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Effect of Gaseous Pollutants (NO_2, SO_2 and O_3) on Cultural Heritage Materials: A Case of MFAs in Brussels, Belgium

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Abstract- The collection of the Royal Museums of Fine Arts (MFA) of Brussels, Belgium covers a period extending from the 15th to the 21st centuries. It provides overview of western arts with remarkable ensembles of works of artists from Belgium. In the museum there a collection of paintings, sculptures, drawings and prints, it also includes, in particular through donations or deposits, items of decorative arts and furniture along with a small number of non-European works. The online catalogue currently contains over 10,000 of the most representative works of the collection. To assess the air quality inside and outside the museums the sampling campaign over a period of April 13, 2015- May 11, 2015 was performed. The gas monitoring of nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and ozone (O_3) was carried out outside the building, in galleries and in showcases by means of using diffusive samplers. The concentrations of gaseous pollutants (NO_2, SO_2 and O_3) were lower inside the museums than the outside with some of them at undetectable levels inside; in addition, the levels of these gases inside the two museums were lower and below the recommended level when compared to that of other museums (in other countries). The air conditioning system inside the museums play a great role in determines the concentrations of the pollutants.

Keywords: *museum, gaseous, pollutants, indoor, outdoor.*

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Effect of Gaseous Pollutants (NO_2, SO_2 and O_3) on Cultural Heritage Materials: A Case of MFAs in Brussels, Belgium

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Abstract- The collection of the Royal Museums of Fine Arts (MFA) of Brussels, Belgium covers a period extending from the 15th to the 21st centuries. It provides overview of western arts with remarkable ensembles of works of artists from Belgium. In the museum there a collection of paintings, sculptures, drawings and prints, it also includes, in particular through donations or deposits, items of decorative arts and furniture along with a small number of non-European works. The online catalogue currently contains over 10,000 of the most representative works of the collection. To assess the air quality inside and outside the museums the sampling campaign over a period of April 13, 2015- May 11, 2015 was performed. The gas monitoring of nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and ozone (O_3) was carried out outside the building, in galleries and in showcases by means of using diffusive samplers. The concentrations of gaseous pollutants (NO_2, SO_2 and O_3) were lower inside the museums than the outside with some of them at undetectable levels inside; in addition, the levels of these gases inside the two museums were lower and below the recommended level when compared to that of other museums (in other countries). The air conditioning system inside the museums play a great role in determines the concentrations of the pollutants.

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I. Introduction

Air born pollutants exhibits a wide range of adverse effects on objects connected to cultural heritage. Both gaseous and particulate air pollutants are responsible for deteriorating processes. Some of these pollutants are encountered in indoor atmospheres have their main sources are in the outdoor environment and enter mainly via air exchange while other pollutants are mainly produced indoors.

Inorganic compounds such as sulphur dioxide (SO_2), nitrogen oxide (NO_2) and ozone (O_3) are the most dangerous gaseous air pollutants. Presence of SO_2 in the atmosphere may be due, as in the case of NO_X, to transport. However, the main emission source is the combustion of sulphur-containing fuels (95% go for SO_2 and 5% go for SO_3) (Geerinckx, 2003). SO_2 is a colourless, water-soluble gas. Similarly as ozone, SO_2 is responsible for the degradation of dyes and damaging of photographic material (Swan, 1981) and leather (Spedding, and Rowlands, 1971). This is the result of an oxidation reaction which causes conversion of the atmospheric SO_2 to sulphuric acid (H_2SO_4) (Pavlogeorgatos, 2003), which can damage the museum objects.

These are mostly objects that are composed of calcium carbonate ($CaCO_3$) (marble, limestone and murals), but also cellulose (paper, cotton and linen), silk, iron (Fe) and steel (Pavlogeorgatos, 2003). Paper will discolour and become brittle, textile and leather weaken and metals will become dull (Spedding and Row lands, 1971, Shahani and Wilson, 1987), Lang well, 1976). Hudson and Milner, 1961, Zeronian, 1970, 1973, Pope et al., 1986). Iron acts as a catalyst for such oxidation reactions, as well as manganese (Mn) or copper (Cu) (Whitmore, P. M. 1987).

Tropospheric ozone caused damage to the health, environment and material. Unlike in the case of most pollutants, there is no direct O_3 emission source. It is formed when sunlight is incident at different atmospheric polluting gases such as NO_X. Ozone is a highly reactive gas because of its strong oxidizing properties. It is capable to damage a variety of oxidation-sensitive materials, especially by ozonolysis reactions with unsaturated organic compounds. Colour change and fading of pigments illustrate this phenomenon. Whitmore and Cass, 1998, Giles, (1965), have investigated the effect of O_3 on a range of pigments and textile dyes. They showed that the materials are at risk only if they are exposed to O_3 for a prolonged period. The discolouration or fading of dyes occurs when organic pigments are sensitive to specific oxidation reactions (Salmon et al, 2000, Shahani, and Wilson, 1987, Newton, 1945). Additionally, O_3 causes damage to photographic material and paper (Morris et al, 1964) and reduces endurance of rubber (Camuffo, 1998).

NO_X-compounds are produced by combustion processes as a result of the oxidation of nitrogen (N_2) in the air. There are both anthropogenic and natural sources. NO_2 is a toxic, reddish brown gas and is similar to SO_2 regarding the damage to the exhibits. In humid air, it is oxidized to volatile nitric acid (HNO_3) by reaction

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with OH-radicals (Pavlogeorgatos, 2003). This acid can then induce fading of textile dyes and photographic film damage and weaken textile fibres (Worobiec et al, 2008).

In this study, we measured O_3, SO_2 and NO_2, concentration in the museum environment (inside, outside and showcase) and these results are probably very important basic information when considering the conservation of cultural property over a longer period of time.

II. Methodology

a) Sampling site

The museums are situated in the capital Brussels, Belgium in the downtown area on the Coudenberg. It is located on the city of Brussels (50.84^0 N, 4.36^0 E, 28 m a.s.l.) and it has a population of 1.187890 million.

b) Gaseous sampling: Radiello diffusive sampler

The diffusive sampler (Fondazione Salvatore Maugeri, Padova, Italy) is a closed box, usually cylindrical. It has two opposite sides, one is transparent to gaseous molecules which cross it, and are adsorbed onto the second side. The former side is named diffusive surface (S), the latter is the adsorbing surface (A) (marked with *S* and *A* in Fig. 1). The diffusive body has a cylindrical symmetry in which the adsorbing cartridge is positioned coaxially (Fig.1). The chemiadsorbing cartridges are positioned in the diffusive bodies and the whole is subsequently attached to a supporting plate, which also act as a closure. When measuring outdoors, the samplers are protected from rain by a small shelter. Sampling periods ideally range from 3 to 7 days.

Since the uptake rate of the gas molecules depends on temperature, the ambient temperature is measured simultaneously to obtain more accurate concentration values, applying a temperature dependent correction factor. After sampling, the chemiadsorbing cartridges are well sealed from ambient air and transported to the lab for analysis.

For the sampling of O_3, SO_2 and NO_2, the same diffusive body was used (code 120-1). It consists of microporous polyethylene with an average porosity of 25 ± 5 µm, opaque to light. The chemiadsorbing cartridges are compound specific. For ozone, the cartridge (code 172) is composed of silica gel coated with 4, 4'-dipyridylethylene. Upon exposure to ozone and water, both trapped in the silica gel, 4-pyridaldehyde is formed (Fig. 1). The analysis is based on colorimetry. The 4-pyridaldehyde is condensed with 3-methyl-2-benzothiazolinone hydrazone (MTBH) to obtain the corresponding aside which is yellow colored. The absorbance of the solutions is subsequently measured with UV-Visble spectrometry at a wavelength of 430 nm. By means of a calibration curve, the ozone mass is deduced (1 µg of 4-pyridylaldehyde = 0.224 µg of ozone). Finally, the average ozone concentration over the whole exposure time is calculated, applying the appropriate temperature correction. The active compound of the chemiadsorbing cartridge for NO_2 and SO_2 (code 166) is triethanolamine (TEA). NO_2 and SO_2 are adsorbed as nitrite and sulphite or sulphate ions. The diffusive body ensures that the sampling is selective for gaseous molecules. The procedure and sam[ling techniques are adapted from (Hitzenberger et al. 2006).

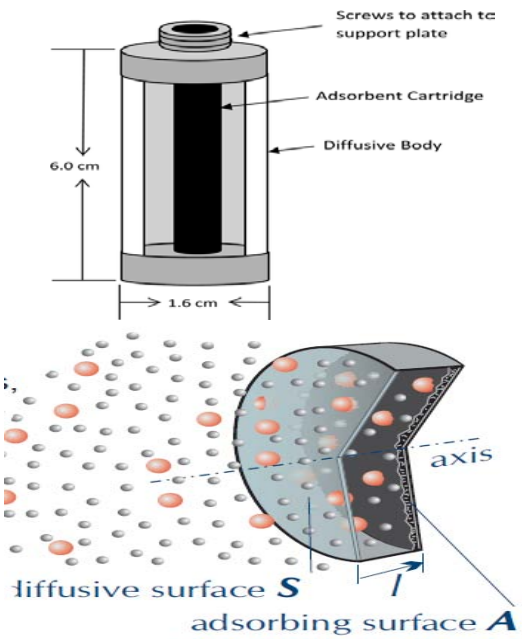


Fig. 1: The Radiello passive samplers and its Schematic of the radial sampler and Diffusion principle.

III. Result and Discussion

Both inside and outside average concentrations of pollutant gaseous such as NO_2, SO_2, and O_3 were measured in Magritte, Magritte Showcase and Reserve OB Museums of Fine Arts. Results of the analysis of investigated gaseous pollutants are summarized in Figs. 2-4

NO_2 concentrations obtained from all location inside the museums were below the detection limit defined by the United States (US) National Bureau of Standards and the Museum Environment (Thomson, G. 1986). The outside concentrations of NO_2 were found to be around 23.8 and 12.6 µg/m^3 Magritte and Reserve OB respectively. In Magritte's' Showcase, NO_2 concentration, which was inside, was below the detection limit (Table 1). Because the showcase is rather a less closed compartment within the gallery that result in a small air exchange. NO_2 is a gas with strong outdoor sources mainly from road traffic, and domestic heating for energy generation (Thomson, 1986, Kontozova-Deutsch et al 2011, Kontozova et al 2005, Ricardo et al 2015). These results also showed that NO_2 enters the museums from outdoor air and there were no

strong sources inside. In the case of Showcase, the concentration of NO_2 decreases inside because of its closed nature (Brimblecombe et al., 2001).

The indoor concentrations of SO_2 were 0.8, 0.4 and 1.5 μg/m^3 in Magritte, Reserve OB and the Magritte Showcase, respectively. SO_2 was also detected in the outdoors of the Magritte (2.4 μg/m^3) and Reserve OB (2.7 μg/m^3). SO_2 was found to be high in the display case than inside Magritte; this could be due to restricted air circulation that leads to pollutants build up over time. The decrease SO_2 concentration inside the museums was due to due to the high deposition velocity of SO_2 which leads to quick adsorption on the surface (Grontoft and Raychaudhuri, 2004)

Table 1: Indoor and outdoor mean concentrations of NO_2, SO_2 and O_3 in Museum of Fine Art.

Location	O_3 (μg/m^3)	SO_2 (μg/m^3)	NO_2 (μg/m^3)	NO_2 (ppb)	SO_2 (ppb)	O_3 (ppb)
Magritte inside	3.1	0.8	<DL	<DL	0.33	1.56
Magritte Showcase	2.1	1.5	<DL	<DL	0.56	1.04
Reserve OB. Inside	1.6	0.4	<DL	<DL	0.17	0.80
Magritte Outside	46.4	2.4	23.8	12.70	0.92	23.20
Reserve OB. Outside	70.9	2.7	12.6	6.73	1.04	35.45

In addition, the inside concentrations of O_3 were found to be much lower than the outside in all three museums. The lowest value was detected 1.6 μg/m^3 in the Reserve OB museum (Table 1). The highest concentrations of O_3 were found outside of the two museums with an average of 46.4 and 70.9 μg/m^3 Magritte and Reserve OB respectively. This might be a result of the continuous opening of the windows in the period of very high temperatures during the sampling period. These results can be also explained by the higher reactivity of ozone which also reflects rather its large deposition velocities. Meteorological parameters have an impact on ozone concentrations. Kgabi and Sehloho (2012) confirmed that there is a direct relation between ozone and temperature and wind; while, an inverse relation between ozone and relative humidity. The concentration values of all analyzed gases were higher outside the building than in the galleries. It may be argued to the fact that part of the gaseous components could have reacted with the art objects, walls, furniture, etc. or with other gases and aerosol particles present in the air and a limited air exchange. In the city main sources of ozone are traffic activities, industrial area and businesses (Kgabi, and Sehloho, 2012).

The most distinct difference between indoor and outdoor concentrations was noticed in the case of O_3 (Fig. 3). This observation applies to all sampling period and is probably due to the higher reactivity of this compound compared to the others.

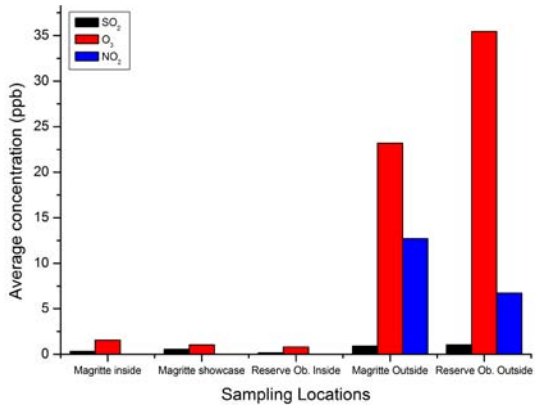
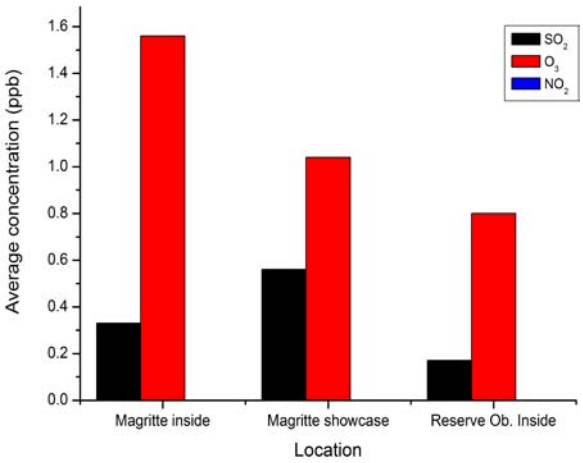
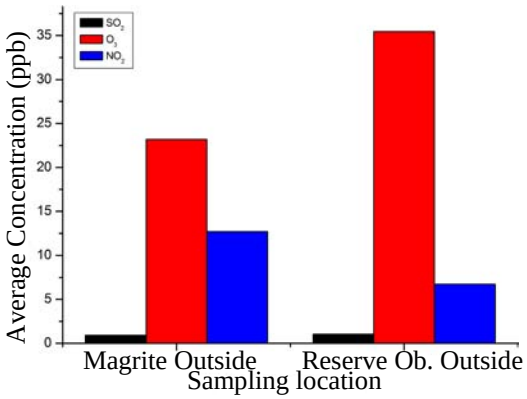


Fig. 2: Average Concentration of SO_2, NO_2 and O_3 in Museum of Fine Arts.



(a)



(b)

Fig. 3: Average Concentration of SO_2, NO_2 and O_3 inside (a) and outside (b) Magritte and Reserve OB.

In general, the levels of NO_2, SO_2 and O_3 inside the two museums are lower when compared to that others as indicated in Fig. 4. However, recommended levels of gaseous pollutants in museums are SO_2< 2 ppb, NO_2< 10 ppb and O_3< 5 ppb (Brimblecombe, 1990). Our findings showed that the level of these gaseous pollutants were below the recommended limits. This may presumably due to centrally heating, ventilation and air conditioning (HVAC) systems used in the museum, which play a significant role for protecting the museum's environment (Magritte and Reserve OB).

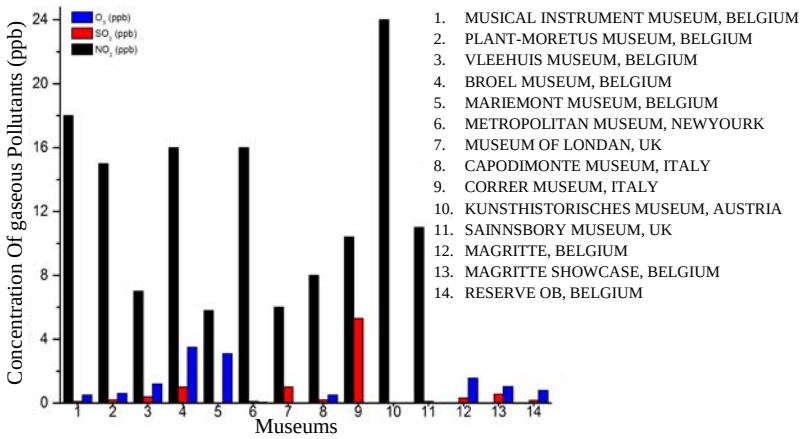


Fig. 4: Gaseous pollutants in MFAs compared with different museums.

IV. Conclusion

Passive diffusion tubes were used for sampling of NO_2, SO_2 and O_3. The results show that the concentration of the gaseous pollutants found in Magritte (NO_2 = <DL, SO_2= 0.8 µg/m^3 and O_3 = 3.1 µg/m^3) and Reserve OB (NO_2 = <DL, SO_2 = 0.4 µg/m^3 and O_3 = 1.6 µg/m^3) is below the recommended level (NO_2 = 19 µg/m^3, SO_2 = 5.2 µg/m^3 and O_3 = 10 µg/m^3). In the case of NO_2, the concentrations measured in inside Magritte and reserve OB and Magritte showcase were below the detection limit but the concentrations SO_2 and O_3were significantly high. In practice, SO_2 and O_3could have reacted with museum objects after inflowing from the outdoor environment, therefore their high indoor concentrations can be high worrying than less concentrations of nitrogen dioxide.

This implies that meteorological conditions i.e., wind, temperature, relative humidity and outside anthropogenic activities such as movement of vehicles and tourists had major influences on the concentrations of pollutants.

It may be argued that a museum, an exhibition space for objects with great cultural and historical value, is ideally considered to be free from internal sources of pollutants. The air pollution comes therefore primarily from outside and is transferred towards inside during the outdoor/indoor air exchange through cracks in walls or other slits in the building, opened windows, doors and ventilation systems. Outside anthropogenic activities such as movement of vehicles and tourists had major influences on the concentrations of pollutants in museums.

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