mm) inversely correlated with wind speed. Larger size range and wind speed correlated with directly proportional.

Camuffo et al. (2001) studied microclimate, the gaseous and particulate air pollution and the biological contamination in four museums. Nitrogen dioxide and sulphur dioxide are pollutants of outdoor sources. The reason of NO's decrease in summer is that the indoor gas-phase reaction of NO and ozone produce NO_2. Therefore, NO_2 concentration increased in summer in museum. The significant counts of fungi were not found out as harmful neither for the exhibited works of art nor for the employees and visitors in these museums.

Worobiec et al. (2010) investigated the influence of outdoor air pollution on the composition of particulate matter and gases inside the museum of Wawel Castle. They

detected that filters which used for PM sampling were darker in winter than in summer. Because the museum was in the centre of the city, this result was probably due to the high soot content, intensive traffic around the castle, and the pollution of domestic heating. Sulphur dioxide concentration was higher in indoor than outdoor in winter season. In summer, the transport inside was limited and the concentrations of sulphur indoors were lower. In addition, I/O concentration ratios of NO_2 were higher but concentrations were lower than in winter.

Mouratidou et al. (2004) study $PM_{2.5}$ and its relation with ionic component concentrations were determined in the Archaeological Museum of Thessaloniki which located at a central site of the city surrounded by heavy traffic. Indoor and outdoor $PM_{2.5}$ samplings were concurrently carried out in three room and back yard of the museum. They determined that re-suspension of soil dust particles introduce by visitors and restoration works carried out during sampling campaign were concluded as major indoor sources for fine particles and associated calcium. Sulphate was found to be the dominant ion in indoor aerosol originating from outdoor penetration more than indoor sources.

Worobiec et al. (2008) study investigation involved in the determination of transport and deposition of particulate matter introduce by visitors to indoor. The suspended particulates samples were collected indoor and outdoor the museum in winter and summer to observe of particulate matter distribution different seasons. The concentration of total suspended particulates and all investigated elements was significantly higher on the days of intensive tourist visits.

Gysels et al. (2004) indoor and outdoor atmospheres of the ‘Koninklijk Museum voor Schone Kunsten’ (KMSK, Royal Museum of Fine Arts) which is located in the south of the city centre of Antwerp near major traffic axes and a river. Campaign aerosol particles, pollutant gases, bacteria and fungi were sampled during two seasons of winter and summer. In additional different indoors microclimatic parameters were measured. Ca-rich, Ca–Si and sea salt particles were identified as the main particle types in winter. S-rich particles were high amount in summer. Particularly for Na and Cl, but also for other elements, the average bulk indoor concentrations were higher in winter than in summer.

Reddy et al. (2005) investigated indoor and outdoor air quality studies in Salarjung museum. They measured some important parameters are; suspended particulate matter (SPM), sulphur dioxide (SO_2), oxides of nitrogen (NO_x), hydrogen sulphide (H_2S), ammonia (NH_3), aldehydes (formaldehyde) and ozone (O_3). Results show thatSO_2, NO_x, H_2S and oxidants levels in the galleries are related to intrusion of pollutants from outdoor atmosphere, whereas aldehydes and NH_3 levels are related to intrusion as well as emanation within the galleries. The background level of outdoor air highly affected the indoor air quality level in the museum.

Tidblad et. al. (2009) studied air pollution effect on materials in and cultural heritage in Asia and Africa. They investigated SO_2, NO_2, HNO_3 and O_3, particles, amount and pH of precipitation, temperature and relative humidity parameters in 12 test sides. They found highly trafficked Kuala Lumpur was high HNO_3 and NO_2 levels. NO_2 is also high for the other traffic intensive cities Bangkok, Chongqing and Hong Kong and they detected that SO_2 is the dominating pollutant which affected the cultural heritage.

Drakou et al. (2008) searched on indoor concentrations of air pollutants in church and a museum. They found indoor concentrations of air pollutants such as O_3, NO, NO_2, HCHO, PAN and HNO_3 were generally higher than most recommended air quality standards.

Saraga et al. (2011) studied to determine the main sources contributing to the air pollution of three indoor environments of different use: a museum, a printing industry and an office. For this purpose, particulate matter (TSP, PM10, and $PM_{2.5}$), inorganic pollutants (NO_x, SO_2 and O_3) and organic compounds (BTX, formaldehyde) were monitored. They found highest concentration values saved in the bookbindery section of the printing industry whilst the lowest in the museum. NO, SO_2 and O_3 seem to originate mainly from external, following a diurnal variation in most cases. Benzene/toluene ratio indicates traffic as a VOCs source. Moreover, ozone detected in low levels in the printing and the museum and relatively higher levels in offices, indicating its outdoor origin.

Kucera (2003) searched corrosion impacts on buildings and cultural heritages caused by emissions of pollutants. The result of the study detected that SO_2 is the most important

pollution parameter. The other important point is that pollution control should be emphasized as the damage related to acid deposition that could be even worse in the warm and humid climate.

1.5 AIM OF THE STUDY

Historical artefacts are the most important inheritance remaining from a nation's past. Owning the heritage means to protect it. However it is known that collections that have historical and cultural value are exposed to damage, harm, wear and corrosion over time in the environments where they are stored and exhibited. Basically most important reason of there damages can be listed as temperature (T, °C), relative humidity values (RH%), light amount and rates, air pollution, incest and other unwanted pests of the environments where they are stored, presented and protected and perhaps the most important, people. In last 20 years, scientific studies clearly showed that air pollution damages the cultural and historical structures and materials.

For this purpose we are aiming to search traffic-related pollutants in the indoor environment of the Dolmabahçe Palace and to discuss the possible effects of the pollution on historical artefacts by available findings. For this purpose, the measurement in indoor environment and outdoor environment of the Dolmabahçe Palace (palace balconies) in two seasons, including winter and summer is summarized briefly as follows;

i) Determine NO_2, SO_2 and aldehydes amounts in 65 points selected in Dolmabahçe Palace
ii) Make measurements and assessments of PM in all rooms in Dolmabahçe Palace in two different ways, with and without visitors
iii) Determine the distribution in indoor and outdoor environment and seasonally in the palace, making Black carbon measurement at certain points selected in the palace
iv) Determine heavy metal distribution according to the size of particulate material in the palace. For this purpose, analysed heavy metals are: Chromium (Cr), copper (Cu), Manganese (Mn), Nickel (Ni), Cadmium (Cd), Lead (Pb).

Values of these parameters measured at selected locations in Dolmabahçe Palace were compared with the limits and the rooms threatened by traffic-related pollutants have been identified.

CHAPTER 2

EXPERIMENTAL WORK

2.1 SAMPLING

2.1.1 Sampling Site & Selection

In Turkey current instructions there is no any limitation what is related with the indoor air quality about museums. In the current research it is observed that the objects that are in the museum are contaminated by these indoor air pollution pollutants. In this research as a palace was chosen. The features of the place are divided into five;

1. Dolmabahçe Palace is located in Beşiktaş, Istanbul. The region is under the effects of heavy ties Ortaköy to Kabataş.
2. It is difficult and important to protect the Dolmabahçe palace which is both a historical wonder and museum. The historical objects inside it have been affected by contamination.
3. Because since Dolmabahçe Palace is a historical place it is impossible to establish any HVAC system.
4. One side of the palace is being directly exposed a heavy street traffic, while the other side looks the Marmara Sea. Thus, the palace is under the risk of being contaminated by both sea and the urban traffic

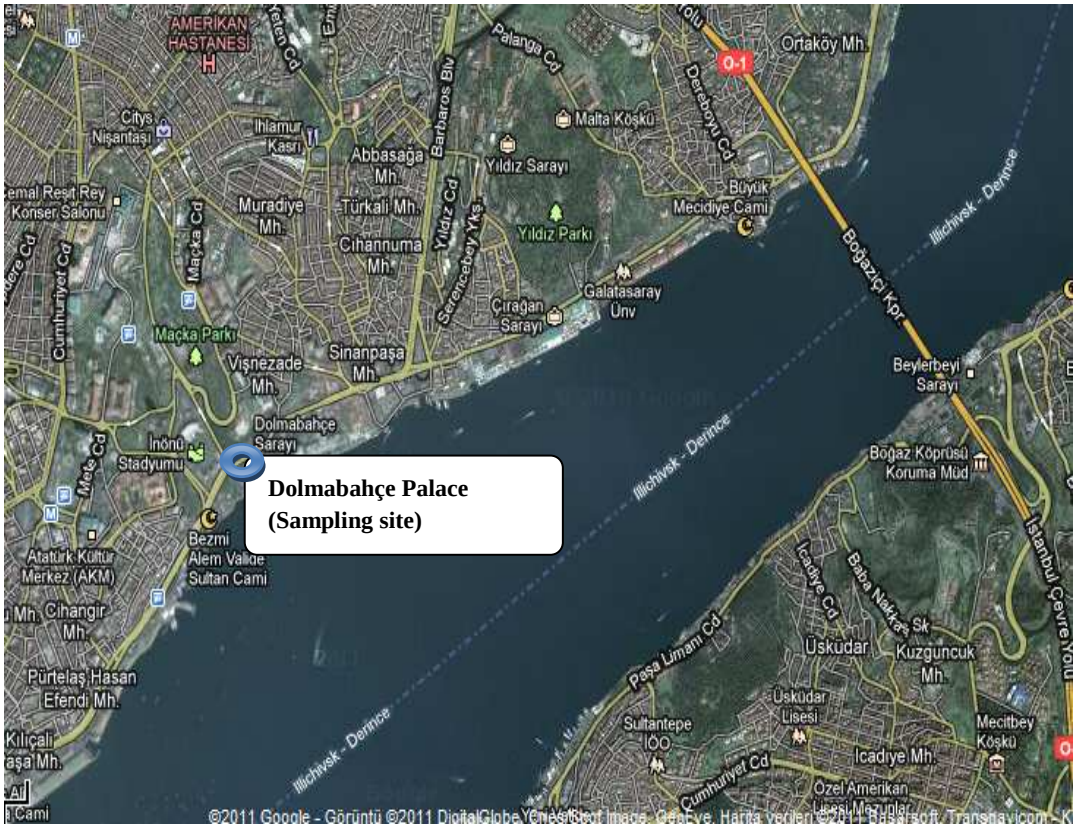

Figure 2.1 The Sampling Site Dolmabahçe Palace (The map was created using Google Earth®)

Compared to the other national palaces Dolmabahçe has strategic importance from the view of air pollution. Because of the settlement of the building it exposed to contamination and also the evener's disaffection by this contamination is very probable.

2.1.2. Sampling Location in Dolmabahçe Palace

The study carried out was held in a total of 65 sampling point of which are some rooms and balconies of the Dolmabahçe Palace. In this section information about Dolmabahçe Palace and important rooms and points of sampling is given. Sampling point shown in Figure 2.2, Figure 2.3 and Figure 2.4.

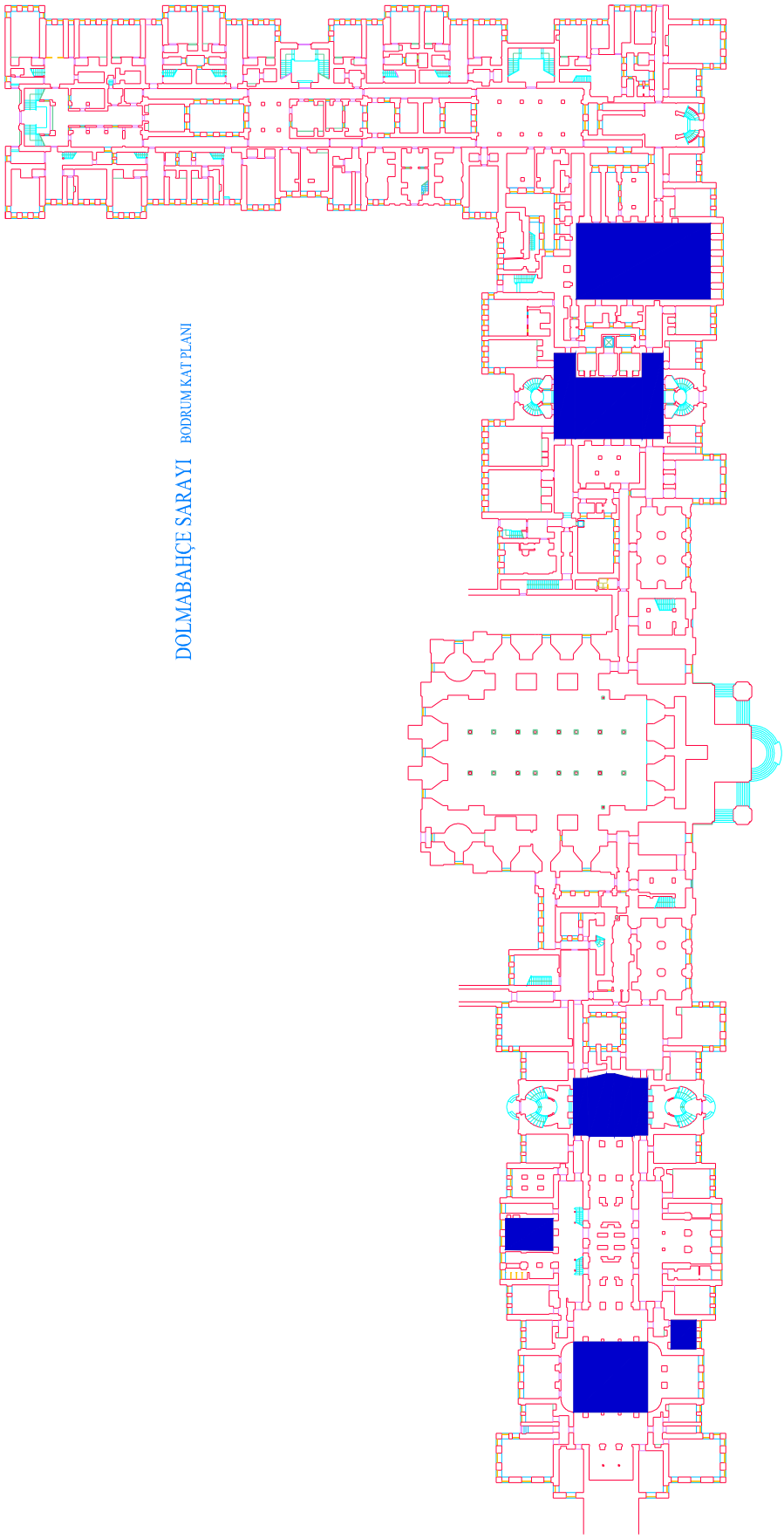

Figure 2.2 Sampling points of the basement in Dolmabahçe Palace

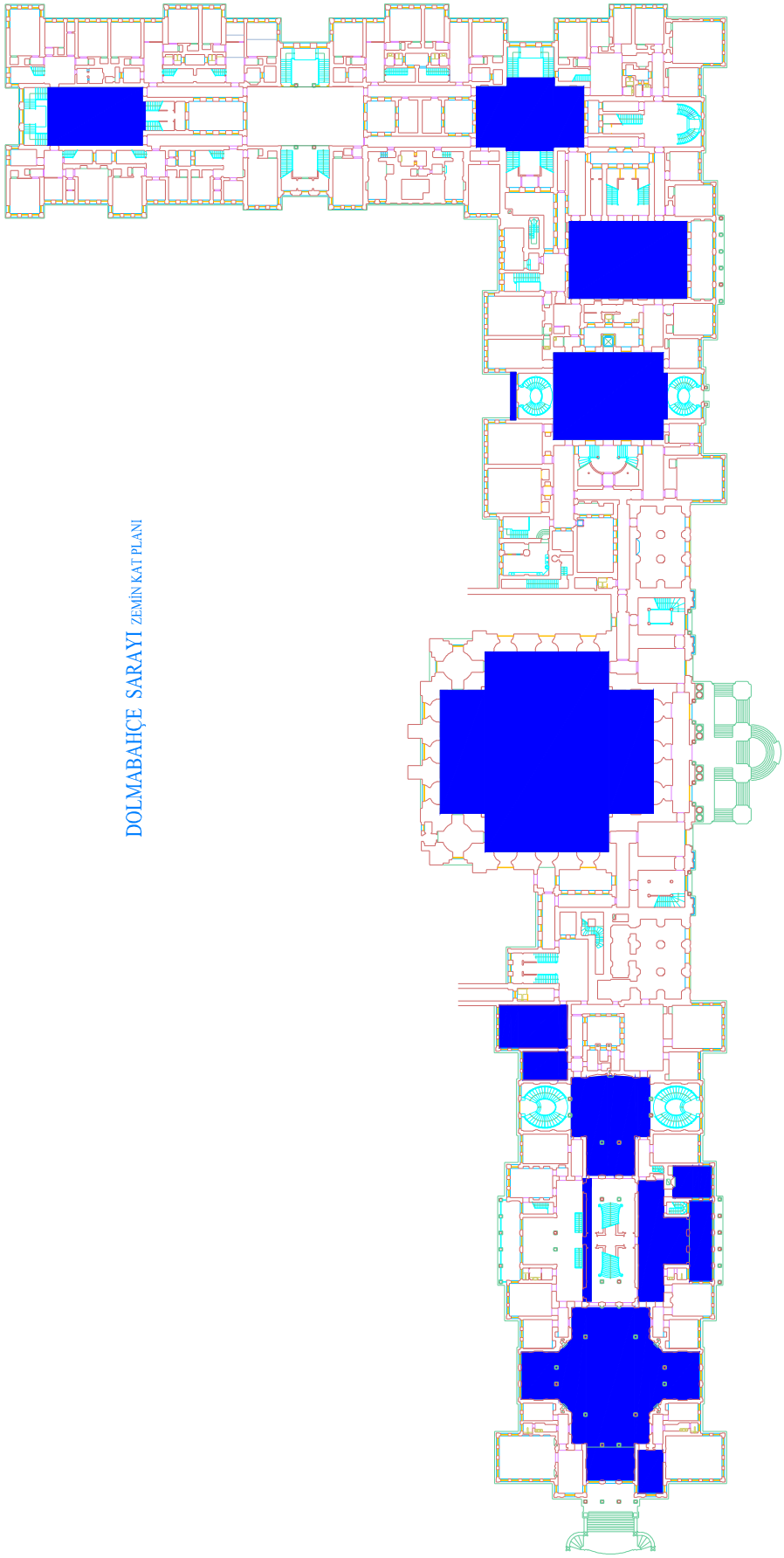

Figure 2.3 Sampling points of the ground floor in Dolmabahçe Palace

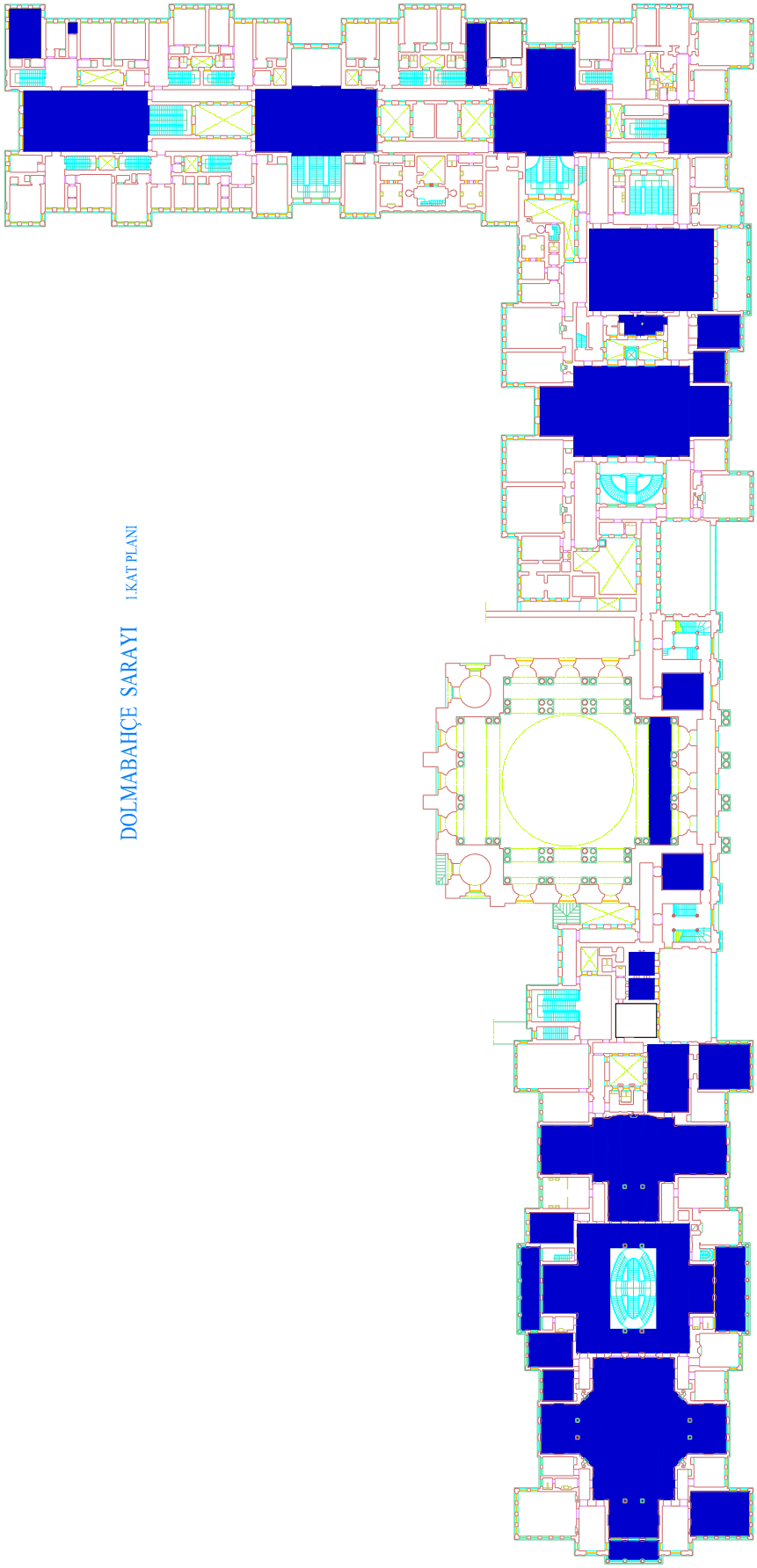

Figure 2.4 Sampling points of the f first floor in Dolmabahçe Palace

2.1.2.1. Dolmabahçe Palace History

Dolmabahçe Palace (shown Figure 2.5) was constructed by Abdülmecit I the Empire's 31st Sultan and completed in 1856. Palace occur 285 rooms, 44 halls and 6 hamams in 45,000 square metre which stands on an area of 110,000 m². The palace mainly consists of three parts, named as the Imperial Mabeyn (State Apartments), Muayede Hall (Ceremonial Hall) and the Imperial Harem. Fourteen tonnes gold used to built the structure.

Figure 2.5 Entrance of Dolmabahçe Palace (By permission of Dolmabahçe Palace Management)

Dolmabahçe Palace was home to six Sultans from 1856. The palace was used as Presidency office between 1927- 1949. Mustafa Kemal Atatürk, the founder of our Republic, used Dolmabahçe Palace for his studies at İstanbul. Atatürk spent the last days of his medical treatment in this palace, where he died on November 10, 1938. The Palace which was partially open to protocol and visits between 1926- 1984 and was opened to visit as a “museum-palace” from 1984. (National Palace, 2011).
Dolmabahçe Palace consists of two main parts Selamlık and Harem.

Part of Selamlık: The part of Selamlık where head of Islamic and Turkish house lives means the part allocated for official business except for the ruler’s family in the palaces.

Part of Selamlık with its West origin décor inspired by Ancient times shows glory of sultanate and state.

Part of Harem: It is the part where Sultan and his family lived. This part where Ottoman dynasty with its crowded number lived in Tanzimat period was established influencing by hierarchy and space traditions of Turkish house plan and Topkapı Palace as well as its plan consisting of apartments arranged side by side in Western Palace style.

2.1.2.2. Medhal Hall

Medhal Hall, in Figure 2.6, is located on the ground floor in part of Selamlık of Dolmabahçe Palace. It is the Hall at the end of stairs from Hasbahçe, the Hall entrance to the palace. It is the main entrance place of the Palace. This entry and exit place where visitors and protocol used is now used for the same purpose since it was established. Still it is used by state protocol in important meetings and receptions. The glass doors opened inward in the middle of the Hall provides access to Crystal Staircase leads to the upper floor.

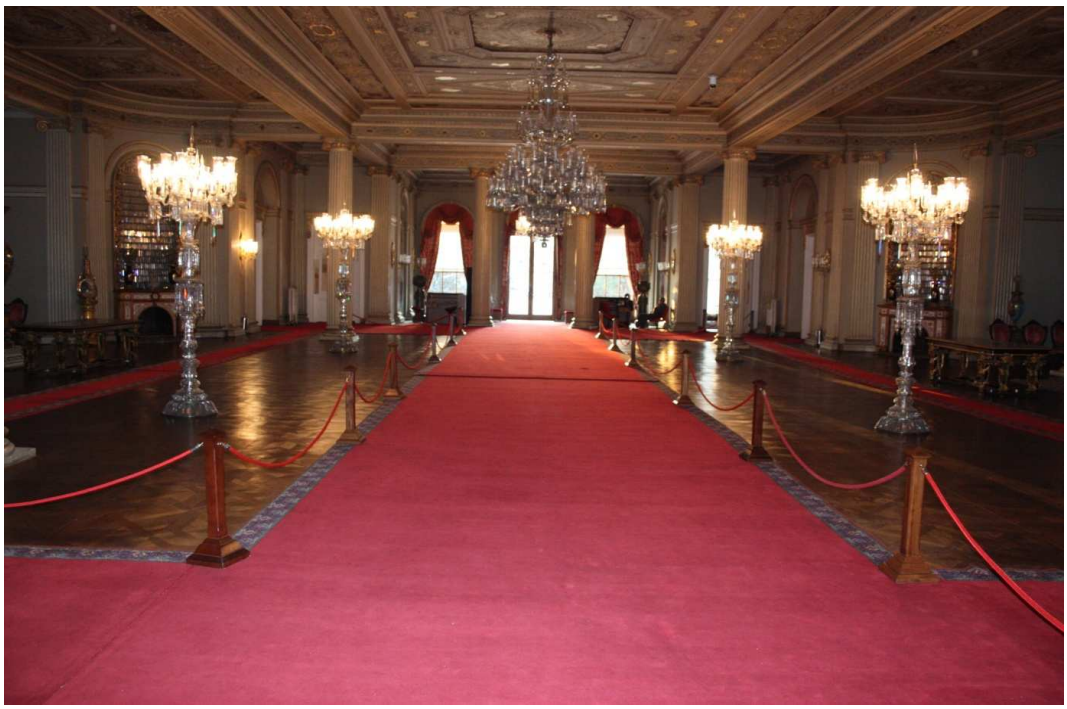

Figure 2.6 Medhal Hall (By permission of Dolmabahçe Palace Management)

2.1.2.3. Crystal Staircase

The protocol section to the upper floor from palace entrance is called as Crystal Staircase because of banister rails made of crystal. Crystals on banister, a large chandelier and glass vault cover that lets the daylight in directly create a bright and light environment. Without exception, it is an area all visitors taken to the palace use. It forms a large volume since there is a sofa in the area including both floors. This area is a transit point that connects the service floor of the Palace and the State floor. Today, it is open to visitors, and is actively used to switch between the two areas similarly. Floor is completely covered with Hereke wool carpets as illustrated Figure 2.7.

Figure 2.7 Crystal Staircase (By permission of Dolmabahçe Palace Management)

2.1.2.4. Süfera Hall

Süfera (ambassadors) Hall is on the first floor of the palace (Figure 2.8). It is one of the major venues that are open to visitors, looking across both the sea and land. It was specially designed to show magnificence of Ottomans before foreign governments.

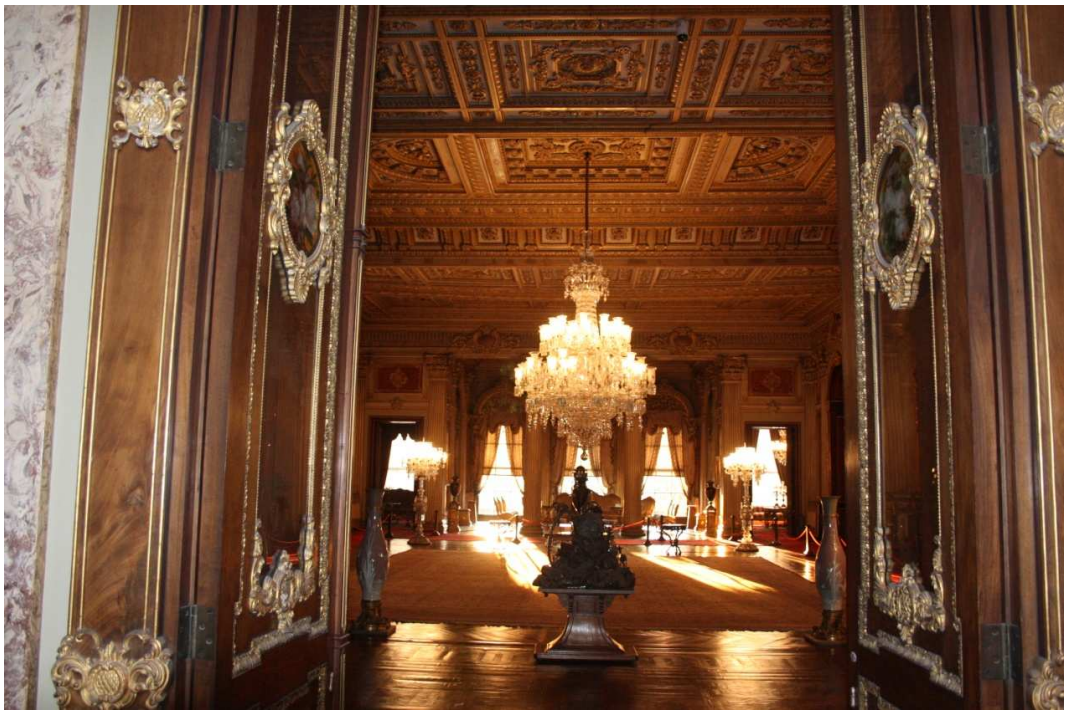

Figure 2.8 Süfera Hall (By permission of Dolmabahçe Palace Management)

2.1.2.5. Muayede Hall

Muayede (Bairam greetings) Hall is the most high and glorious part of the palace between Mabeyn-i Humayun and Harem-i Humayun as shown in Figure 2.9. There is a dome in 36 m height inside the Hall and it has a roof outside. Baroque-style architecture composition and columns draw attention.

Figure 2.9 Muayde Hall (By permission of Dolmabahçe Palace Management)

2.1.2.6. Blue Hall

Blue Hall, Figure 2.10, is the place where Sultan reaches climbing the Halife stairs after bairam greeting in Muayede Hall and accepted congratulations of people of harem and it is known as ceremonial Hall of the harem. It is in the harem section, on the first floor. This Hall is centre of Sultan's flat in harem and it has been named like that because of the blue colour used in its decoration.

Figure 2.10 Blue Hall (By permission of Dolmabahçe Palace Management)

2.1.2.7. Library

There three interconnected rooms on the sea side of the Sülvecheyn Hall. The last caliph Abdulmecid Efendi used to live in this room some time and his belongings that he brought from Veliaht room when moving from Dolmabahçe Palace. This room is now used a library in Dolmabahçe Palace. This library (Figure 2.11) enriched with books and magazines received and donated in the periods of Ataturk and Inonu as well as books and magazines which Abdulmecid Effendi collected. Here are more than 10 thousand books, majority of them are Ottoman and French (Dolmabahçe Palace, 2011).

Figure 2.11 Library (By permission of Dolmabahçe Palace Management)

2.2 MEASURING EQUIPMENT & ANALYSIS METHODS

The measurement campaigns were carrying out two-seasonal campaign (i.e. summer and winter). During this time measurements were performed on a monthly basis both indoors and outdoors. The main aim of the nine months measurement campaign was to perform a characterization of the indoor air pollution based on monthly integrated measurements. Therefore a wide range of gaseous pollutants such as NO_2, SO_2, and O3, aldehydes, black carbon (BC), particular matter and heavy metal were measured.

The two-seasonal measurement campaigns were performed in February 2010 and July 2011 in 65 different indoor locations in order to evaluate possible seasonal variations. NO_2, SO_2, O_3 and aldehydes were selected as indicators of outdoor and indoor generated pollutants, respectively. Black carbon measurements were made in the selected rooms in two different categories, including indoor-outdoor or winter-summer. Particulate matter measurements were made in all rooms so as in summer and winter and with or without visitors. Heavy metal sampling was made in selected rooms.

2.2.1 Sampling Equipment

Sampling of many pollutants were made in Dolmabahçe Palace in order to examine the effects of traffic-related pollutants to the palace. In this section, information about gas pollutants NO_2, SO_2, O_3 and aldehydes; particulate matter, devices and analysis methods used in sampling of BC and heavy metal is given.

2.2.1.1 Sampling Gases (NO_2, SO_2, O_3, Aldehydes) Pollutants with Passive Diffusion Tubes

Passive samples are small and doesn't need an electricity source, they are very useful for producing samples. Passive sample method is preferred about searching in both museum and cultural buildings (Schieweck A.et al., 2007, Salmon L. G., 2000).
The principles of the passive samples can be shortly expressed as:

The diffusive sampler is a closed box and it occur two sides. Fist side is "transparent" to gaseous molecules which cross it and second side is adsorbed gaseous onto the surface. The former side is named diffusive surface and second side is the adsorbing surface.

The sampling amount of analyte by sampling time and rate (5) are used to determine the concentration of sample.

$$\frac{dm}{dt} = DS\frac{dc}{dl} \qquad (5)$$

Where m is the adsorbed mass of sample, t is exposure time and D is the diffusion coefficient of measured sample. S is diffusive surface area and C environment air concentration.

$$\frac{m}{t} = D\frac{S}{l}(C - Co) \qquad (6)$$

Q is the sampling rate and has the dimensions of a gaseous flow (if m unit in μg, t in minutes and C in $\mu g \cdot l^{-1}$, Q unit is in $l \cdot min^{-1}$).

$$C = \frac{m}{t\,Q} \qquad (7)$$

In which Q is the sampling rate of o specific compound in the radial diffusion tube, having the dimensions of a gas flow. Finally, the radial dimensions of the Radiello diffusion tube, high and constant sampling rate values are accomplished (Radiello, 2006).

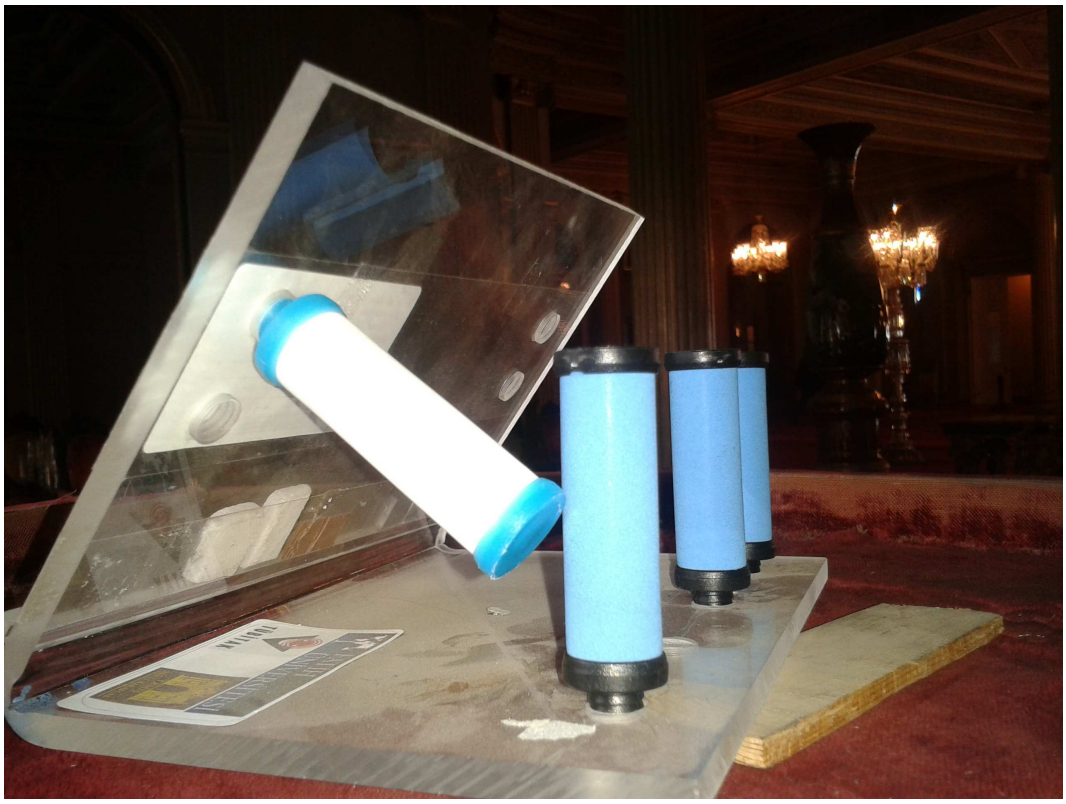

Figure 2.12 Radiello Passive Sampler (By permission of Dolmabahçe Palace Management)

2.2.2.1.1 Sampling of NO_2 and SO_2

The pollutant gases that SO_2 and NO_2 are adsorbed on the adsorbing cartridge which is made of mycroporous polyethylene coated with triethanolamine (TEA). Nitrogen (NO2) and sulphur (SO_2) dioxide is bound on TEA form of the nitrite (NO_2) and sulphite (SO_3) or sulphate (SO_4) ions. This method is selective for gaseous molecules and any airborne nitrite, sulphite or sulphate will not cross the diffusive membrane.

The sampling rate value at 298 K (25°C) and 1013 hPa for NO_2 and SO_2 sampling are 0.141 ± 0.007 ng NO_2 ppb^{-1} min^{-1} and .466 ± 0.022 ng SO_2 ppb^{-1} min^{-1}. The ambient temperature influences the sampling rate of NO_2 whereas the sampling rate of SO_2 does not vary with temperature in the range between 263 and 313 K (-10 to 40 C). Sampling adsorbing cartridges extracted with 5 ml ultra-deionise water and samples wait vortex for one minute. Otherwise samples analysed in ion chromatography (Radiello, 2006).

2.2.2.1.2 Sampling of Aldehydes

Code 165 is a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil. Aldehydes react with 2,4-DNPH to give the corresponding 2,4-dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazones are then extracted with acetronitrile. The sampler added 2 ml HPLC grade acetonitrile waited for 30 minutes. Later samples analysed by the HPLC after filtering with 0.45 μm micropore filter membrane (Radiello, 2006).

2.2.1.2 Sampling of Heavy Metals

Heavy metal sample cascade experimented with impactor. Cascade impactors operate on the principle of inertial impaction i.e. separation is provided on the basis of differences in inertia - a function of particle size and velocity. Cascade impactor occur a series of stages each in a plate, with specific nozzle setting and collection surface. Sample air which has particulate matter is go into the impactor, flowing sequentially through the stages; nozzle size and total nozzle area decrease with stage number (Hafkenscheid et al., 2009). Andersen Cascade Impactor with 8 different impaction stages with cut-off diameters 9, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7 and 0.4 mm as shown in Table 2.1 respectively .For an optimal size fraction the air flows through. The impactor was adjusted to 28 l/min (Nichols, 1998).

Table 2.1 Cut off Cascade Impactor

	Size Range mm	**ECD mm**
Stage 0	9.0-10.0	9
Stage 1	5.8-9.0	5.8
Stage 2	4.7-5.8	4.7
Stage 3	3.3-4.7	3.3
Stage 4	2.1-3.3	2.1
Stage 5	1.1-2.1	1.1
Stage 6	0.7-1.1	0.7
Stage 7	0.4-0.7	0.4
Stage F	0-0.4	0

Thermo Scientific® Andersen Series of Non-Viable Cascade Impactor branded particulate matter sampler given in Figure 2.13 is used in this study. Particulate matter collected on different stage plates was extracted with 20 ml ultra-pure water in ultrasonic bath. Heavy metal analyses of the samples of which extraction processes were completed were made with Graphite furnace atomic absorption spectrometry.

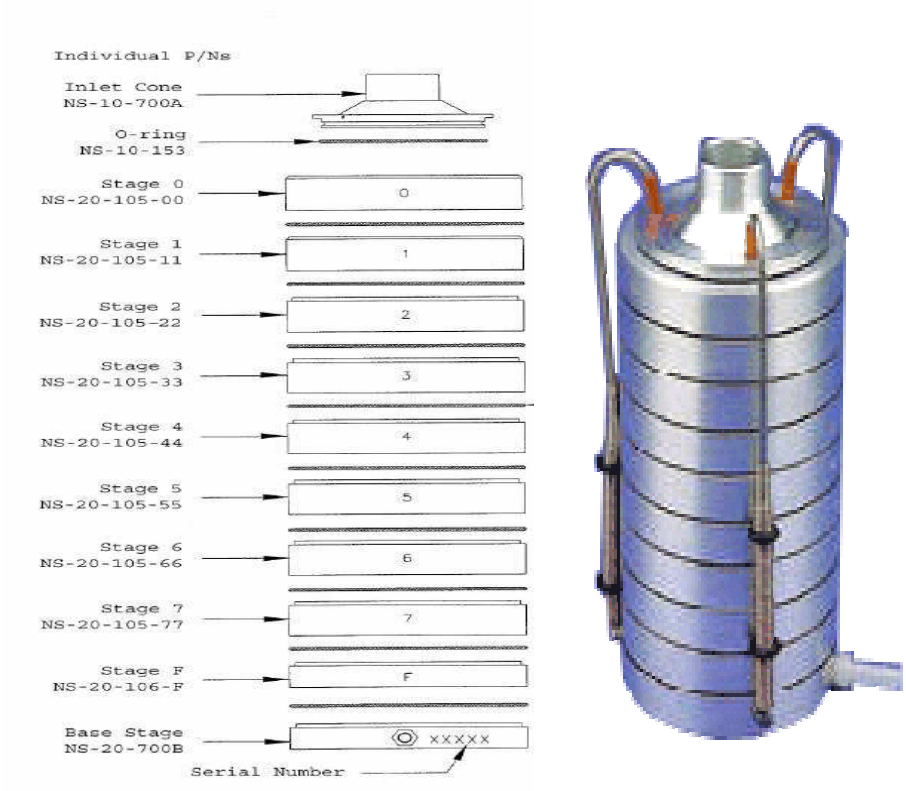

Figure 2.13 Sampler of PM Cascade Impactor (Petro- Instruments Corp. Ltd, 2008)

2.2.1.3 Sampling of Particulate Matter

Particulate matter sampling was made with online particle counter CLJ-H6003® in this study. Particle counter used makes the sampling in 6 different stage including 0.3, 0.5, 1.0, 2.0, 3.0 and 5.0 micrometer in size. Weights of particulate matters collected in different stages were calculated. Particulate matter concentration that is calculated arithmetically is considered as 2 g/cm^3.

2.2.1.4 Sampling of Black Carbon

Black carbon analyses were made with Magee Scientific Portable ® Model AE 42 in Aethalometer the study conducted in Dolmabahçe Palace. In the investigation, sampling was made in two different groups including indoor-outdoor and summer-winter in the rooms that can be considered important in respect of traffic pollution.

Figure 2.14 The Portable Aethalometer Model AE 42 (Magee Scientific, 2010)

The Portable Aethalometer Model AE 42 (shown as Figure 2.14) measures light absorption by suspended aerosol particles at two wavelengths: 880 nm (IR), quantitative for the mass of 'Black' Carbon; and 370 nm (UV), indicating aromatic organic compounds. The Portable Aethalometer may also be supplied with 7 wavelength light sources upon request (Hansen, 2005).

2.2.2 Analysis Method

2.2.2.1 Ion Chromatography (IC)

SO_2 and NO_2 are respectively determined as sulphate and nitrite with analysis of extract by chromatography in a same run. An ICS-1100 Ion Chromatography with an Ion Pac AS9-HC column, suppressor ASRS-4mm and an auto sampler AS 1000 is used for analysis. Analytical conditions for this system are as follows: eluent 9 mM Na_2CO_3; 1 ml/min flow rate. Calibration was performed using certified standard Combined Seven Anion Standard II (Dionex, 2009).

2.2.2.2 Graphite Furnace Atomic Absorption Spectrometry

Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) technique were used for heavy metal analysis. Analysed heavy metals are: Chromium (Cr), copper (Cu), Manganese (Mn), Nickel (Ni), Cadmium (Cd), Lead (Pb). In Table 2.2 is given optimized parameters for GFAAS in analysis.

Table 2.2 Optimized Parameters for GFAAS

	Cr	**Cu**	**Mn**	**Ni**	**Cd**	**Pb**
λ nm	357.9	327.4	400.1	232	228.8	217
Inject Volume (µl)	20	12	20	40	20	40
Lamp Current (mA)	10	10	10	10	10	10

The results of the pyrolysis and atomization temperature studies are presented in Table 2.3 for analysed heavy metals. Significant tree stage temperature; ashing, atomization and cleaning are different for each of metals.

Table 2.3 Oven program of GFAAS

	Oven Temperature (℃)					
	Drying 1	Drying 2	Drying 3	Ashing	Atomization	Cleaning
Cr	85	95	120	100	2600	2600
Cu	85	95	120	800	2300	2300
Mn	85	95	120	700	2400	2400
Ni	85	95	120	800	2400	2400
Cd	85	95	120	250	1800	1800
Pb	85	95	120	400	1200	1200
Time(sec.)	5	15	10	8	2.8	2

2.2.2.3 High-Performance Liquid Chromatography (HPLC)

In the study a Shimadzu model LC20A HPLC was used to determine formaldehyde and acetaldehyde amount. The column was the Mediterranea™ sea18 column (5 µm 15x0.46) size at 40 °C. Acetonitrile is used for eluent. Injection volume is 20 µl, flow rate 1.2 ml/min wave range is 250- 400 nm.

Table 2.4 Eluent gradient program

Time	**0-10**	**10-20**	**20-25**
%B	62	25	62

The eluents were (A) ultrapure water and (B) acetonitrile (ACN). The flow rate of the eluent was 1 mL/min and the gradient program as follows in Table 2.4. Calibration curves for aldehydes are obtained with standard solutions of the corresponding 2,4-dinitrophenylhydrazones with Radiello Code 302.

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CHAPTER 3

RESULTS AND DISCUSSION

During this study exposure levels of the gaseous indoor air pollutants (NO_2, SO_2, O_3, and aldehydes) and particulate matter (PM) samples were collected in Dolmabahçe Palace. Chemical compositions of the PM samples were investigated by means of metal and ion compositions. In addition to the indoor measurements, we also conducted some outdoor exposure sampling. Indoor (61) and outdoor (4) samples were collected, totally, at 65 different places which were micro environments, e.g. rooms, Halls, cabinets, library, baths, and archives in Dolmabahçe Palace. All the samples were collected in two seasonal campaigns; winter and summer. However, PM samples in different spaces were not collected simultaneously, but sequentially, due to unavailability of multiple sampling equipments. We had only one PM sampling equipment and one aethalometer to monitor and sample the indoor particulate matters and black carbon (BC), and then we used this equipment during each of the seasons, one by one by moving one room to another.

3.1 GASEOUS AIR POLLUTANTS

3.1.1 Nitrogen dioxide (NO_2)

Annual natural outdoor concentrations of nitrogen dioxide ranges between less than 1 $\mu g/m^3$ to more than 9 $\mu g/m^3$. In literature it was reported that indoor levels of nitrogen dioxide range between 20 and 40 $\mu g/m^3$ in living rooms and up to 70 $\mu g/m^3$ in kitchens (measured in five European countries over 2 to 7 days)(Health Council of the Netherlands, 2004) The average value of indoor and outdoor NO_2 exposure level during winter and summer periods were found to be 52.8 $\mu g/m^3$, and 46.47 $\mu g/m^3$; and 56.8 $\mu g/m^3$, 106.08 $\mu g/m^3$, respectively. All the measurements for indoor and outdoor nitrogen dioxide exposures measurements were given in Figure 3.1, Figure 3.2.

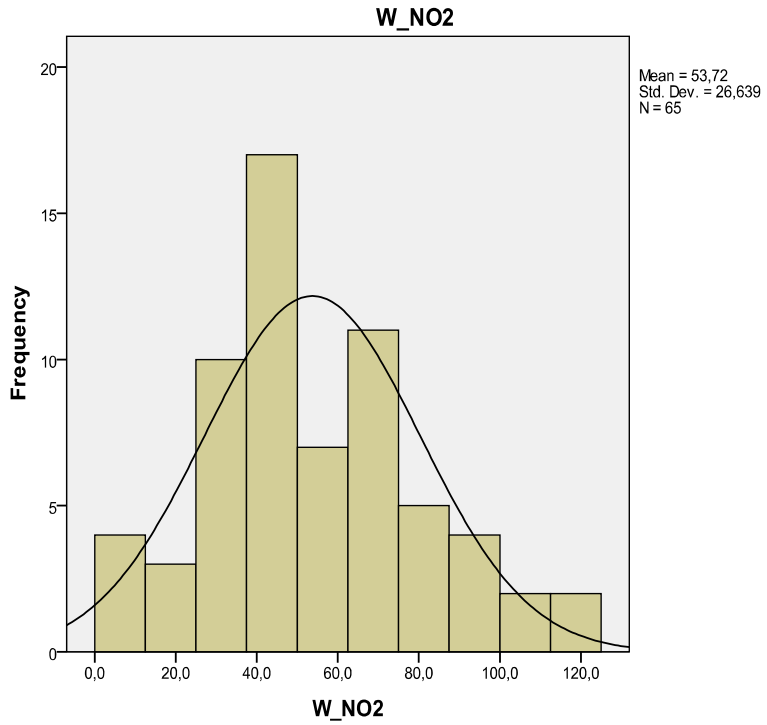

Figure 3.1 Histogram graph for wintertime NO_2 exposure levels (units are in $\mu g/m^3$)

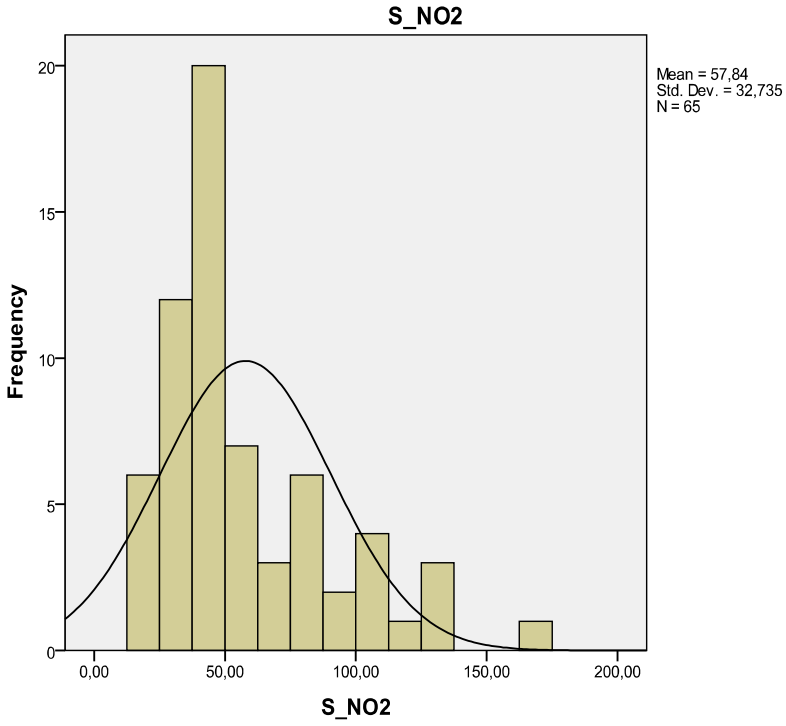

Figure 3.2 Histogram graph for summertime NO_2 exposure levels (units are in $\mu g/m^3$)

NO_2 is a strong outdoor sourced pollutant. Main outdoor sources of this pollutant are road traffic, domestic heating and combustion plants for energy generation.

Dolmabahçe Palace's northern side is bordered by about 10 m exterior walls to protect this structure from outer environment. A main city road characterised by heavy daytime traffic follows these outer walls. That street has high heavy traffic volumes and densities around the Dolmabahçe Palace surroundings to the extent possible to maximize the automobile emission in a phased manner.

NO_2 emissions were higher in the summer around the Dolmabahçe Palace. However looking at the indoor environment, close values of summer and winter shows that NO_2 pollutant penetrates into indoor environment only in a certain amount. On the other hand, when looking at histogram distributions (Figure 3.1, Figure 3.2), it is seen that NO_2 amount increases in most rooms. In our national regulations there is not any NO_2 limit for material and cultural heritage safety. The limit values of the criteria air pollutants in ambient atmosphere for the urban areas were set in the directive on ambient air quality assessment and management (HKDYY, 2008). According to the directive, the 24-hr NO_2 short-term limit value and yearly mean value are 200 $\mu g/m^3$ and 40 $\mu g/m^3$ will be decreased to 100 $\mu g/m^3$ and 20 $\mu g/m^3$ in 2014. Our measurements are higher than annual mean limit value for outdoor environments. In literature there is some health-based recommended occupational exposure limit for nitrogen dioxide (Health Council of the Netherlands, 2004). The recommended WHO long-term guidance value for children is 40 mg/m^3 annual average and NO_2 concentration high to 30 $\mu g/l$ limits in Dolmabahçe Palace. Although there is not any agreed limit or warning, NILU – Norwegian Institute for Air Research was developed an Early Warning device (The EWO dosimeter) for the protection of Cultural Heritage objects in Museum, Historic Buildings and Archives. They set threshold values on NO_2 in museums or archives (López-Aparicio S., 2009). These values were given in ppb, so we converted them into $\mu g/m^3$ by using a conversion factor; 1 ppb =1.91 $\mu g/m^3$. Threshold values are 1.91 $\mu g/m^3$ in archive stores, 4.78 in purpose built museums, 9.55 $\mu g/m^3$ in house museums, 19.1 $\mu g/m^3$ in open structures, 28.65 $\mu g/m^3$ in external stores with no control. Based on these threshold values it can be easily said that some warning activities should be activated in Dolmabahçe Palace, due to higher level NO_2 exposure levels.

3.1.2 Sulphur dioxide (SO_2)

Sulphur dioxide concentrations were decreased dramatically during last two decades In Istanbul, due to the increased usage of natural gas and high-quality coal in the residential areas (Elbir T.et al., 2010). Annual yearly average values of SO_2 measurements in Besiktas, Istanbul was ranged between 4.8 $\mu g/m^3$ and 12.04 $\mu g/m^3$ during since 2007. However our indoor and outdoor SO_2 exposure levels are still considerably high. In the Multi Assess model final report the SO_2 interval between 0-20 $\mu g/m^3$ and 60-80 $\mu g/m^3$ are defined as moderate and high, respectively (Multi Assess, 2005). Our results are classified as moderate according to that criterion.

All the measurements for indoor and outdoor sulphur dioxide exposures measurements were given in Figure 3.3, Figure 3.4. While SO_2 gas amount is about 3.32 $\mu g/m^3$ indoor in winter, this value is measured 5.53 $\mu g/m^3$ in summer period. In outdoor facade measurements in winter, SO_2 value is 10.64 $\mu g/m^3$, while this value is 11.03 $\mu g/m^3$ in summer. SO_2 exposure levels do not change indoor and outdoor seasonally, it was determined that indoor SO_2 gas amount is lower. Looking at the overall distribution of SO_2 gas, we see a normal distribution. The distribution characteristics of the SO_2 exposure levels are skewed left and having sharp decreases followed by a long tail. This type of distribution represents typically the lognormal distribution characteristics. So we suggest that SO_2 exposure levels are distributed log-normally. Statistically this type of distributions suggests that the origins of pollutant are not natural and most probably from some or any external sources.

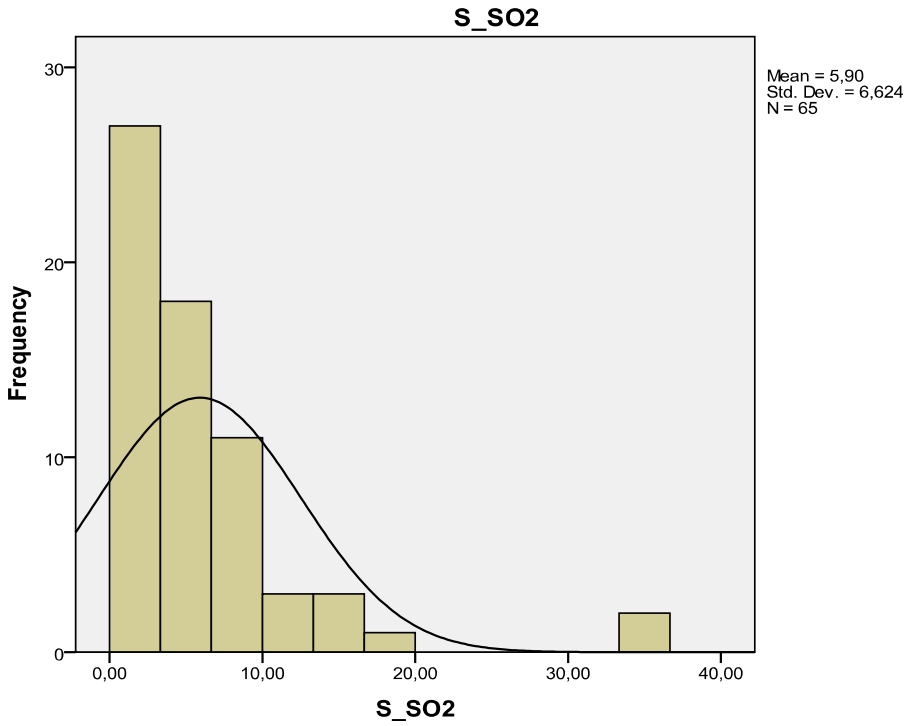

Figure 3.3 Histogram graph for summertime indoor SO_2 exposure levels (units are in $\mu g/m^3$)

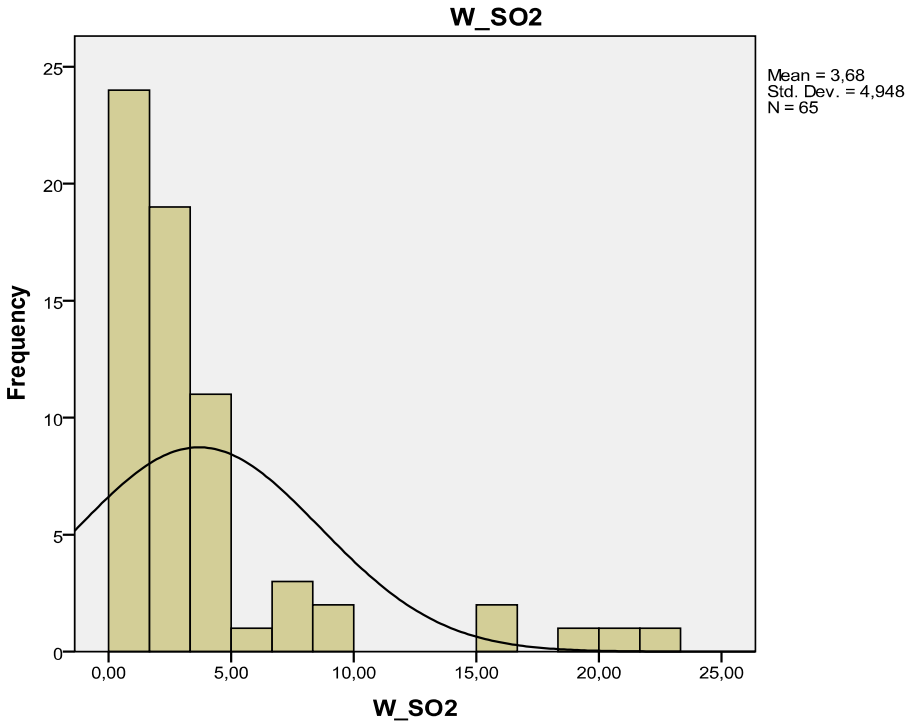

Figure 3.4 Histogram graph for wintertime indoor NO_2 exposure levels (units are in $\mu g/m^3$)

U.S. National Ambient Quality Standards (NAAQS) for sensitive area (Table 3.1) SO_2 24 hr average value is 30 $\mu g/m^3$ while annual average value is 15 $\mu g/m^3$. The concentrations inside the palace were below the U.S. NAAQS of sensitive area limit. The limit values for sensitive areas in our national regulation can be considered as regulatory limits. These values are summarised in Table 3.1.

Table 3.1 US. National Ambient Air Quality Standards (NAAQS) for sensitive area

Pollutant	**Time Weighted Average**	**Sensitive Area**
Sulphur dioxide (SO_2)	Annual Average	15 $\mu g/m^3$
	24 Hours Average	30 $\mu g/m^3$
Nitrogen dioxide (NO_2)	Annual Average	15 $\mu g/m^3$
	24 Hours Average	30 $\mu g/m^3$
Suspended particulate Matter(SPM)	Annual Average	70 $\mu g/m^3$
	24 Hours Average	100 $\mu g/m^3$
Reparable particulate matter (Size less than 10 mm) (RPM)	Annual Average	50 $\mu g/m^3$
	24 Hours Average	70 $\mu g/m^3$
Lead (Pb)	Annual Average	0.50 $\mu g/m^3$
	24 Hours Average	0.75 $\mu g/m^3$

In the literature, in some studies that have examined air quality in museum, museum outdoor quality was compared with these limit values (Reddy, M. K, 2005). Results show that the SO_2 outdoor levels are observed to be low in accordance with U.S. National Ambient Air Quality Standards (NAAQS) for sensitive area. The recommended OSHA short-term exposure limit of sulphur dioxide is 5 ppm (13100 $\mu g/m^3$) in workplace atmospheres. According to EU project MULTI ASSESS SO_2 concentrations resulting from combining the dose-response functions; the tolerable corrosion rates for two different scenarios are given in Table 3.1 (Multi Assess, 2005). A dose-response function together with the tolerable corrosion rates enables the specification of a tolerable climate/pollution situation. For SO_2 a level of 10 $\mu g/m^3$ is proposed protecting 80% of the European territory at present HNO_3 levels (Multi Assess, 2005). Sulphur dioxide scenario 2 “urban” limit values were determined for limestone; 9 $\mu g\ m^{-3}$, for copper, for bronze; 9 $\mu g/m^3$, for zinc; 5 $\mu g/m^3$, for carbon steel; 6 $\mu g\ m^{-3}$. EU project MULTI ASSESS SO_2 (Table 3.2)is in average limit value, indoor sulphur dioxide values are under these values, while outdoor values are over limestone, bronze, zinc and carbon steel limit values, except copper.

Our outdoor measurements are close these risk levels, although indoor SO_2 exposure levels are lower. As a result, it can be said at Dolmabahçe Palace is under the pollution risk which was mostly generated from outdoor sources mainly vehicle and ship transportation.

Table 3.2 Tolerable SO_2 levels for corrosion of cultural heritage materials for two different scenarios (Multi Assess, 2005)

Material	**Scenario 1 "average" ($\mu g/m^3$)**	**Scenario 2 "urban" ($\mu g/m^3$)**
Limestone	25	9
Copper	5	13
Bronze	21	9
Zinc	11	5
Carbon steel	11	6

However the SO_2 exposure level which was sampled on a sea-front balcony was significantly higher than the other outdoor locations. We note that it was not possible to make any accurate decision using only one sample, but we speculate that one of the main reasons for this difference can be related to ship transportation over the Bosporus, since ships are among the world's highest polluting combustion sources per quantity of fuel consumed and the Bosporus strait has very high level of sea traffic. Even though we did not observe any statistically significant differences between indoor locations with respect to SO_2 exposure levels, the winter measurements in first floor shows an interesting indoor SO_2 distribution characteristic. During that period, the eastern part of the seaside direction of the building complex has significantly higher SO_2 levels. This can also be related to higher level SO_2 emissions from ship emissions. Kesgin and Vardar (2001) estimated the daily sea transportation in Istanbul is met by 348 ships cruising between the sides of Europe and Asia, along the Bosporus and into the Golden Horn. Most of these ships are motor boats which are typically operated by high speed diesel engines. While Kesgin and Vardar (2001) stated that 4% of all motor vehicle emissions correspond to ship emissions which are transporting over the Strait, Deniz and Durmusoglu (2008) stated significantly higher emission levels which are up to 45% of vehicle emissions (Kesgin and Vardar, 2001; Deniz and Durmusoglu, 2008).

3.2 BLACK CARBON (BC)

Elemental carbon (EC) and black carbon (BC) are often used interchangeably. It is a by product of incomplete combustion of biomass, fossil fuels, and biofuel. EC or BC can be emitted in both anthropogenic and naturally occurring soot to the atmosphere. In the design of this study, we planned to use EC results as a tracer to evaluate the effect of traffic related emissions into indoor air quality of Dolmabahçe Palace. Some recent studies showed that EC is not a unique tracer for diesel exhaust and efforts to utilize EC as an indicator of diesel exhaust must properly address other sources of EC to avoid significant biases (Schauer, 2003). It is clear that the relative contributions of EC sources will vary significantly as a function of location and time, due to multiple source characterisations in urban environments. For example; regions with significant primary particulate matter emissions from coal-fired power plants, fuel oil-fired power plants and biomass combustion sources will have dominant EC contributions to ambient PM budget. But in our case study, this is not likely to possible, because there is not any nearby such plants. We believe that the most important EC differences as a function of time observed in our measurements is governed by the relative contributions of EC emissions from the motor vehicle fleet emissions changes and indoor ventilation characteristics (e.g. opening windows, or doors for ventilation or access purposes) during summer period. It is also possible to have relative BC contribution from space heating, which is a typical seasonal change in biomass burning, during wintertime measurements. Schauer (2003) summarised the source contributions to fine particle EC determined in a group of source apportionment studies. According to these results, EC contributions from diesel exhaust, gasoline-powered vehicle, combined motor vehicles, biomass burning, and other sources in percentages (%) are in the ranges of 20-94, 0.1-42, 86, 0.7-39, and 0.6-35, respectively. To take in the consideration of the location of Dolmabahçe Palace, we are convenient to say that the monitored BC concentrations in Dolmabahçe palace is mostly related to diesel exhaust and gasoline-powered vehicles emissions. We also note it that there is not any possibility to have any indoor BC source in Dolmabahçe palace.

EC, therefore, often referred to as BC measurements were made in the palace in order to examine effect of the traffic to the Dolmabahçe Palace. These measurements were made in selected rooms in two different groups, including winter and summer or indoor and

outdoor. Outdoor measurements were made only in winter and were discussed. In this study, increasing of BC amount occurred with increasing of traffic jam outdoor. In many studies it is determined that BC concentration increases when number of vehicles in traffic increase (Pakkanen et al., 2000; Redriguez et al., 2008). In addition to that, we conducted several indoor and outdoor BC monitors in several different places, rooms, Halls and balconies. Some of the places selected according to their physical conditions, e.g. location and size, while some of them were based on operational situations, e.g. open to visitors during day time, secure rooms (no entry and no ventilation), and office rooms used by official personnel. In this part we only reported the results some selection of the measurements, which are the representative of the all measurements or belong to a unique or important microenvironment.

The Sultan Reşat room is one of the most important rooms in harem department of the palace with its three windows on the sea side. Indoor and outdoor BC measurement in Sultan Resat Room is given in Figure 3.5 and Figure 3.6. In measurements made in winter in this room, the highest BC value was measured indoor in the morning hours. While BC value was 4.00 $\mu g/m^3$ in the room in the morning, this value continuously decreased in the day and it was about 2.00 $\mu g/m^3$ in the last measurement hour at 15:00. While BC value measured outdoor environment of the Sultan Reşat room was 5.50 $\mu g/m^3$ in the morning, this value increased between 10:00 and 11:00 hours up to 8.00 $\mu g/m^3$.This times interval is the typical morning traffic peak hours for the surrounding road and area. Between 11:00- 13:00, BC value decreased seriously, although an increase of a certain amount in the value of BC occurred between 13:00-14:00, a second increase was determined after 15:00. This second peak is the typical evening traffic peak hours, which is a result of back to house traffic. Based on our measurements, it is seen that the indoor BC concentrations were not have a quick response to outdoor changes; due to ventilation characteristics (windows are not always open). Sultan Reşat room indoor BC value is not affected by fluctuations of BC value outdoor and has a parallel change to the graphic decreasing until 15:00 observed in outdoor general graphic.

The accumulated concentration at the beginning of the day (at 9:00 o'clock) is related to daily operation of the palace. In such a manner that, the palace are being closed every day after 5:00 pm and opens at 8:00 am. During this closed period, the indoor pollutants including BC as well as the other suspended particulate matters (SPM), enriches to their

maximum concentrations, just at the beginning of the opening hours the indoor concentrations starts to decrease steadily. But outdoor peaks within this day time have only little effects on this trend. This expression doesn't mean that the indoor pollution levels are independent to outdoor levels; on the contrary there is a clear relation between outdoor and indoor concentrations. Indoor concentrations are not changing as fast as outdoor because of the buffer effects of ventilation and infiltration characteristics of the building materials.

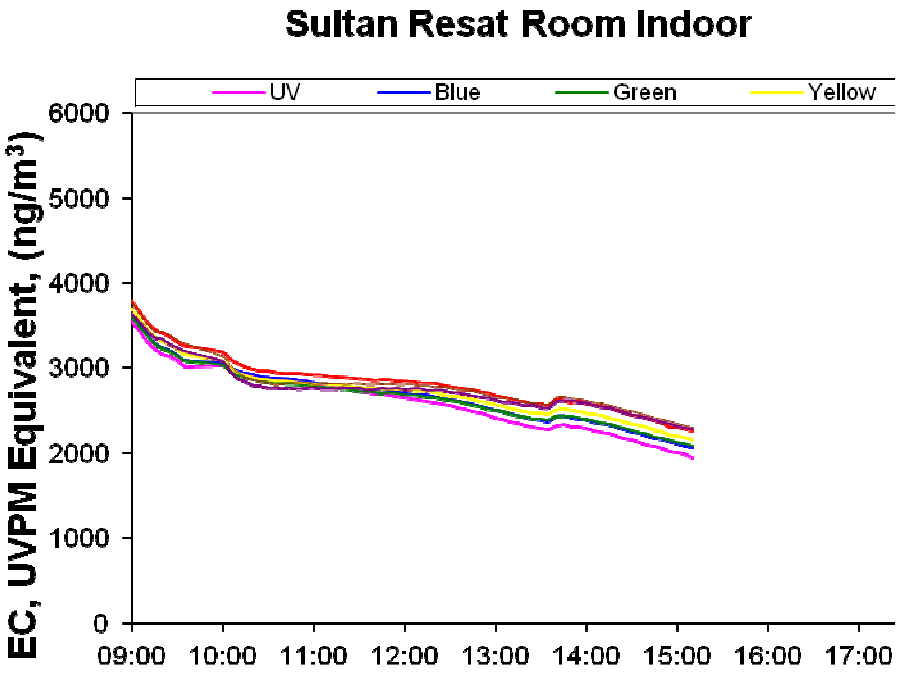

Figure 3.5 Indoor BC monitors in Sultan Resat Room

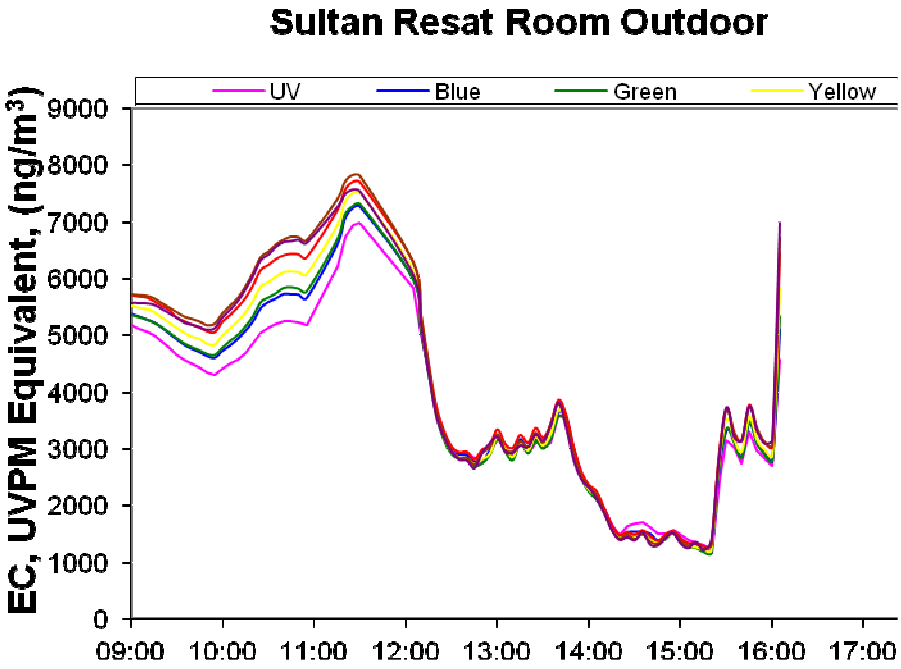

Figure 3.6 Outdoor BC monitors in Sultan Resat Room

Medhal Hall is located in Selamlık department of Dolmabahçe Palace on the ground floor. It is the Hall where people enter the palace at the end of the stairs climbed from Hasbahçe. It is main entrance place of the palace. Reasons for this place to be selected especially in this study are that its location in the palace, it is an entry place, it exposures to very intense visitor and other environmental effects, it is one of the large Halls, it is always open to visitors and use and it has many significant artefacts. Indoor and outdoor BC measurements in Medhal Hall (Entrance Hall) are given in Figure 3.7 and Figure 3.8. Measurements in Medhal Hall were made on the days when it was open to visitors, so effect of outdoor environment to BC concentrations in the entry was observed clearly.

In winter season measurements of Medhal Hall reach 6.00 μg/m^3 highest degrees. BC value continuously decreased between 11:00-14:00 and became about 3.00 μg/m^3. But began to increase after 14:00 and reached a value of 6.00 μg/m^3 in the morning at 17:00. In the measurements made in summer season of Medhal Hall, the highest BC rate is observed similarly in the morning as 3.00 μg/m^3. During the day this rate has fallen consistently and at 16:00 BC value was measured as 1.00 μg/m^3.

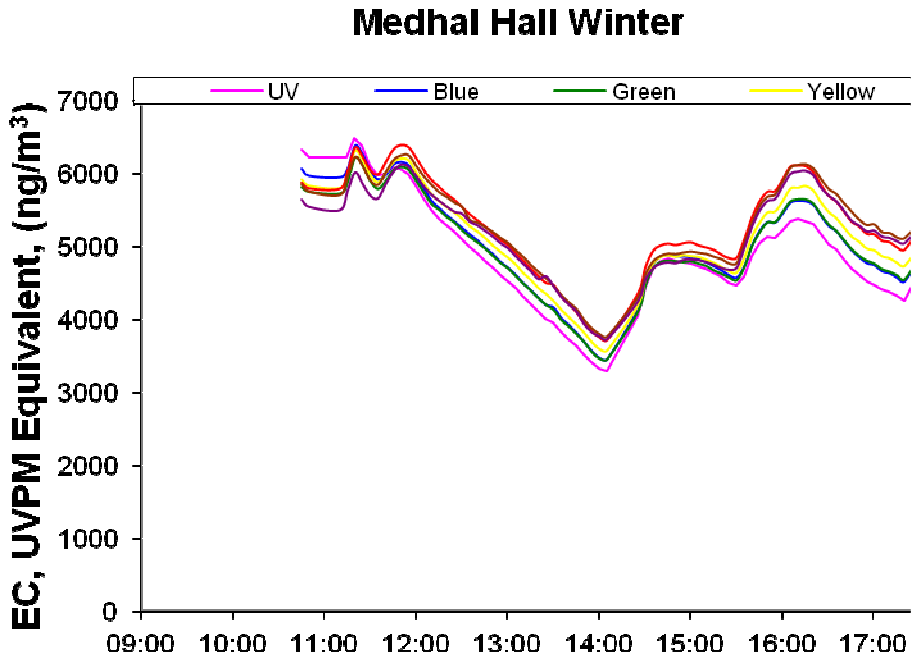

Figure 3.7 Winter BC monitors in Medhal Hall

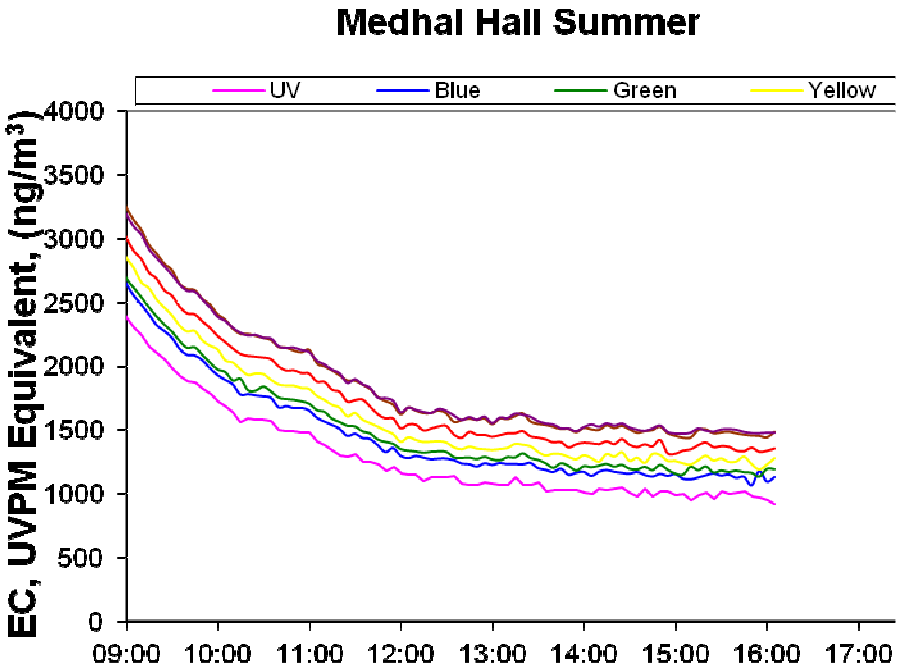

Figure 3.8 Summer BC monitors in Medhal Hall

Prayer room was selected because the main road is crossing along with this direction of the palace. Thus, it will give an idea about change of traffic-related BC value in the

rooms looking across the land. Indoor BC measurements in Medhal Hall (Entrance Hall) are given in Figure 3.9 and Figure 3.10 for winter and summer periods, respectively. BC value Prayer room indoor BC value experienced its highest value with 2.50 μg/m^3 in winter in the morning. This value decreased until 14:00 and become 1.70 μg/m^3. After 14:00 BC value began to increase again and reached its value in the morning that is 2.50 μg/m^3.

Unfortunately, there is not any available area, e.g. balcony, outdoor stand, etc, to monitor outdoor concentrations, so we were not able to conduct any outdoor monitors in a nearby location. On the other hand we have winter and summer measurements which make possible to draw some conclusions related to seasonal indoor BC concentration differences. Summer season indoor prayer room BC measurements were made 4.00 μg/m^3 in the morning and this value increased until 12:00 and reached the value of 9.00 μg/m^3. This value is one of the highest BC values ever reached in our indoor measurements. This value decreased to 5.00 μg/m^3 until 14:00, but again increased again and reached 7.00 μg/m^3 at 16:00. It was observed in the measurements in prayer room in summer and winter that BC value is higher in summer period, even it never decreases to the values measured in winter period.

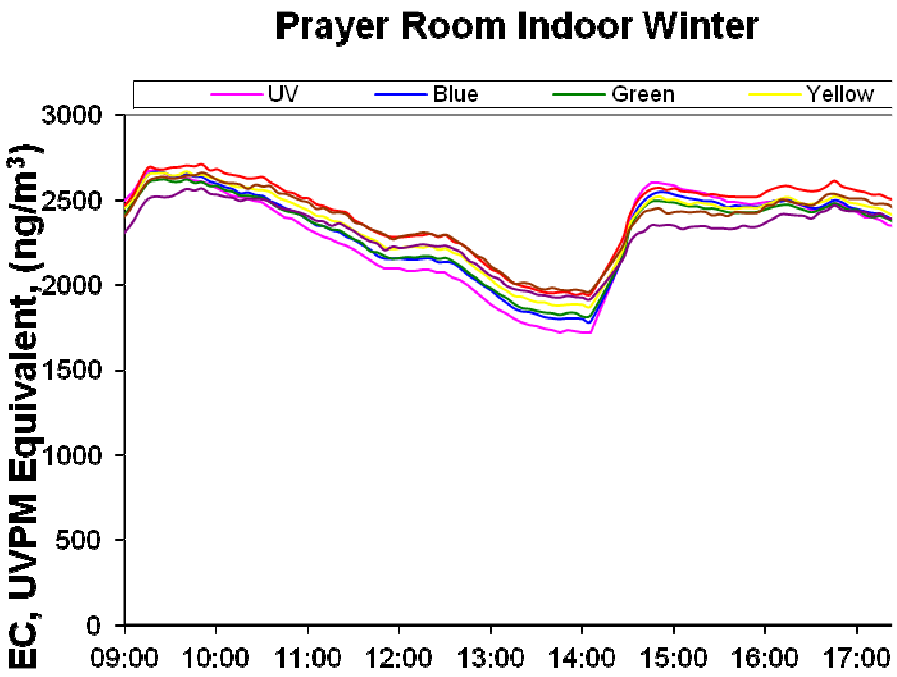

Figure 3.9 Indoor BC monitors in Prayer Room during winter

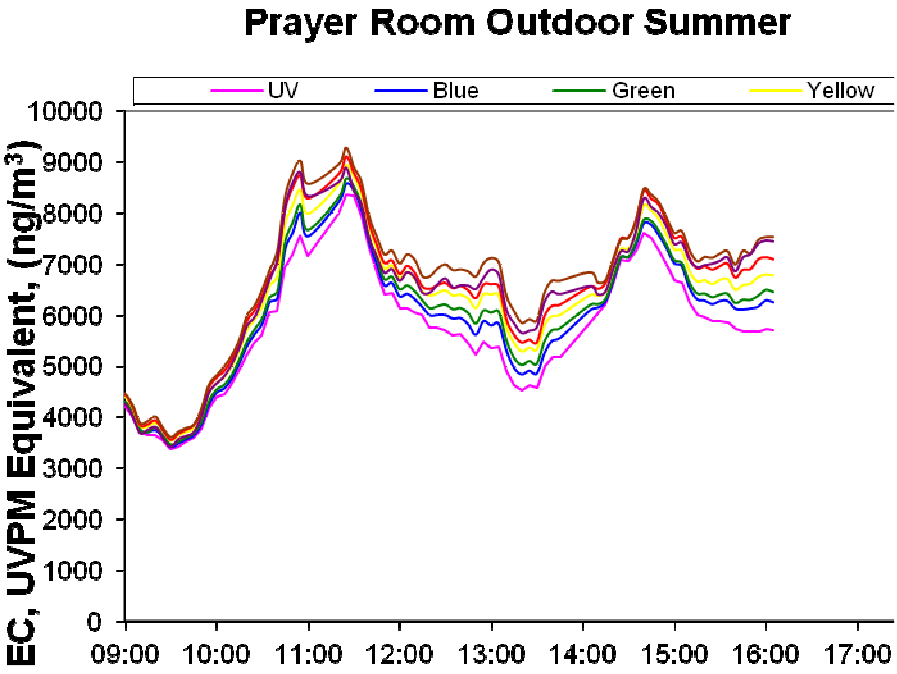

Figure 3.10 Outdoor BC monitors in Prayer Room during summer

Blue Hall is the place where Sultan reaches climbing the Halife stairs after bairam greeting in Muayede Hall and accepted congratulations of people of harem and it is known as ceremonial Hall of the harem. . It is in the harem section, on the first floor. This Hall is centre of Sultan's flat in harem and it has been named like that because of the blue colour used in its decoration. Indoor BC measurements in Blue Hall are given in Figure 3.11 and Figure 3.12 for winter and summer periods, respectively. The highest BC value in Blue Hall in winter is measured as 2.50 μg/m^3 in morning. This value decreased until 14:00 and began to increase again after this hour. BC value in Blue Hall in summer was measured in morning hours like in winter. BC value that was 6.00 μg/m^3 in the morning continuously decreased and finally become 2.00 μg m^{-3}. BC value measured in Blue Hall in both seasons is higher in summer similarly to prayer room and in both seasons the highest value of BC parameter was measured in morning.

Higher level indoor BC concentrations are not likely if we only consider that it is related to outdoor concentrations. In our case study we also observed that the ventilation methodologies in Dolmabahçe place are completely different in both of the seasons that effect the infiltration of outdoor pollutants to indoor locations. During winter time due to cold climate, the palace never ventilated using windows, on the contrary, summer

period is very hot and humid, and most of the windows were open that increase the level of indoor ventilation. This is the main reason why we have higher level of indoor summer BC pollution levels. The pollutants generated in outdoor sources (in our case it is BC) can easily transport into confined areas from the open windows, and then indoor pollution levels are likely to close the levels which were observed in outdoor.

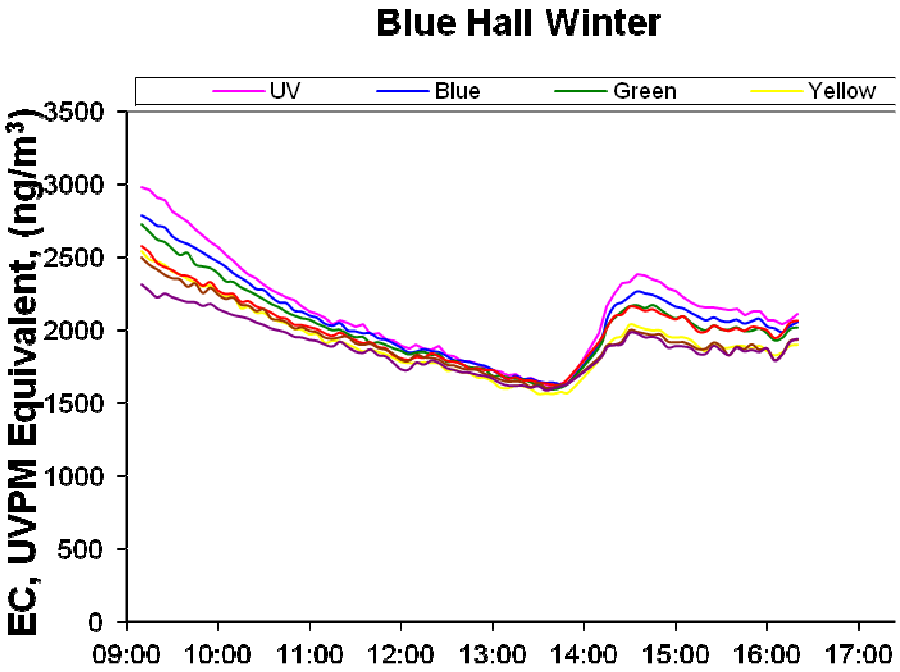

Figure 3.11 Indoor BC monitors in Blue Hall during winter

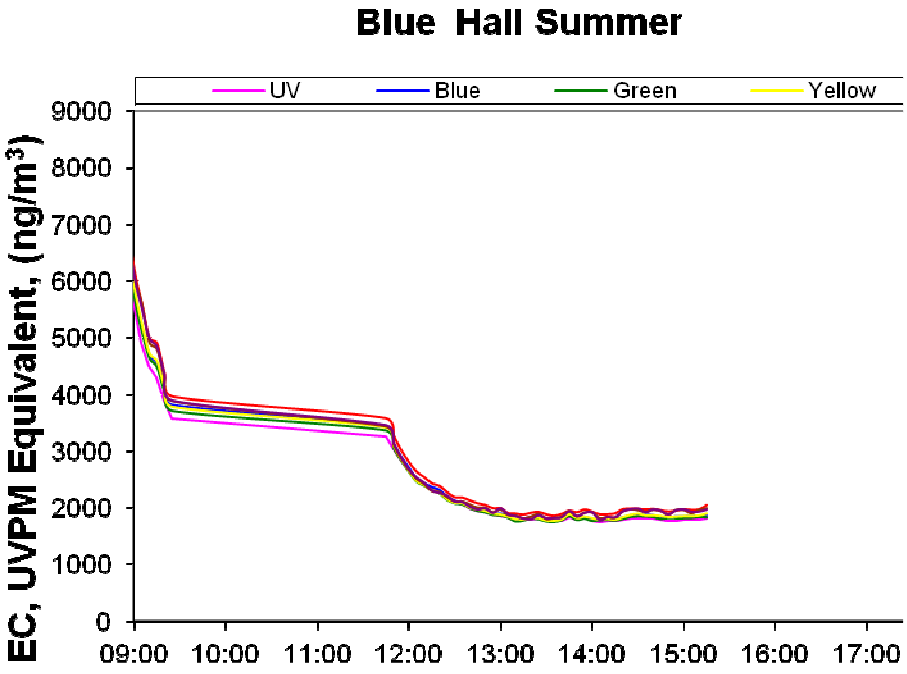

Figure 3.12. Indoor BC monitors in Blue Hall during summer

3.3 PARTICULATE MATTER (PM)

In the study carried out, particulate matters that affect Dolmabahçe Palace indoor environment quality were investigated. For this purpose, 5 µm, 3 µm, 2 µm, 1 µm, 0.5 µm, 0.3µm sized particulate matters were measured. These dimensions represent the average aerodynamic diameter (d_p) of any PM groups. However we focused on anthropogenic particulate matter ($PM_{2.5}$) because the study carried out aimed to investigate traffic-related pollutants.

Coarse fraction of the PM data will be evaluated by in the scope of another study (Kilic, 2012).

In the study carried out, measurements were made in summer and winter and with or without visitors in Dolmabahçe Palace, both particulate matter ($PM_{2.5}$) values were measured and how visitors affect ht particulate matter concentration in the palace.

As a result of measurements made in Dolmabahçe Palace indoor environment in winter-summer and with or without visitor, course PM concentration was measured higher than fine particulate matters as in some studies in literature. As shown in Table 3.3, PM_5 (here it represent the particles which are smaller and equal aerodynamic diameter, d_p=5

µm) value was measured as average 65.62 µg/m^3 in winter with visitors, average 38.42 µg/m^3 in summer with visitors.

PM5 value was measured as average 31.88 µg/m^3 in winter without visitors, average 33.73 µg/m^3 in summer without visitors. Looking at the distribution of fine particulates, while PM_2 value winter season with visitors is 9.85 µg/m^3 on average, this value was measured as 5.81 µg/m^3 in summer. While PM_2 value average in winter with visitors is 10.30 µg/m^3, this value was measured as 6.39 µg/m^3 in summer. When total course PM and fine PM concentration values are examined, visitors' effect on PM concentration in the palace is clearly seen. It is seen in the measurements both in winter and summer that course particulate matter amount increases in palace on the days Dolmabahçe Palace is open to visitors and fine particulate matter decreases. On the days palace is close to visitors, course PM amount decreases while fine PM_2 amount increases. These values show that; this is rising of settled dust with visitors' movements and/or spread of the dust carried or produced by people. In a study conducted, it was emphasized that particulate matter amount in the museum increases on the days museum is open to visitors, outdoor air pollution and effect of visitors on museum indoor source of particulate matters (Krupińska, et al., 2011).

Table 3.3 Distribution of particulate matter in Dolmabahçe Palace (µg/m^3). *Fine fraction means the particle range between 0.3 µm-2 µm dimensions

	0.3 µm	**0.5 µm**	**1 µm**	**2 µm**	**3 µm**	**5 µm**	**Total**	**Fine* PM**
Winter with visitor	0.87	1.73	3.26	3.99	25.47	30.30	65.62	9.85
Summer with visitor	0.46	0.94	2.03	2.38	14.78	17.83	38.42	5.81
Winter non visitor	2.11	3.84	2.33	2.02	10.84	10.82	31.88	10.30
Summer non visitor	0.95	1.46	1.87	2.11	12.60	14.82	33.73	6.39

According to the visiting and non-visiting days measurements two different PM behaviours for fine and coarse sized PM groups were observed. Firstly always higher indoor ambient levels were observed in coarse PM fractions during winter and summer periods. This difference is more significant in wintertime measurements, which is about two times higher. Summertime visitor-no visitor difference, about 10 percent, is also significant but as not high as the wintertime measurements. These results clearly show that visitors make a significant PM contribution to indoor air quality profile in Dolmabahçe Palace. However, the results in Table 3.3 indicate an interesting result for

the fine PM fraction. During visiting periods, there is a decreasing trend in fine PM fractions, but not significant (about 5%), in both of the season. Actually this is not a surprising result, because we know that, during non visiting times, all the windows and doors were closed, that decreases the ventilation efficiency of the building. It is clearer that Dolmabahçe palace was ventilated to provide a better indoor conform for visitors during summer times during visiting hours. Maybe windows were not opened during winter period as it is a standard application during summer, but it is likely to have better ventilation due to visitors' movements in the buildings. This second results showed that visitors were not making any contribution to fine PM fraction, but significant contributions to coarse PM fractions.

No limit value is given for $PM_{2.5}$ in Air Quality Assessment and Management Regulations (HKDYY) implemented in Turkey, PM_{10} limit value is given 50 $\mu g/m^3$ for 24-hour measurement and 40 $\mu g/m^3$ for a year. It was observed that PM5 value in Dolmabahçe Palace is under HKDYY limit values. WHO (World Health Organization) 2005 Air Quality Guidelines gave PM10 value as 20 $\mu g/m^3$ for year and 50 $\mu g/m^3$ for 24-hour limit value for the purpose of human and public health protection; $PM_{2.5}$ annual limit value was given as 10 $\mu g/m^3$ and 24-hour limit value was given as 25 $\mu g/m^3$ (WHO AQG, 2005). While PM5 value remains under these values when there are visitors in Dolmabahçe Palace, this value remains over 24-hour limit value when no visitors in winter.

U.S. Environmental Protection Agency (EPA) gave PM_{10} 24-hour limit value as 150 $\mu g/m^3$; $PM_{2.5}$ annual limit value as 15.0 $\mu g/m3$**,** 24-hour limit value as 35 $\mu g/m3$ (EPA, 1997). It was seen in the measurements in palace that PM_5 and PM_2 values remained under the limit values set by EPA. California Environmental Protection Agency Air Resources Board (ARB) accepted PM limits of the regulation "Children's Environmental Health Protection Act" intended to protect children's' health in 2002. In mentioned regulation, PM_{10} annual limit value was given as 20 $\mu g/m^3$**,** 24-Hour limit value as 50 $\mu g/m^3$**,** $PM_{2.5}$ annual limit value as 12 $\mu g/m^3$ (ARB, 2002). It was observed in the study carried out in Dolmabahçe Palace that PM_2 value remained under limit values of California Environmental Protection Agency ARB.

EU project MULTI ASSESS determined the PM_{10} limit value as 15 $\mu g/m^3$ in order to prevent corrosion on historical artefacts (Multi Assess, 2005). This value was determined basing on allowable PM_{10} values of painted steel, white plastic, limestone shown in Table 3.4. In the investigation of EU project MULTI ASSESS, no limit value

was given for $PM_{2.5}$. PM_5 value that we measured in Dolmabahçe Palace indoor environment is much more than this value. Even it is seen that PM_2 winter value is in these limit values.

As a result of all above evaluations, we conclude that the indoor PM air quality in Dolmabahçe Palace may not be dangerous for workers and visitors, but it is significantly higher than the desired level for the protection and conservation of cultural heritage objects.

Table 3.4 Tolerable PM_{10} levels for painted steel, white plastic and limestone based on dose-response functions and a tolerable loss of reflectance of 35% (Multi Assess, 2005)

Material	5 years	10 years between	15 years maintenance	20 years
Painted steel	40 μg/m^3	20 μg/m^3	13 μg/m^3	10 μg/m^3
White plastic	45 μg/m^3	22 μg/m^3	15 μg/m^3	11 μg/m^3
Limestone	36 μg/m^3	18 μg/m^3	12 μg/m^3	9 μg/m^3
Average	40 μg/m^3	20 μg/m^3	13 μg/m^3	10 μg/m^3

3.4 ALDEHYDES

Formaldehyde (FA) and acetaldehyde (AA) are one of the sources of both primary and secondary air pollution and they are most common aldehydes in the environment. Formaldehyde and acetaldehyde consist of both natural and anthropogenic emission sources. However they are composed of traffic emissions and photochemical reactions of volatile organic compounds in outdoor environment anthropogenically (Machado et al., 2010). In many studies it is stated that Formaldehyde and acetaldehyde amount in outdoor environment affects solar flux, vehicular emissions and temperature parameters (Vartiainen et al., 2000; Machado et al., 2010). On the other hand, the indoor sources for FA and AA have completely different profile. Formaldehyde in the vapour form is emitted from wooden enclosures (e.g display or storage cabinets), which comprise synthetic wood boards (e.g. plywood, particleboard, chipboard and fibreboards containing urea–formaldehyde (UF) or phenol–formaldehyde (PF) resin binders) (Gibson et al., 2010). In addition to that, acetaldehyde and formaldehyde are known to be emitted from paper and other cellulose-based materials during degradation (Fenech et al., 2010). Of the typical characteristics of an indoor museum environments is well-sealing, which result low level air exchange rates and in-out filtration. In our study, measured FA and AA values in indoor environments are mostly attributed to

biodegradation process of the aged wooden materials which are the dominant building and structural material in Dolmabahçe Palace.

When gas pollutants measured indoor and outdoor of Dolmabahçe Palace were assessed, formaldehyde and acetaldehyde amount was determined to be higher in internal environment. Seasonal average values of AA and FA measurements are given in Table 3.5. These results are also confirmed that the indoor FA and AA values were originated from any indoor source. Formaldehyde and acetaldehyde was measured in winter period indoor respectively as 3.30 $\mu g/m^3$ and 2.27 $\mu g/m^3$, outdoor as 1.50 $\mu g/m^3$ and 1.68 $\mu g/m^3$. Also in summer period indoor it was measured respectively as 8.96 $\mu g/m^3$ and 3.11 $\mu g/m^3$, while it was measured outdoor as 3.16 $\mu g/m^3$ and 5.53 $\mu g/m^3$. It is thought that much amount of Formaldehyde and acetaldehyde in palace is due to organic decay on palace inventory as stated in many studies. [Salthammer et al., 2010].

Table 3.5 Average values of formaldehyde and acetaldehyde exposure levels observed in Dolmabahçe Palace indoor and outdoor places ($\mu g/m^3$)

	Formaldehyde	**Acetaldehyde**	**Formaldehyde**	**Acetaldehyde**
	Summer		**Winter**	
Indoor	8.96	3.11	3.3	2.27
Outdoor	3.16	0.53	1.5	1.68

No limit value is given for Formaldehyde and acetaldehyde in Air Quality Assessment and Management Regulations (HKDYY) implemented in Turkey. The World Health Organization (WHO) has developed a guideline for formaldehyde in non-occupational settings at 100 ppb (0.1 mg/m^3) for 30 minutes. USA-NIOSH (National Institute for Occupational Safety and Health, 2005) gives TWA limit as 0,016 ppm (13 $\mu g/m^3$), for STEL 1 ppm (0.81 mg/m^3); and no limit for acetaldehyde. USA-OSHA (National Institute for Occupational Safety and Health, 2005) gives TWA limit for formaldehyde as 0,75 ppm (0.61 mg/m^3), for STEL 2 ppm (1.63 mg/m^3); TWA limit for acetaldehyde as 200 ppm (111 mg/m^3), for STEL 150 (83.3 mg/m^3) ppm. UK (Health &Safety Executive, 2005) gives TWA limit 2 mg/m^3, for STEL 2 mg/m^3. In the study carried out in internal and external environment of Dolmabahçe Palace, formaldehyde and acetaldehyde values were determined to remain under these limits.

Two of the factors affecting the formation of formaldehyde and acetaldehyde are the amount of heat and sunlight. In the same way, formation of ozone gas was expressed as a photochemical reaction. When correlation between FA, AA and ozone is examined, (Table 3.6) it was determined that there is a correlation in level of R=0.88 between aldehydes and ozone amount in summer measurements where photochemical oxidation and temperature are higher. Contrary to this fact, a perfect negative correlations (R=-1.0) are calculated for wintertime concentrations. This is quite interesting result, which indicates while ozone was increasing, the aldehydes decreased, or vice versa. It is easy to explain the decreasing level of ozone formation under the winter climate, but this should be also associated by the same trends in the level of biodegradation. It is not likely to have a perfect negative correlation. These findings are open question and more detailed studies and investments should be performed to have a better explanation.

Table 3.6 Correlation table of seasonal formaldehyde, acetaldehyde and ozone measurements in Dolmabahçe palace indoor environments

	Winter O_3	**Summer O_3**	**Summer FA**
Summer FA		0.88	
Summer AA		0.88	1.00
Winter FA	-1.00		
Winter AA	-1.00		

Outdoor FA/AA ratios measured in Dolmabahçe Palace in winter and summer season are given in Table 3.7.

In the measurements made in Dolmabahçe Palace external environment, FA/AA ratios were determined. While average FA/AA ratio was about 1 in winter measurements, FA/AA ratios in summer analyses were respectively determined as 4.25, 5.97 and 6.39. Such high ratios show that formation of FA occurs more in summer period.

Table 3.7. Formaldehyde and acetaldehyde ratio

Summer FA/AA	**Winter FA/AA**
4.25	2.13
5.97	0.71
6.39	0.69

3.5 HEAVY METALS

Traffic-related heavy metals components were also investigated in sampling of particulate matter in the study that was carried out in order to examine the effect of traffic-related pollutants to indoor environment of the palace. For this purpose, heavy metals such as Chromium (Cr), Copper (Cu), Manganese (Mn), Nickel (Ni), Cadmium (Cd), Lead (Pb) were analysed in particle materials that sampling was made in 8 different sizes with Cascade Impactor. Averages of heavy metals according to size distribution whose samplings were done in indoor environment are given in table 3.9. Results were assessed according to the sizes stated in Table 2.1 (method part cascade Impactor). Traffic-related pollutants are in $PM_{2,5}$ fine particle sizes. For a better interpretation of the results, coarse (stage 0, 1, 2, 3) and fine (stage 4, 5, 6, 7) particle size distributions and percentages are given in Table 3.8.

Table 3.8 Average concentrations of heavy metals in PM samples collected by a cascade impactor

	Stage 0 (ng/m^3)	**Stage 1 (ng/m^3)**	**Stage 2 (ng/m^3)**	**Stage 3 (ng/m^3)**	**Stage 4 (ng/m^3)**	**Stage 5 (ng/m^3)**	**Stage 6 (ng/m^3)**	**Stage 7 (ng/m^3)**
Cr	0.08	0.06	0.64	0.64	2.61	3.22	1.95	1.80
Cu	2.90	3.55	8.12	5.23	6.88	8.89	7.31	4.91
Mn	2.70	4.03	7.41	5.29	7.50	7.50	4.01	3.19
Ni	2.06	1.28	6.37	1.95	2.00	5.31	5.75	6.69
Pb	2.35	6.92	25.08	7.90	8.65	7.10	3.09	4.76
Cd	0.03	0.04	0.11	0.09	0.13	0.44	0.42	0.38

Table 3.9 Average heavy metals concentrations in coarse and fine PM fractions

	Course (ng/m^3)	***Fine (ng/m^3)***	***% Course***	***% Fine***
Cr	1.42	9.58	13	87
Cu	19.80	27.98	41	59
Mn	19.42	22.20	47	53
Ni	11.66	19.75	37	63
Pb	42.25	23.60	64	36
Cd	0.27	1.37	16	84

According to our results, as shown in Table 3.9, fine particulate matter concentration was 9.58 ng/m^3, while Cr coarse particulate matter concentration was 1.42 ng/m^3. While 13% of the Cr element detected in the palace is in the coarse particulate matter, 87% of it is in fine particulate matters. While coarse particulate matter concentration of Cu

element is 19.80 ng/m^3, its fine particulate matter concentration is measured 27.98 ng/m^3. 59% of Cu element measured is in fine particulate matter while 41% of it is in coarse particulate matter. Another element measured Mn has 19.42 ng/m^3 concentration in particulate matter, while its quantity in fine particulate matter is 22.20 ng/m^3. While 47% of the Mn element detected is in coarse particulate matter, 53% of it is in fine particulate matter. While concentration of Ni element measured indoor environment of Dolmabahçe is 11.66 ng/m^3 in coarse particulate matter its concentration in fine particulate matter is 19.75 ng/m^3. When we consider percentage distribution of Ni element according to its particulate size, coarse particulate matters are 37% of total particulates, while fine particulates are 63% of total particulates. While coarse particulate matter amount of Pb element is 42.25 ng/m^3, its fine particulate matter amount is 23.60 ng/m^3. While 64% of Pb element measured is in coarse particulate matter, 36% of it is in fine particulate matter. While coarse particulate matter amount of Cd element is 0.27 ng/m^3, its fine particulate matter amount is 1.37 ng/m^3. While 16% of the Cr element detected in Dolmabahçe Palace is in coarse particulate matter, 84% of it is in fine particulate matter.

As a result of heavy metal sampling in Dolmabahçe Palace, it is determined that all elements except Pb were found more in fine particulate matter size. There is no source in the palace that can cause fine particulate sized heavy metal pollution. We conclude that heavy metals measured indoor are anthropogenic pollutants outdoor. We attributed that the most significant anthropogenic fine PM source is traffic related exhaust emissions.

The amount of Pb was higher than the amount of coarse particulate matter in palace. This is an unexpected result, since the atmospheric sources of lead is mainly related the lead containing fossil fuel combustion, mostly gasoline, which emits lead mostly in form of fine sized PM into the atmosphere. However, the sources of environmental lead are wide-ranging in the literature, one of the main indoor lead contribution and poisonings were attributed to lead based paints, which were common in earlier times (Montgomery and Mathee, 2005). Even though we did not perform any chemical analysis on the wall painting samples obtained from anywhere in Dolmabahçe Palace; we speculate that the enriched indoor lead concentrations can be attributed to wall and structural material deformations which may contain higher level of old lead based paints

used in the palace. Because, this elevated lead concentrations perfectly coincidence with wall and other structural restoration activities performed in the closer rooms and micro environments to sampling points.

Especially high amounts of Pb in coarse particulate matter in measurements in Medhal Hall are thought to be due to the restoration in Crystal Stairs that are always open and connected to Medhal Hall. Some parts of Crystal Stairs are in restoration since 2009, but on the date of measurements inventories and the room of Medhal Hall were being cleaned. We conclude that coarse particulate matter containing Pb increased due to this cleaning.

In order to identify the common sources of heavy metals, we performed a factor analysis with use SPSS. Results of this analysis are summarised in Table 3.10. Two main factors were identified and 84% of the variance explained with these two factors. Components of the each factor groups are given in bold fonts in the table. These are the factor components which have common.

Table 3.10 Factor groups of heavy metal pollutants

	Component	
	1	**2**
Cr	0.882	0.137
Cu	0.708	0.675
Mn	0.264	0.885
Ni	0.733	0.196
Pb	-0.150	0.918
Cd	0.972	-0.176

In the first group, Cr, Cu, Ni, and Cd are located, and in the second factor group Mn, and Pb are located. In the second factor, lead and manganese falls in the same factor groups that also confirms our previously assumption. Manganese is naturally occurring element and found abundantly in nature; 0.1% of the earth crust is manganese. Its association with the lead confirms that both elements are abundant in paint materials used in the palace, which was get scrapped during the restoration activities, settled down to surfaces, then re-suspended during any space cleaning activities.

3.6 EVOLUTION OF RESULTS ACCORDING TO TWO MODELS

3.6.1 Dose-Response Calculations

European Union Fifth Frame Work Programme (EU5FP) for the purpose of preventing corrosion on cultural structures, a project named MULTI-ASSESS, Model for Multi-Pollutant Impact and Assessment of Threshold Levels for Cultural Heritage was completed in 2005. Comprehensive aim of the project is to investigate corrosion and soiling effects of parameters such as HNO_3, SO_2, NO_2 and O_3 main sources of air pollution and particulate matter on historical artefacts and to model the amount of damage mathematically. Weather conditions during the modelling; parameters such as temperature, moisture and pH value are included in modelling. In order to investigate dose- response relation (dose-response function) in terms of corrosion, carbon steel, zinc, copper, bronze and limestone materials were selected. Mathematical formulas developed for these materials are given in the Table 3.11 Relative deposition model given;

$$K= K_{dry} (SO_2, NO_2, O_3, Rh, T) + K_{wet} (Rain, H^+) \quad (8)$$

Deposition- dose-response formulas become two parts which are dry deposition and wet deposition (8). Dry deposition part is significant to evaluate the result because of the study carried out inside of the Dolmabahçe Palace. Therefore gases air pollutants; SO_2, NO_2 and O_3 additional relative humidity values important in the study.

Only parameters forming dry deposition values were used in indoor assessment. As already stated, SO_2 and PM_{10} limit values of the study Multi-Assess (2005) are given. These values are given respectively as 10 $\mu g/m^3$ and 15 $\mu g/m^3$.

Table 3.11 Dose-response functions for the multi-pollutant situation, including temperature function, for unsheltered materials (Multi-Assess, 2005).

Material	**Dose-response function***	**Temperature function**
Carbon steel	$ML=29.1+\{21.7+1.39[SO_2]^{0.6}Rh_{60}e^{f(T)} +1.29Rain[H^+] + 0.593PM_{10}\}t^{0.6}$	$f(T) = 0.15(T-10)$ when $T<10°C$, $-0.054(T-10)$ otherwise
Copper	$ML=3.12+\{1.09+0.00201[SO_2]^{0.4}[O_3]Rh_{60}e^{f(T)} 0.0878Rain[H^+] \}t$	$f(T) = 0.083(T-10)$ when $T<10°C$, $-0.032(T-10)$ otherwise
Cast Bronze	$ML=1.33+\{ 0.00876[SO_2]Rh_{60}\cdot e^{f(T)} + 0.0409Rain[H^+] + 0.0380PM_{10} \}t$	$f(T) = 0.060(T-11)$ when $T<11°C$, $-0.067(T-11)$ otherwise
Portland limestone*	$ML=3.1+\{0.85+0.0059[SO_2]RH+0.054Rain[H^+] + 0.078[HNO_3]Rh_{60} + 0.0258PM_{10} \} t$	-
Zinc*	$ML = 1.82 + \{ 1.71 + 0.471[SO2]^{0.22} e^{0.018Rh+f(T)} + 0.041Rain[H^+] + 1.37[HNO3] \} t$	$f(T) = 0.062(T-10)$ when $T<10°C$, $-0.021(T-10)$ otherwise

* The annual HNO_3 concentrations were calculated:
$HNO_3 = 516\ e^{-3400/(T+273)}\times([NO_2][O_3]Rh)^{0.5}$

** Units of the used parameters are: corrosion attack [ML] in g m^{-2}, gaseous pollutants in µg/m^3, time (t) in years, temperature (T) in °C, relative humidity (Rh) in percent (%), amount of precipitation (Rain) in mm, and H^+ of precipitation [H^+] in mg/l.

While SO_2 is common parameter in modelling of all materials, PM_{10} is the other pollutant parameter that affects carbon steel and cast bronze materials, HNO_3 is the other pollutant parameter that affects zinc, O_3 is the other pollutant that affects copper, HNO_3 and PM_{10} are the other pollutants that affect Portland calcareous cement. Parameters which have synergetic effects on the materials are given in Table 3.12. This table includes only dry deposition parameters.

Table 3.12 Parameters which have synergetic effects on the materials

Material	**T**	**Rh**	**SO_2**	**NO_2**	**O_3**	**HNO_3**	**PM_{10}**
Carbon Steel	X	X	X				X
Zinc	X	X	X			X	
Copper	X	X	X		X		
Bronze	X	X	X				X
Limestone	X	X	X			X	X
Glass		X	X				
	X	X	X	X			

While NO_2 and O_3 do not affect directly materials but the gaseous occur synergistic effects cause HNO_3 formation.

PM_{10} parameter affects especially in form of soiling. Effects of particulate matters on painted steel (9), white plastic (10), polycarbonate membrane (11) and limestone (12) are stated with the formulas below.

Painted Steel: $R = Ro\ [1\text{-}exp\ (-\ CPM_{10} \times t \times 5.9 \times 10^{-6})]$ (9)

White Plastic: $R = Ro\ [1\text{-}exp\ (-CPM_{10} \times t \times 5.3 \times 10^{-6})]$ (10)

Polycarbonate Membrane: $R = Ro\ [1\text{-}exp\ (-CPM_{10} \times t \times 2.4 \times 10^{-6})]$ (11)

Limestone: $R = Ro\ [1\text{-}exp\ (-CPM_{10} \times t \times 6.5 \times 10^{-6})]$ (12)

Multi Assess Dose-response functions used to calculated the effect of related traffic resources in Dolmabahçe Palace. We determined the risk values of micro environments (e.g. rooms, Halls, etc.) with Dose-response function of SO_2, NO_2, O_3 and PM_{10}.

Humidity values of Dolmabahçe Palace are high because it is a museum on the sea side. Humidity values measured by Dolmabahçe Palace administration are very high both in winter and summer. As mentioned in formulas, humidity value is over 60% and this causes humidity parameter to become active for materials exposed to corrosion. Unfortunately, even the humidity values measured in winter season in Dolmabahçe Palace are over 60%.

Highest risk rooms for Carbon Steel, bronze materials; Hall 76, Süfera Hall, Head clerk room, Hall Nr. 18, silver room and room for preparation to worship. Rooms at risk for Zinc, cooper and limestone; Hall 76, Süfera Hall, Head clerk room, Hall Nr. 18, silver room and room for preparation to worship, room Nr.33and room Nr.162. For Glass; Hall 76, Süfera Hall, Head clerk room, Hall Nr. 18, silver room and room for preparation to worship, room Nr.33and room Nr.162.

All rooms in the palace are at risk because PM_{10} value is over 15 mg/m^3 for the materials painted steel, white plastic, polycarbonate membrane, limestone that are exposed to soiling due to high value of PM_{10}. The biggest reason for this is that too many visitors come to palace during the day, floors are covered with carpets and palace is located on a street where traffic is intense. The highest PM value on the day's close to visit are in 127th room, 129th room, 96,97th and 99th rooms, 212th room, 166, 168th and 170th rooms, 119, 122, 157,161, 163, 167 and 157th corridor.

The highest PM value on the days open to visit are; 122nd room, 154th room, 157th room 152nd corridor, 161, 163 and 166, 167, 168 and 170th rooms.

3.6.2 EU Project Master Early Warning Dosimeter for Organic Materials (EWO Dosimeter)

The study carried out by NILU Norwegian Institute for Air Research refers to air pollutants that affect objects in museum and possible effects of these pollutants. Two investigations EU project MASTER and PROPAINT, were made by NILU Norwegian Institute for Air Research for indoor materials and air pollution.

EWO dosimeter work with this principle; develop an early warning system based on an effect sensor for organic materials, assessing deterioration on organic materials indoor, based on the end-user identified needs.

There are two different calibration equations including MASTER Early Warning Dosimeter for Organic Materials (EWO Dosimeter) Showcase (10) and galleries (11) belonging to sensors used (Lopez-Aparicio S., 2010). These are;

Showcase: $EWOG1000=4.53+T^{-1/2}\ (0.16[NO_2] +0.052[O_3])$ (13)

Galleries: $EWOG1000=8.67+UV^{-1/2}+T^{-1/2}\ (0.11[NO_2] +0.1[O_3])$ (14)

Table 3.13 Threshold values of Early Warning Dosimeter for Organic Materials (EWO Dosimeter)

	Calibration point	**Trigger values**					
						T (^{o}C)	
		NO_2 (ppb)	O_3 (ppb)	UV (mW/m2)	RH = 45 %	RH = 55 %	RH = 65 %
1		1	1.15	1	20.8	19.3	18.2
2	Increasing deteriorating ↓	2.5	3	3.75	22.9	21.4	20.2
3		5	6.5	15	24.5	23	21.8
4		10	12.5	37.5	26.8	25.3	24.1
5		15	25	37.5	29	27.6	26.2

Most significant pollutants for organic materials are NO_2 and O_3 which illustrated Formula 1 and 2. Additional the other important parameter is SO_2 which given range 0-3.5 ppb.

1 ppb= 1.91 µg/m^3 NO_2, 1 ppb= 2 µg/m^3 O_3 and 1ppb= 2.62 µg/m^3 SO_2.

According to calculated values between 1- 5 classifications; 1- 5 between classifications determined NO_2 between 1.91- 28.65 µg/m^3, O_3 between 2.3– 50 µg/m^3 and SO_2 between 0- 9.2 µg/m^3.

The classification given in Table xxx different kind of places as; Archive store, Purpose built museum, House museum, Open structure, External store with no control. We evaluate the result according to the house museum for Dolmabahçe Palace.

Table 3.14 Early Warning Dosimeter for Organic Materials response level after exposure

Determined	**Classification of Levels**				
Expectation	**1**	**2**	**3**	**4**	**5**
Archive store	Expected environment (acceptable)	Environment could be better	Environment is poor	Something is wrong with control	Serious problem with building or control
Purpose built museum	Environment is very good	Expected environment (acceptable)	Environment could be better	Environment is poor	Something is wrong with control
House museum	Excellent environment	Environment is very good	Expected environment (acceptable)	Environment could be better	Environment is poor
Open structure	Dosimeter is not responding	Excellent environment	Environment is very good	Expected environment (acceptable)	Environment could be better
External store with no control	Dosimeter is not responding	Dosimeter is not responding	Excellent environment	Environment is very good	Expected environment (acceptable)

Our results are compared with the values specified in the Dolmabahçe Palace. NO_2 gas was measured respectively on average of 52.8 µg/m^3, and 46.47 µg/m^3 in summer in the palace. Dolmabahçe Palace is 5th group in terms of NO_2 pollutant. O_3 concentration was determined as 4.30 µg/m^3 and 4.48 µg/m^3 on average in winter and summer seasons. Dolmabahçe Palace is in 2nd group in terms of O_3 values.

Rooms at highest risk with actual measurements in Dolmabahçe Palace are as follows; Hall 76, Hall 118, Süfera Hall, Room 33, Selamlık Sultan Bath, Silver Room, Harem of passenger Hall, Yellow Hall, 162 Medhal Hall, Hall 41 and Glass Pavilion.

CHAPTER 4

CONCLUSIONS

In the study carried out, traffic-related pollutants and possible effects of them on inventory of the palace were researched in indoor and outdoor (Palace balconies) of Dolmabahçe Palace. For this purpose, in Dolmabahçe Palace NO_2, SO_2, O_3, particulate matter (PM), black Carbon (BC), heavy metal and aldehydes (formaldehyde and acetaldehyde) were investigated and the results were discussed.

NO_2 value from traffic-related main gas pollutants has been determined very high in indoor and outdoor environment of the palace. Even, when amounts of all pollutants measured in the palace, it is seen that NO_2 has the most pollutant value. NO_2 amount remains over the NILU limits in 65 points where measured in the palace. Also NO_2 is a main pollutant that will lead to formation of corrosion on the inventory in the palace because it causes formation of HNO_3 in humid environment with ozone. Therefore, inventories in the palace are under high risk in terms of pollutant NO_2.

SO_2 gas, with its average values in indoor and outdoor environment of the palace, is in the group of “moderate” according to limit values of Multi Assess 2005. However, SO_2 value has not been determined in high degree in any room.

One of the traffic-related pollutants, Black Carbon value has been determined higher in summer period in the rooms facing to the traffic in analysis results. This result indicates that traffic-related pollutant increases during the summer period. Similarly, it has been identified that the values of NO_2 and SO_2 also increase during the summer in support of this conclusion. In indoor and outdoor BC measurements of Dolmabahçe Palace, it is notable that the highest value measured in indoor environment is in the morning. It is determined that BC value generally decreases during the day but also affected by fluctuations in outdoor environment. However, BC value decreases at noon while it has high values in the morning and near the end of the working hours.

Course and fine particles amount was determined to be highly affected by visitors. The measurement results carried out in Dolmabahçe Palace were determined to be over the limit values determined for historical objects.

The most remarkable results regarding the Aldehydes measurements are that aldehydes amount is higher inside the palace than out of the palace. With this result, it has been identified that objects in the palace are suffering from organic deterioration.

Although heavy metal pollution is not in Dolmabahçe Palace, heavy metals are mostly in fine particulate matter sizes, also it is determined that restoration works in the palace increase Pb value in course size.

Because Dolmabahçe Palace is a museum palace, an HVAC system, unfortunately, cannot be established for the purpose of protecting the historical objects. Absence of HVAC system in the palace increases exposure of the inventory in the palace to outdoor pollutants. Nevertheless, especially the pollutants that cause damage on the historical artefacts and determined in high degrees in Dolmabahçe Palace indoor environment pose a threat to the inventory of the palace.

This study that is conducted was supported by TUBITAK with project number 109Y272. Furthermore, this study is the first study in Turkey that examines the air quality in the museum and discusses possible effects of the air quality to the objects in the museum. This study will be guiding the projects and researches in respect to air quality in museum in the future in Turkey

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