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# Indoor particulate matter in four Belgian heritage sites: case studies on the deposition of dark-colored and hygroscopic particles

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## Abstract

Atmospheric total suspended particulate (TSP) was passively sampled by means of deployed horizontal and vertical filters in various rooms of four Belgian cultural heritage buildings, installed with various heating/ventilation systems. Soiling/blackening and deposition of inorganic, water-soluble aerosol components were considered. The extent of soiling was determined by means of two independent methods: (1) in terms of the covering rate of the filters by optical reflection microscopy and (2) the reduction in lightness of the filters using the CIE L\*a\*b\* color space by spectrophotometry. A correlation was found between both methods. The inorganic composition of the deposited water-soluble TSP was quantified by means of ion chromatography. Compared to controlled environments, uncontrolled environments showed a higher water-soluble aerosol fraction in the total deposited mass. On horizontal surfaces, higher chloride deposition was observed compared to vertical surfaces.

**Keywords:** Indoor air quality, particulate matter, deposition, museum, preventive conservation

## 1. Introduction

The primary concern of airborne particles (particulate matter, PM) in heritage environments is often their ability to soil or blacken surfaces, altering the aesthetic appearance of the object (Ford and Adams 1999; Adams and Ford 2001; Yoon and Brimblecombe 2001; Adams et al. 2002; Brimblecombe and Grossi 2005; Lloyd et al. 2007; Urosevic et al. 2012). Once deposited, PM can also accelerate deterioration processes on underlying surfaces (Tétreault 2003). Particles can, for example, act as catalysts in many degradation processes, such as the iron-catalyzed oxidation of S(IV) to S(VI), e.g., conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> (Saxena and Seigneur 1987; Elfving et al. 1994). They also transport harmful substances indoors, which can deposit onto various surfaces, such as walls, carpets, and artworks. Soot particles, for example, adsorb reactive gases from the ambient air. Once the soot particles are deposited, they bring and release the harmful adsorbed compounds in close proximity to the (artwork) surfaces (Van Grieken et al. 2000; Yoon and Brimblecombe 2001). Moreover, all particles, even inert ones, act as condensation nuclei, via absorbing humidity from air, thus increasing their water content (Brimblecombe et al. 2009). However, for insoluble particles such as silica, the water uptake is only significant in the extreme conditions of a supersaturated vapor. Water-soluble particles possess a moisture absorption capacity and show already considerable water uptake under moderate conditions (Hinds 1982). Such hygroscopic particles attract water on the deposition surface, accelerating any degradation process favored in humid conditions such as the oxidative degradation of paper and textile (Feller 1994; Havlíková et al. 2009), corrosion of metals, discoloration of pigments (Saunders and Kirby 2004), etc. The inorganic, water-soluble PM-fraction principally consists of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, mainly originating from sea salts (e.g., NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>), secondary inorganic aerosols (e.g., NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), and mineral dust (e.g., (Ca,Mg)CO<sub>3</sub>, CaSO<sub>4</sub>) (Colbeck 1995).

In the current study, two aspects, the blackening of surfaces by total suspended particulates (TSP) as well as the deposition of inorganic, water-soluble aerosol components, have been studied in various indoor heritage locations in Belgium, *i.e.*, three museums and a church. Focus was on the inorganic aerosol fractions, due to their characteristic hygroscopic properties. Such particles not only do facilitate (degradation) reactions at their deposition surfaces, they also promote particle growth when the particles are suspended in the air, thus increasing their settling velocity. Moreover, when a surface is soiled with a hygroscopic contaminant, the liquid film easily adheres other particles that touch the surface, thus increasing the rate of particle deposition (Camuffo 1998). Constituents of PM deposited on horizontally and

vertically oriented surfaces were compared, as well as the effects of the absence or presence of a central climate system controlling the indoor air.

Once the deposited (water-soluble) particles are identified, further experiments could be performed to study their interactions with the heritage surfaces on which they deposit. Such research could be performed by monitoring the degradation under real conditions (e.g., Urosevic et al. 2012), or by studying mocked-up samples that are aged in laboratory conditions (e.g., accelerated aging experiments). Such accelerated aging experiments are commonly used in the study of heritage material degradation (Feller 1994). The aging experiments study the influence of environmental parameters such as relative humidity, temperature, light and gaseous air pollutants. Airborne (salt) particles are not yet considered. However, in other research areas, examples exist of the use of climate chambers to simulate material interactions with airborne (salt) particles (e.g., Frankenthal et al. 1993, Litvak et al. 2000). Recently, Anaf et al. (2014) developed an electrochemical monitoring method to study the influence of different airborne salts on their deleterious effects towards pigment degradation.

## **2. Experimental**

### **2.1. Instrumentation, material and methods**

Particles were passively collected simultaneously on Teflon, silicon and sticky labels, positioned vertically as well as upward-facing horizontally. For each location, the substrates were mounted on a Plexiglas support of 20 by 21 cm. Sampling started in September 2012 and lasted for 250 to 300 days.

In order to study the coverage rate of dark-colored and black particles, a collection substrate was made by sticking rectangular white adhesive labels on cardboard frames, creating a '*sticky sampler*' with a sticky surface area of 150 mm<sup>2</sup> (Yoon and Brimblecombe 2001). After eight to ten months of sampling, the vertically oriented *sticky samplers* were analyzed by means of spectrophotometry to study the change in lightness L\* (model AvaSpec-2048 L, Avantes BV, Apeldoorn, The Netherlands) and optical reflection microscopy (model BX41, Olympus, Hamburg, Germany). For the latter, microscopic images were manually converted to a binary format, and subjected to automated image analysis with the 'SigmaScan Pro' software (Systat Software, San Jose, CA, USA). Particles were counted and particle areas were calculated. Only dark-colored and black particles were taken into account. Fibers were not incorporated, since they are not expected to deposit on vertically oriented non-adhesive surfaces due to their large size (Yoon and Brimblecombe 2000).

Teflon filters with 37 mm diameter (Pall, East Hills, NY, USA) were applied for gravimetric (model MX5 microbalance, Mettler Toledo, Columbus, OH, USA) and ion chromatographic (IC, model Dionex DC-120, Dionex, Sunnyvale, CA, USA) analyses, in order to determine the mass and water-soluble fraction of the deposited particles per cm<sup>2</sup>, respectively. For the IC-analysis, the filters were ultrasonically leached in 5 mL of deionized water. After filtering up to 0.2 µm, the solutes were analyzed with IC, with an IonPAC AS14 and CS16 column for the analysis of anions and cations, respectively. The eluents used, were a buffer solution of 1 mM NaHCO<sub>3</sub> and 3.5 mM Na<sub>2</sub>CO<sub>3</sub> for anion analysis, and a 0.017 M aqueous H<sub>2</sub>SO<sub>4</sub> solution for cation analysis. For each sample, 20 µL of analyte was injected and loaded into the column with an eluent flow rate of 1 mL min<sup>-1</sup> (anions) or 1.2 mL min<sup>-1</sup> (cations). Teflon filters are advantageous for this type of sampling and analyses, since they are chemical resistant with ignorable electrostatic forces (Ferm et al. 2006). Therefore, collection of suspended material takes place mostly via gravitational settling and/or adsorption onto these surfaces. Silicon wafers were mounted to sample individual particles, subjected to scanning electron microscopic analysis (model Quanta 250 FEG, FEI, Hillsboro, Oregon, USA).

## 2.2. Description of the study sites

Three Belgian museums (Mu.ZEE, MAS|*Museum Aan de Stroom*, and the Rubens House) and the Saint-Augustine church housing a concert hall were chosen as study sites, representing various atmospheres (sea side/urban) and/or the controlled indoor climate (heating, ventilation and air conditioning (HVAC)/uncontrolled atmosphere). The obtained data were compared with previously published results of deposition experiments in the *Museo Nacional do Azulejo* (National Tile Museum) in Lisbon (Anaf et al. 2013).

The Mu.ZEE is located in Ostend at the coast of the Belgian North Sea. The museum, mostly displaying Belgian art dating from 1850 to present days, is housed in a modernist building characterized by an imposing glazed facade. For sampling purposes, a vertical sampling platform was attached to the wall in the entrance hall. Additional horizontal and vertical panels were positioned on the first floor. On both locations, the deposition plates were mounted around 2.5-3 m above the floor level. During exhibition movement/replacement, the sampling platforms were covered with Plexiglas plates to prevent the influence of extreme conditions in terms of air pollution (*e.g.*, artefacts from exceptional events of indoor dust re-suspension). The museum climate is controlled with a central HVAC-system with particulate air filtration.

The MAS is a museum, built between 2007 and 2011, located in the north of Antwerp next to the river Scheldt. It is build-up as a cochlea: in the outer shell, anyone can visit the tall building, with – as a highlight – the magnificent viewpoint on the roof. The inner building shell

consists of the museum rooms, divided on seven floors. The test setup was placed within the permanent exhibition, called “World Port. On trade and shipping” (6<sup>th</sup> floor). One horizontal and one vertical sampling plate were installed next to each other between displayed ship models around 1 m above the ground level. The indoor air is controlled by an HVAC system equipped with a particulate glass fiber air filter of class F7 (average efficiency  $Em$  for 0.4  $\mu\text{m}$  particles between 80 % and 90 %, according to EN779:2002). These filters are renewed 3 to 4 times a year. Temperature and relative humidity are set at 21°C and  $50 \pm 10$  %, respectively.

The Rubens House, a two-floor high building, located in the center of Antwerp, is the house of one of the most famous paint artists in the world. The building is divided into a living area and a workshop area, connected by an impressive portico. Sampling was performed in both parts of the building, on the ground floor. Within the living area, the samples were installed in the semi-circular museum around 1 m above the floor level. In this part of the building, instead of the central climate system, heating is performed with the use of radiators in cold weather, and humidity control is made with (de)humidifiers. In the workshop area, the sampling panels were positioned in the large studio on top of a wooden tympanum around 2.5 m above the floor level (Fig. 1). Rubens painted most of his work in this room. In this part of the museum the indoor air is controlled by a central climate system with air filtration.

The 17<sup>th</sup> century Saint-Augustine church, recently being fully renovated, acts as a concert hall for the international music center ‘AMUZ’. The samples were positioned in the nave, just below some paintings (Fig. 1). On the left side, only a vertical panel was placed, while on the right side, one horizontal and one vertical panel were installed. The indoor climate is controlled by an HVAC system, effecting a 21°C temperature and 56 % relative humidity. A minimum of 15 % outdoor air is pumped through the installation, passing a particulate air filter of class F7 ( $80 \% \leq Em \leq 90 \%$ , EN779:2012). Filters are replaced annually. Due to the height of the sampling location (~6 m above the floor level), impact of visitors or the cleaning staff on the sampling was restricted. Limited air motion due to human action is expected due to the adjusting of the spotlights and electricity provision at this height.



*Fig. 1: Picture of the sampling locations in the St.-Augustine church and the Rubens House (workshop) in Antwerp. The red circles indicate the sampling locations.*

The *Museo Nacional do Azulejo* in Lisbon is housed in a historic cloister building. One sampling location was selected to be in the big ambulatory, enclosed with glass panes, while the other was in an exposition room inside the building. Local heating and ventilation takes place through several individual air conditioning systems installed in each room of the building. Detailed sampling conditions can be found elsewhere (Anaf et al. 2013).

### **3. Results and discussion**

#### **3.1. Gravimetric and morphologic analysis**

Gravimetric results of the filters show higher amounts of deposited PM mass on the horizontal filters compared to the vertical ones (Fig. 2a). Horizontal-to-vertical ratios vary between 1.5 (Tile Museum, inside) up to 7.7 (Rubens House, hemisphere). Fine particles (aerodynamic diameter < 2.5  $\mu\text{m}$ ) prevalently deposit due to Brownian diffusion (Seinfeld 1986), inducing similar deposition probabilities for horizontal as well as vertical surfaces. Coarse particles (aerodynamic diameter > 2.5  $\mu\text{m}$ ) mainly deposit by gravitational settling, which effect prevails on horizontally oriented surfaces. Part of the particles deposited on horizontal surfaces, such as textile fibers, are giant (>> 100  $\mu\text{m}$ ) and strictly do not adhere to the definition of PM. Such particles are generally of less reactive chemical composition than fine PM. However, small, often more reactive particles can agglomerate and form coarse, even giant particles (*e.g.*, fine PM on mineral particles, skin flakes, fibers) as illustrated in Fig. 2b. Thus, although particle size is related to the deposition mechanism and linked to the particle composition, the latter predominates when considering particle-induced material degradation.

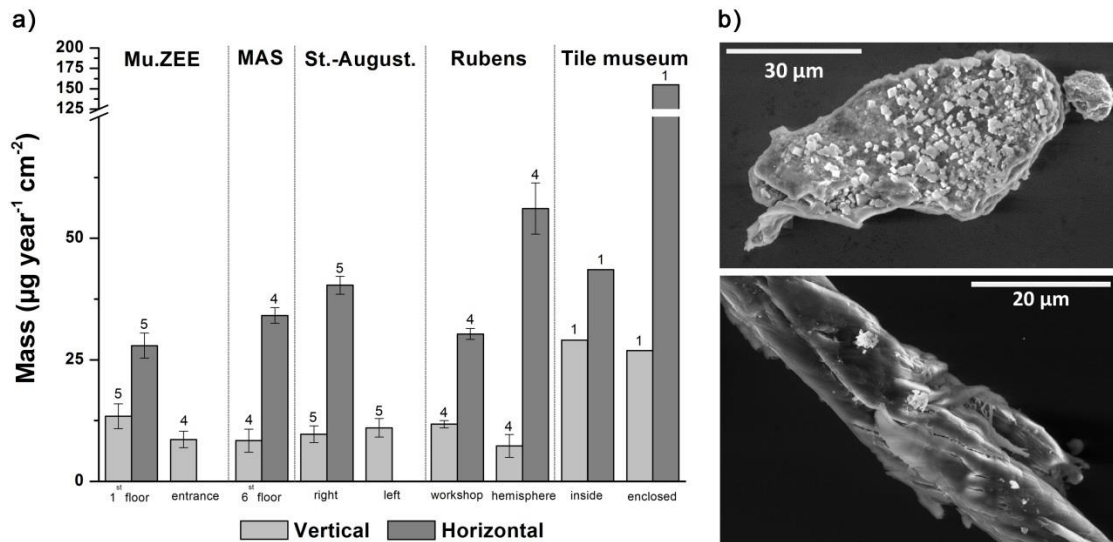


Fig. 2: (a) Total mass deposition on the filters in various indoor environments. Error bars denote the standard deviation, the values above the bars indicate the number of concurrent filters.

(b) Secondary electron images: small particles agglomerating onto bigger particles (top: carbonaceous particle with NaCl-rich particles; bottom: magnified picture of a fiber with different types of small particles).

### 3.2. Evaluation of soiling rates

The degree of blackening of each vertically positioned sticky sampler was analyzed first with optical microscopy to determine the covering rate, and then with spectrophotometry to define the decrease in lightness ( $L^*$ ) (Fig. 3a). Evaluation on the basis of the lightness value of the CIE  $L^*a^*b^*$  system are scarce (*e.g.*, Ferm et al. 2006)(Grossi et al. 2003; Urosevic et al. 2012) and assessment concerning a critical value whereby soiling becomes visible is not yet available in the literature. Nevertheless, the spectrophotometric method is less time-consuming compared to the microscopic determination of the covering area. Moreover, this method takes into account the different shades and possible transparency of particles. The results of both methods are strongly correlated ( $R = 0.95$ ) (Fig. 3b). The following relationship could be deduced: *covering area (%) = (98.2 -  $L^*$ )/107*. Nevertheless, due to the limited number of statistical data, additional experiments have to be performed to validate the accuracy of this equation. During data processing, the  $L^*$  value for a blank sticky sampler was not subtracted from the measured values, since longer exposures of the samplers under indoor conditions probably change slightly the color of the sticky label, *e.g.*, under the influence of (natural) light.



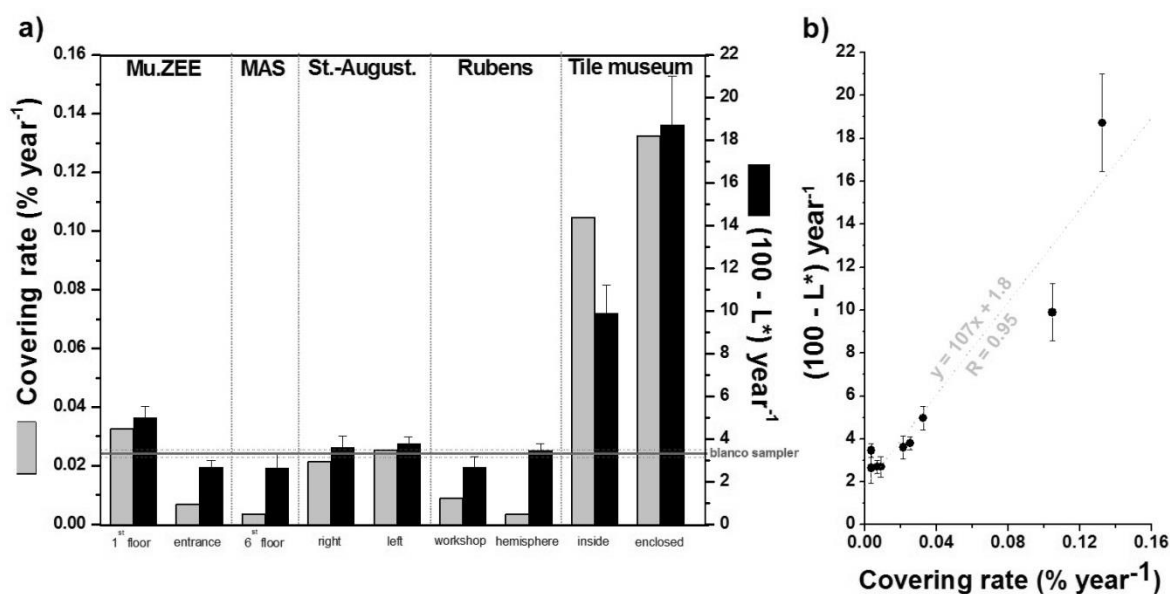


Fig. 3: Blackening of the vertically oriented sticky samplers, determined with microscopy and spectrophotometry in various heritage buildings (a). Linear relationship between the spectrophotometric and optical microscopy method (b).

Since visual damage is all about human perception, it is difficult to determine it accurately. Efforts have been made to set thresholds whereby soiling becomes visible for the naked eye. Literature values for critical covering areas range from 0.2 to 12 % (Carey 1959; Bellan et al. 2000). Other parameters such as particle size, distribution, particle color, etc. play an important role in the perception. According to Bellan et al. (2000), a surface covered with small black spots (diameter: 60-160  $\mu\text{m}$ ) is perceived as 'soiled' over 3.6 % coverage of its area when compared to a clean surface, exposed next to it. When considering this threshold for vertical surfaces, soiling would become visible already after less than 30 years in the Tile Museum (enclosed exposition hall), but more than 1000 years have to pass before vertical surfaces in the MAS would visually darken. Moreover, it was estimated by Yoon et al. (2000) that the fluxes determined with sticky samplers are approximately three times higher compared to non-adhesive substrates.

No clear correlation could be found between the degree of blackening and the total mass of deposition, nor between the degree of blackening and the presence of climate control. The former indeed depends on the local PM composition, whose fraction of dark-colored particles varies, depending on the percent contribution of soot and the types of minerals. The latter is related to the efficiency of particulate filters of climate controllers/HVAC, which hinder most of the coarse particles from entering the indoor environment.

### 3.3. Composition of water-soluble deposited matter

The total composition of the water-soluble inorganic fraction was defined by the sum of the determined ion concentrations with adjustment of the ion balance with either addition of  $\text{CO}_3^{2-}$  or  $\text{H}^+$ , as described earlier (Horemans et al. 2011; Anaf et al. 2013). The water-soluble fraction is only a limited fraction of the total deposition amount (Fig. 4). The non-identified PM mass consists of insoluble mineral particles, soot, low molecular weight organic materials, such as textile fibers, skin fragments, pollens, mold spores, etc.

In general, the indoor water-soluble fraction in total PM mass observed here (0.8 to 21.8 %), is smaller than that found for several outdoor TSP deposition sampling campaigns over Europe (MULTI-ASSESS project) where a fairly constant ratio of 24 % has been noted (Ferm et al. 2006). However, the indoor air composition is not only determined by the outdoor air, but also by internal sources, filtering, heating, climate control, human activity, etc. A difference between environments with and without climate control can be seen in terms of aerosol deposition. For uncontrolled environments (Tile Museum and Rubens House, hemisphere), the water-soluble fraction in total PM mass varied from 14.0 to 21.8 % with a 17.1 % average for horizontal surfaces, and from 4.1 to 10.2 % with a 7.3 % average for vertical surfaces. On the contrary, museum environments with climate control (Mu.ZEE, MAS and Rubens House, workshop) have a lower water-soluble content, ranging from 2.5 to 8.0 % (average = 4.7 %) and from 0.8 to 3.2 % (average = 2.1 %) for horizontal and vertical surfaces, respectively. This difference can be explained as follows. Climate control, including the filtering of the incoming outdoor air, results in a decrease in the concentration of coarse particles indoors. However, fine particles ( $< 1 \mu\text{m}$ ) are less efficiently retained on PM filters. On the other hand, visitors easily transport soil dust and textile fibers on their clothes/shoes into indoor environments (Yoon and Brimblecombe 2000; Worobiec et al. 2008). These particles highly contribute to the total mass, but generally contain relatively low amounts of water-soluble compounds, apart from NaCl, being used to deice the pavements/roads in wintertime (Worobiec et al. 2008). This explanation is supported by the values found in the St.-Augustine church, which was considered separately. Its values for water-soluble fraction in total PM mass are situated in between these of controlled and uncontrolled environments, with a water-soluble content of 12.6 % for horizontal surfaces and 4.1 % for vertical surfaces. Although the church has a climate control system, this is probably due to the height of the sampling location resulting in a lower visitors' contribution. For vertically oriented surfaces, the effect between a controlled and an uncontrolled environment is generally less manifested, since the deposited fraction mainly originates from fine particles, being less efficiently captured by air filtering, and also visitors increase mainly the abundance of coarse particles.

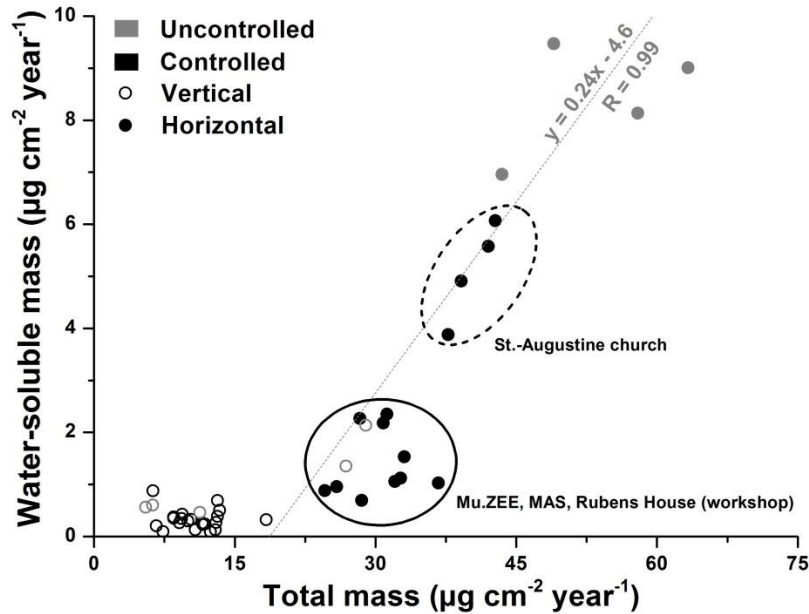


Fig. 4: Water-soluble inorganic PM mass as a function of the deposited total aerosol mass. Open and closed symbols: vertically and horizontally oriented filters, respectively; grey: uncontrolled climate; black: controlled climate.

Fig. 5 depicts the concentration of the main inorganic anions and cations of the deposited PM:  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . For horizontal surfaces, basically all anions are present, whereas for vertical surfaces nitrates mainly dominate. The Lisbon Museum is an exception with its high indoor chloride concentration. Sea salt related particles were segregated from the bulk. Based on the composition of typical sea water (Cotruvo 2005) and starting from the  $\text{Na}^+$  concentration, exclusively brought into the atmosphere by sea spray, the concentrations of all sea salt related ions were estimated ( $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$ ). Anion deficits were compensated by adding mainly  $\text{NO}_3^-$ , associated to aged sea salt. The method is described in detail elsewhere (Anaf et al. 2013). Subsequently, the sea salt related  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations were plotted against each other for the horizontally as well as vertically oriented substrates (Fig. 6). For the horizontal filters, the enclosed exposition hall of the Tile Museum is out of the range of the graph, containing around 5 times more  $\text{Cl}^-$  compared to the Rubens House hemisphere, though without detectable  $\text{NO}_3^-$  concentration. The vertical filter sampled inside the Tile Museum is also out of range, having around 2.5 times higher  $\text{Cl}^-$  concentration compared to the enclosed exposition hall in the same museum. No  $\text{NO}_3^-$  could be detected. A clear aerosol deposition trend is observed: on the horizontal filters, the detected  $\text{Cl}^-$  is mostly dominant, whereas on the vertical surfaces the  $\text{Cl}^-$  level for each Belgian location is lower than the detection limit of the IC method. The filters exposed in the Tile Museum in Lisbon, however, show fairly

high  $\text{Cl}^-$  deposition on the vertical filters. This is probably due to the high indoor/outdoor ventilation rate (Anaf et al. 2013), the close proximity of the Tile Museum to the Atlantic Ocean and the prevailing marine winds, often experiencing freshly formed sea salt. Likewise, the sea spray formed over the Ocean spends relatively short time in the continental air till deposition, which prevents considerable mixing, *e.g.*, its transformation/ageing to aerosol mixtures, the effect that is also observed for marine aerosols over Northern Belgium at increasing distance from the sea (Bencs et al. 2008; Horemans et al. 2009). On the other hand, Mu.ZEE at Ostende, also located close to the sea, differs from the Tile Museum by the presence of a climate control system, which efficiently reduces the sea salt influence indoors. The  $\text{Cl}^-/\text{NO}_3^-$  difference between horizontal and vertical deposition finds its origin in the particle size. Small sea salt particles have a high surface-to-volume ratio, thus they are aging more rapidly compared to larger ones (Laskin et al. 2003). Since deposition onto vertical surfaces is mainly due to Brownian diffusion of fine particles, vertical surfaces are much enriched with aged sea salts as compared to horizontal surfaces. Deposition experiments in five South Californian museums showed analogous results: deposition rates for  $\text{Cl}^-$  on vertical surfaces were below the detection limit, whereas on horizontal surfaces, high  $\text{Cl}^-$  deposition rates were noticed (Ligocki et al. 1990).

The  $\text{Mg}^{2+}$  deposition correlates well with the  $\text{Na}^+$  deposition ( $R=0.98$ ). Though, the  $\text{Mg}^{2+}$ -to- $\text{Na}^+$  molar ratio is in most cases higher than 0.12 (ranging from 0.13 to 2.78), the corresponding ionic ratio for typical sea water, indicating other  $\text{Mg}^{2+}$  sources such as minerals. Indeed,  $\text{Mg}^{2+}$  also has a good correlation with  $\text{Ca}^{2+}$  ( $R=0.96$ ) and the Ca-to-Na ratio is for all cases significantly larger (0.065 to 1.36) than the one for sea salt (0.039). Two filters from the St-Augustine church (horizontal filters) were excluded due to their outlying high  $\text{Mg}^{2+}$  content. The reason for this is not clear. The carbonate ( $\text{CO}_3^{2-}$ ) concentration was not determined in this study, but estimated from the cation-anion balance by filling up the anion deficit, as suggested in Anaf et al. (2013). The highest concentrations were observed for horizontally oriented surfaces, most pronounced for the uncontrolled environments. Since carbonate is expected to be present mainly as a mineral component in the larger particle fractions, its concentration on vertical surfaces is expected to be limited. Indeed, for almost all of the vertically oriented surfaces, a cation deficit could be demonstrated.

For nearly all locations,  $\text{NH}_4^+$  is below the detection limit. This may have several reasons. Ammonium-rich particles are mainly situated in the particle fraction with intermediate size (0.1-1  $\mu\text{m}$ ), for which the deposition rate is found to be minimal (Seinfeld 1986). Moreover,  $\text{NH}_4^+$ -rich particles, certainly nitrates and chlorides, are sensitive towards temperature and humidity gradients (Lunden et al. 2003; Hu et al. 2011). Thus, even once deposited, dissociation can occur.

Sulfates were detected in all samples, except for the vertical filters in the MAS. The origin of these sulfates can be products of secondary reactions of anthropogenic  $\text{SO}_2$ , (aged) sea salt,

and/or mineral related sulfates (*e.g.*, from gypsum). Strong correlation ( $R=0.94$ ) between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  was found for the horizontally oriented surfaces, on which main mineral deposition is expected. For the same reason, no significant correlation was observed for the vertical filters.

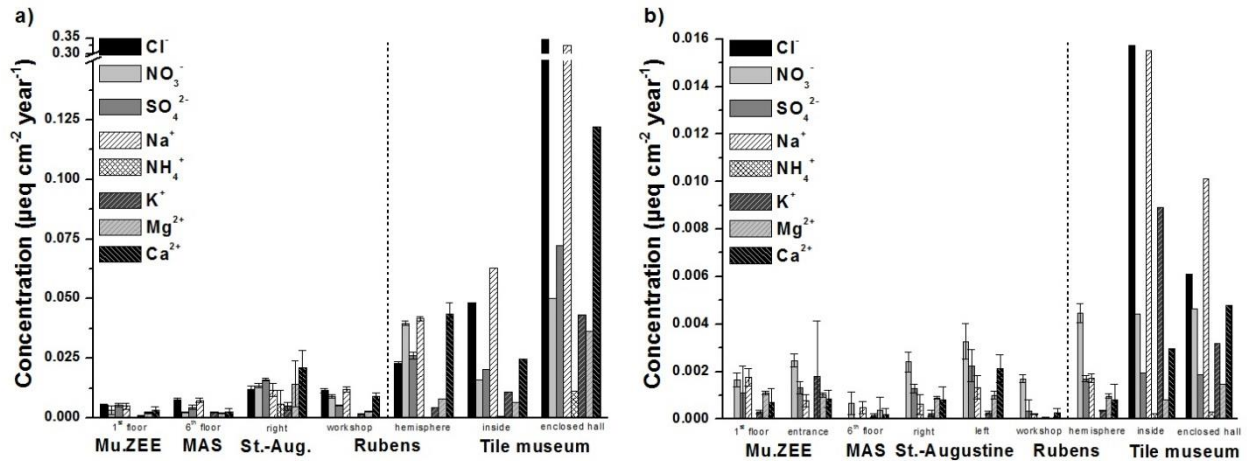


Fig. 5: Total anion and cation concentrations deposited on horizontal (a) and vertical (b) filters in heritage buildings with controlled and uncontrolled indoor climates, on left and right sides of the dashed lines, respectively.

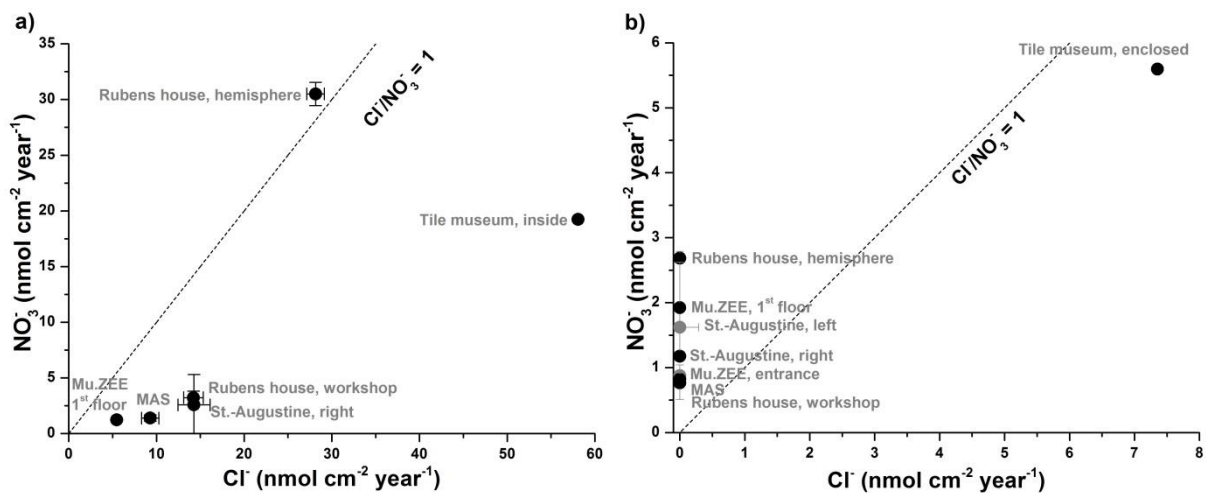


Fig. 6: Measured  $\text{Cl}^-$ -to- $\text{NO}_3^-$  ratios related to sea salt particles. Relationship of genuine ( $\text{NaCl}$ ) and aged ( $\text{NaNO}_3$ ) sea salts for horizontal (a) and vertical (b) filters. Horizontal filters are enriched in  $\text{Cl}^-$ , whereas vertical filters are enriched in  $\text{NO}_3^-$ . Averages of 3 to 4 filters with the standard deviation as error bars, except for the Tile Museum where only one filter has been sampled.

The hygroscopicity of the water-soluble particles highly depends on their chemical composition. Table 1 gives an overview of some inorganic salts occurring in atmospheric PM. At

the deliquescence relative humidity (DRH), a sudden phase transition from solid particle to a saturated solution droplet occurs. Above the DRH, the particle goes on absorbing water to maintain equilibrium with the water vapor content of the ambient air. During the reverse process, water desorbs from the particle by evaporation, which causes a gradual decrease in particle size and mass. Though, particles do not recrystallize at the DRH, but become highly supersaturated until the efflorescence or crystallization relative humidity (CRH) is reached. At this point, the excess of the absorbed water is abruptly expelled and the droplet crystallizes suddenly. This delayed recrystallization is called 'hysteresis' (Hinds 1982; Tang and Munkelwitz 1994; Wise et al. 2005). The DRH and CRH depend on several other factors too. Each high-purity inorganic salt has a characteristic DRH and CRH. However, aerosol particles are rarely pure salts, but mixtures, which have different deliquescence behavior. For instance, a mixed salt particle of NaCl and Na<sub>2</sub>SO<sub>4</sub> with a composition whereby both salts have reached their solubility limits, has a DRH of 74 %, while the corresponding nominally pure salt components have DRH's of 75.5 and 83.5 %, respectively (Tang and Munkelwitz 1994). Highly hygroscopic magnesium and potassium salts, present in sea salt particles, already show deliquescence behavior at RH 30-40 %, partly dissolving these multicomponent salt particles (Liu et al. 2008). Moreover, volatile organic compounds (VOCs), which are known to adsorb on atmospheric particles, often behave as a surfactant coating for inorganic aerosols, thus affecting their water uptake, as well as the deliquescence behavior (Bruzewicz et al. 2011). Likewise, the particle size influences the deliquescence behavior (Hu et al. 2010).

Recently, it was experimentally proven that crystalline nitrate particles only possess an abrupt deliquescence behavior in the first hydration cycle. Accordingly, after (sub)micron nitrate particles are deliquesced, they remain as supersaturated droplets (Liu et al. 2008; Hu et al. 2010; Hu et al. 2011). NO<sub>3</sub><sup>-</sup> is the anion that occurs with the highest average concentrations deposited on vertical surfaces. At 50 % RH, which is a common standard for museums, the water-to-solute molar ratio for NaNO<sub>3</sub> particles is already estimated to be 2 (Liu et al. 2008). This implies that, for example, a deposit of 0.2 µg cm<sup>-2</sup> NO<sub>3</sub><sup>-</sup> entails deposition of 0.12 µg cm<sup>-2</sup> H<sub>2</sub>O. At a slightly higher RH of 60 %, the ratio amounts already up to 3.

*Table 1: Deliquescence and crystallization relative humidity at 20-25 °C for some inorganic salts present in atmospheric aerosols.*

| <b>Salt</b> | <b>DRH (%)</b>       | <b>CRH<sup>(1)</sup> (%)</b> | <b>Reference(s)</b>  |
|-------------|----------------------|------------------------------|--|
| NaCl        | 75-78 <sup>(2)</sup> | 45-48                        | (Tang and Munkelwitz 1994; Chang and Lee 2002; Ebert et al. 2002; Wise et al. 2005; Hu et al. 2010; Möller 2010) |

|   |                      |                   |  |
|---|----------------------|-------------------|--|
| NaNO <sub>3</sub>                               | 76-80 <sup>(3)</sup> | -( <sup>4</sup> ) | (Tang and Munkelwitz 1994; Möller 2010)  |
| Na <sub>2</sub> SO <sub>4</sub>                 | 82-83 <sup>(5)</sup> | 58                | (Tang and Munkelwitz 1994; Chang and Lee 2002; Ebert et al. 2002; Hu et al. 2010)  |
| MgCl <sub>2</sub>                               | 33                   | -                 | (Möller 2010)  |
| NH <sub>4</sub> NO <sub>3</sub>                 | 61-62 <sup>(3)</sup> | < 20-30           | (Frankenthal et al. 1993; Chang and Lee 2002; Ebert et al. 2002; Möller 2010; Sanjurjo-Sánchez and Alves 2011)                       |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | 80-81                | 31-48             | (Frankenthal et al. 1993; Ebert et al. 2002; Lobnig et al. 2003; Wise et al. 2005; Ciobanu et al. 2010; Hu et al. 2010; Möller 2010) |
| NH <sub>4</sub> HSO <sub>4</sub>                | 30-40                | -                 | (Frankenthal et al. 1993; Möller 2010; Sanjurjo-Sánchez and Alves 2011)  |
| NH <sub>4</sub> Cl                              | 77                   | 45                | (Chang and Lee 2002; Sanjurjo-Sánchez and Alves 2011)  |
| CaCO <sub>3</sub>                               | 97                   | -                 | (Zhao et al. 2010)   |
| H <sub>2</sub> SO <sub>4</sub>                  | < 5                  | -                 | (Frankenthal et al. 1993)  |

<sup>(1)</sup> The given CRH is valid for PM in the atmosphere. Once deposited on a certain material, the metastable state of the supersaturated droplet can be shifted (Ebert et al. 2002).

<sup>(2)</sup> Ebert et al. (2002) demonstrated that NaCl already adsorbs a substantial amount of water before reaching the DRH. This adsorption becomes visible around an RH of 75 %. According to these researchers, the DRH is situated at a RH of around 78 %.

<sup>(3)</sup> Abrupt deliquescence behavior is only present in the first hydration cycle (Liu et al. 2008).

<sup>(4)</sup> Not found in literature.

<sup>(5)</sup> Metastable Na<sub>2</sub>SO<sub>4</sub> formed in aerosols.

#### 4. Conclusions

A microscopic and a spectrophotometric method for the evaluation of the soiling of surfaces due to particle deposition have been compared in various cultural heritage environments. The former is a well-known method used by several researchers and provides information about the covering area. The latter provides information on the reduction in lightness, based on the CIE L\*a\*b\* color space. Its use is rather scarce. In the current study, a correlation was found between the covering area and the reduction in lightness L\*. Main advantage of the spectrophotometric method is its fastness, which makes it useful as a first indication in a comparison of different locations.

Deposition studies in buildings displaying cultural heritage are useful to evaluate the degradation potential of airborne particles. Particle deposition depends on many factors such as the indoor air composition, climate, air turbulence, indoor-outdoor ventilation rates and the number of visitors. Nevertheless, the analysis of the inorganic water-soluble deposition indicated some interesting trends. (1) The water-soluble fraction in the total deposited PM mass was smaller in controlled environments. This was explained by a lower concentration of outdoor airborne particles entering the museum, and equal influence of (insoluble) coarse particles

brought in by visitors. This makes the latter relatively more important in controlled environments. (2) The water-soluble fraction differed between horizontal and vertical surfaces. Vertical surfaces were mainly characterized by the deposition of nitrates and sulfates, whereas on horizontal surfaces also important amounts of chlorides were present. The difference is due to surface-to-volume ratio of sea salt particles (NaCl). Small sea salt particles have a high surface-to-volume ratio. Therefore, they age more rapidly compared to larger ones, forming nitrates and sulfates. Since the deposition on vertical surfaces is characterized by small particles, they are enriched with aged sea salts (nitrates and sulfates) as compared to horizontal surfaces.

Is the control of indoor air of the buildings suitable?

Preventive conservation strategies.

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