



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



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## HIGHLIGHTS

- Deposition study of total suspended particulates in four Belgian heritage sites.
- Controlled vs. uncontrolled environments, horizontally vs. vertically oriented surfaces.
- Evaluation of surface blackening with microscopic and spectrophotometric method.
- Analysis of hygroscopic inorganic particles.
- Higher chloride deposition on horizontal compared to vertical surfaces.

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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 samplers by optical reflection microscopy and (2) the reduction in lightness of the samplers using the CIE L\*a\*b\* color space by spectrophotometry. A fairly good 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 increased water-soluble aerosol content of the total deposited mass. Higher chloride deposition was observed on horizontal surfaces, compared to vertical surfaces.

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## 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 (Adams and Ford, 2001; Adams et al., 2002; Brimblecombe and Grossi, 2005; Ford and Adams, 1999; Lloyd et al., 2007; Urosevic et al., 2012; Yoon and Brimblecombe, 2001). 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> (Elfving et al., 1994; Saxena and Seigneur, 1987). 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 can bring and release harmful adsorbed compounds in close proximity to artwork surfaces (Van Grieken et al., 2000; Yoon and Brimblecombe, 2001). Moreover, all suspended 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

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paper and textile (Feller, 1994; Havlínová et al., 2009), corrosion of metals, discoloration of pigments (Saunders and Kirby, 2004), etc. The inorganic, water-soluble PM-fraction consists principally of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , mainly originating from sea salts (e.g.,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ), secondary inorganic aerosols (e.g.,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ), and mineral dust (e.g.,  $(\text{Ca,Mg})\text{CO}_3$ ,  $\text{CaSO}_4$ ) (Colbeck, 1995).

In the current study, two aspects, the blackening of surfaces by total suspended particulates (TSP), as well as the deposition of inorganic aerosol fractions, have been studied in various indoor heritage locations in Belgium, i.e., three museums and a church. The work focuses on the water-soluble aerosol components, due to their characteristic hygroscopic properties. Such particles not only do facilitate (degradation) reactions at their deposition surfaces, but 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 are present. Such research could be performed by (1) monitoring the degradation of the surface under real conditions (e.g., Urosevic et al., 2012), or by (2) studying mocked-up samples aged in laboratory conditions (e.g., accelerated aging experiments). Accelerated aging experiments are commonly used in the study of heritage material degradation (Feller, 1994), to examine the influence of environmental parameters such as relative humidity (RH), air temperature ( $T_{\text{air}}$ ), light and gaseous air pollutants. Airborne (salt) particles have not yet been considered. However, in other research areas, examples exist on the use of climate chambers to simulate material interactions with deposited (salt) particles (e.g., Frankenthal et al., 1993; Litvak et al., 2000). Recently, Anaf et al. (2014) developed an alternative laboratory method based on electrochemical principles to monitor the influence of different airborne salts and their deleterious effects towards pigment degradation.

## 2. Experimental

### 2.1. Instrumentation, material and methods

The TSP was passively collected simultaneously on Teflon, silicon substrates and sticky labels, positioned vertically as well as upward-facing horizontally. For each location, the substrates were mounted on a Plexiglas support of 20 cm by 21 cm. The sampling campaign 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 both 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) to determine the covering rate. 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, 2000b).

All the applied chemicals and materials were of analytical grade or better. Teflon filters with 37 mm diameter (Pall, East Hills, NY, USA) were subjected to 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, first the filters were leached in 5 ml of deionized water for 15 min using a Model Branson 2210 ultrasonic bath (Branson, Danbury, CT, USA). After filtering the leachate through a 0.22 µm Millex-GV syringe driven filter unit (Millipore, Carrigtwohill, Co. Cork, Ireland), the solution was analyzed by IC, using Dionex IonPAC AS14 and CS16 columns for the analysis of anions and cations, respectively. The eluents were a buffer solution of 1 mmol l<sup>-1</sup>  $\text{NaHCO}_3$  and 3.5 mmol l<sup>-1</sup>  $\text{Na}_2\text{CO}_3$  for anion analysis, and a 17 mmol l<sup>-1</sup> aqueous  $\text{H}_2\text{SO}_4$  solution for cation analysis. A 20 µl aliquot of each sample/standard solution was dispensed onto the IC columns, working with an eluent flow rate of 1 ml min<sup>-1</sup> (anions) or 1.2 ml min<sup>-1</sup> (cations). For suppressing the conductivity of the eluent, Dionex ASRS-ULTRA and CSRS-ULTRA suppression units were applied during the anionic and cationic analyses, respectively. The calibration was performed against two sets of standard solutions. The IC limits of detection (LODs) for  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , were found to be 0.004, 0.010, 0.008, 0.017, 0.008, 0.117, 0.103, and 0.074 µg m<sup>-3</sup> respectively. 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, which were subjected to scanning electron microscopic analyses (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., artifacts from exceptional events of indoor dust re-suspension. The museum climate is controlled by a central HVAC-system equipped 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 into seven floors. The test setup was placed on the 6th floor within the permanent exhibition, called "World Port. On trade and shipping". One horizontal and one vertical sampling plate were installed next to each other between displayed ship models around 1 m above the floor level. The indoor air quality and climate is controlled by an HVAC system equipped with a particulate glass fiber air filter of class F7 (average efficiency ( $Em$ ) for 0.4 µm particles between 80% and 90%, according to EN779:2002). These filters are renewed 3 to 4 times a year.  $T_{\text{air}}$  and RH are set at 21 °C and 50 ± 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



**Fig. 1.** Picture of the sampling locations in the St.-Augustine church (left) and the workshop section of the Rubens House (right) in Antwerp. The red circles indicate the sampling locations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 fitted also with air filtration.

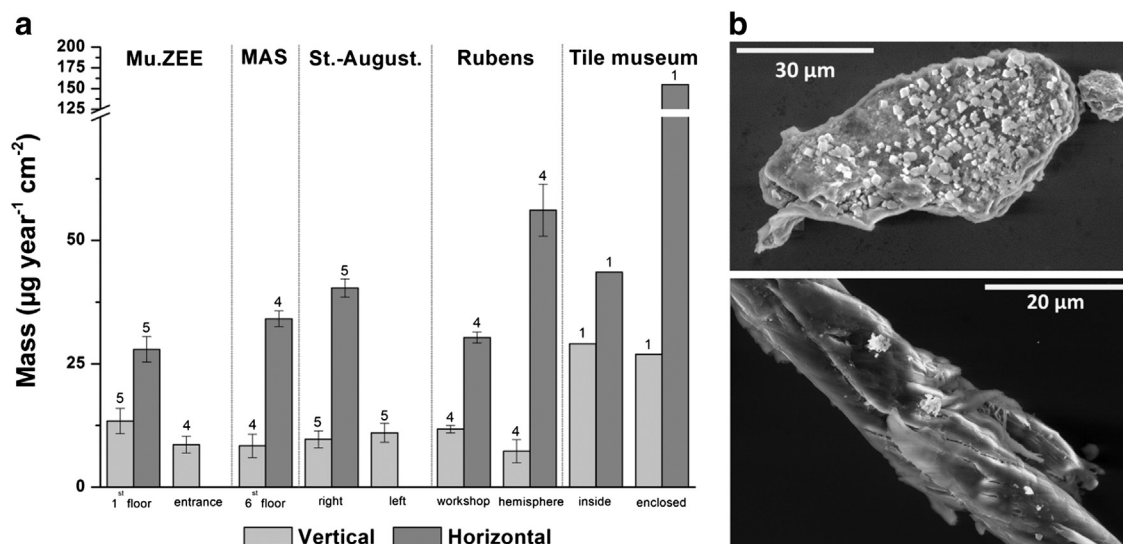
The 17th century Saint-Augustine church, recently being fully renovated, acts as a concert hall for the international music center 'AMUZ'. The samples were positioned in the nave, just below some paintings (Fig. 1). On the left side, only a vertical panel was placed, while on the right side, one horizontal and one vertical panel were installed. The indoor climate is controlled by an HVAC system, set to maintain a  $T_{\text{air}}$  of 21 °C and 56% RH. 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.

The *Museo Nacional do Azulejo* in Lisbon is housed in a historic cloister building. One sampling location was selected to be in the large 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. Sampling conditions can be found in detail 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) and 7.7 (Rubens House, hemisphere). Fine particles (aerodynamic diameter ( $AD$ )  $< 2.5 \mu\text{m}$ ) prevalently deposit due to Brownian diffusion (Seinfeld, 1986b), inducing similar deposition probabilities for horizontal as well as vertical surfaces. Coarse particles ( $AD > 2.5 \mu\text{m}$ ) are mainly deposited 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, fine, often more reactive particles can agglomerate and form coarse, even giant particles,



**Fig. 2.** Total mass deposition on the filters in various indoor environments (a). Error bars denote the standard deviation, the values above the bars indicate the number of concurrently sampled filters. Secondary electron images: small particles agglomerating onto larger/coarser particles (b). (Top: carbonaceous particle with NaCl-rich particles; bottom: magnified picture of a fiber with different types of small particles).



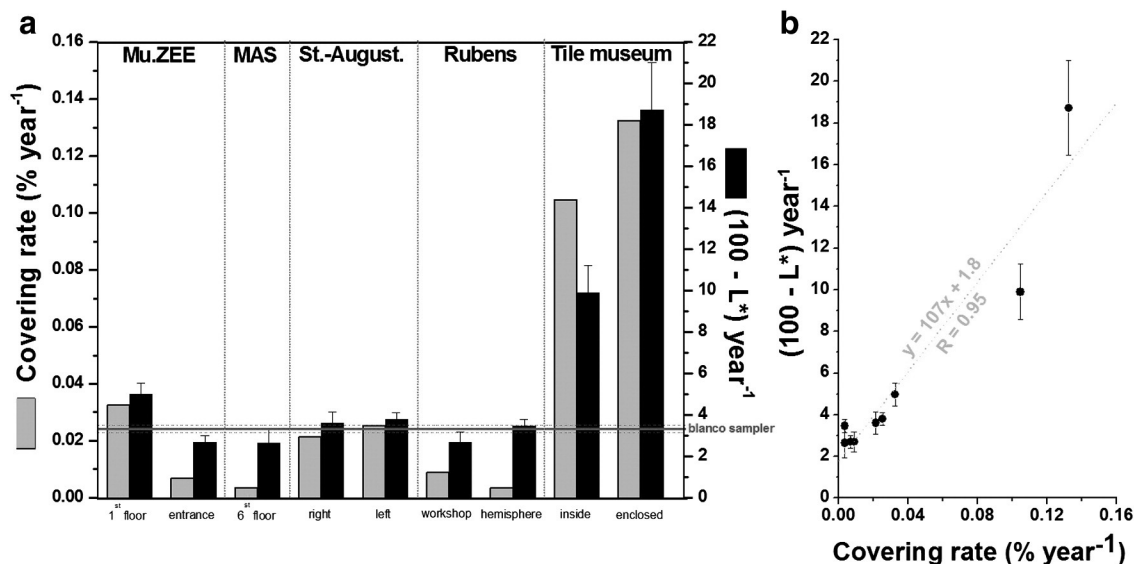


Fig. 3. Blackening of the vertically oriented sticky samplers determined with microscopy and spectrophotometry in various heritage buildings (a). Linear relationship between the results of the spectrophotometric and optical microscopy methods for the five studied buildings (b).

e.g., fine PM on mineral particles, skin flakes, and/or fibers, as illustrated in Fig. 2b. Thus, particle size and growth rate are related to the deposition mechanism and linked to the particle composition, but the latter predominates when considering particle-induced material degradation.

### 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 is scarce (e.g., Ferm et al., 2006; Grossi et al., 2003; Urosevic et al., 2012). However, 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. An assessment concerning a critical value whereby soiling becomes visible was proposed by Lanting (1986), using the reflectance as an estimate for the percentage of area covered by particles. However, the equation requires the reflectance of the settled particles, which is often assumed to be 30% for simplicity (Grossi et al., 2003; Urosevic et al., 2012).

The results of the optical microscopic and spectrophotometric methods are strongly correlated ( $R = 0.95$ ) (Fig. 3b). The following relationship could be deduced: covering area (%) =  $(98.2 - L^*) / 107$ . During data processing, the  $L^*$  value obtained for a blank sticky sampler was not subtracted from the  $L^*$  values determined for samples, since longer exposures of the samplers under indoor conditions probably change slightly the color of the sticky label (blank), e.g., under the influence of natural light, which could lead to inaccuracy in the determination of the  $L^*$  values.

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% (Bellan et al., 2000; Carey, 1959). 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 and Brimblecombe (2000b) that the TSP deposition 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 of the deposited matter 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 (Anaf et al., 2013; Horemans et al., 2011).

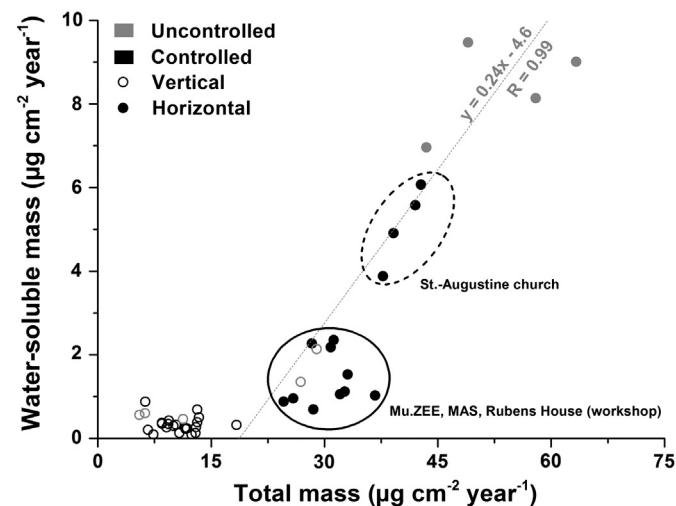


Fig. 4. Water-soluble inorganic PM mass as a function of the deposited total aerosol mass. Open and closed symbols: vertically and horizontally oriented filters, respectively; gray: uncontrolled climate; black: controlled climate.

Water-soluble inorganic species appear to be 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 inorganic 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 (e.g., MULTI-ASSESS project), where a fairly constant ratio of 24% has been reported (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 considerable difference between environments with and without climate control can be seen in terms of aerosol deposition. For uncontrolled environments (i.e., Tile Museum and hemisphere section of the Rubens House), 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 (i.e., Mu.ZEE, MAS, and the workshop of the Rubens House) have a lower water-soluble content of the deposited material, 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. Filtering of the incoming outdoor air results in a decrease in the indoor concentrations of coarse particles. 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 (Worobiec et al., 2008; Yoon and Brimblecombe, 2000a). These particles significantly contribute to the total mass, but generally contain relatively low amounts of water-soluble compounds, apart from NaCl, being used to deice pavements and roads in wintertime (Worobiec et al., 2008). This explanation is supported by the percentages for the water-soluble inorganic fraction of the total PM mass found in the St.-Augustine church, i.e., a water-soluble content of 12.6% for horizontal surfaces and 4.1% for vertical surfaces. These values lay in between those of the controlled and the uncontrolled environments. Although the church has a climate control system, the contribution/transport of water-soluble aerosols by visitors is expected to be low, due to the quite large height of the sampling location (~6 m above the floor level). For vertically oriented surfaces, the effect between a controlled and an uncontrolled environment is generally less manifested, since the deposited aerosol fraction mainly originates from fine particles, which are less efficiently captured by air filtering. Moreover, visitors increase mainly the abundance of coarse particles indoors.

Fig. 5 depicts the site-specific indoor concentrations 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 nitrate salts dominate mainly. However, the Lisbon Museum is an exception with its high indoor chloride concentration. Sea salt related particles are segregated from the rest of the bulk PM. 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 horizontal filters, the values from the enclosed exposition hall of the Tile Museum are well over the usual concentration range, with around 5 times higher  $\text{Cl}^-$  levels compared to the Rubens House (hemisphere section), though without detectable  $\text{NO}_3^-$  concentration. The vertical filter sampled inside the Tile Museum lays also well above the generally observed concentration range, having around 2.5 times higher  $\text{Cl}^-$  concentration compared to the enclosed exposition hall in the same museum. There, 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 LOD of the presently applied 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 connection with continental air till deposition, which prevents considerable mixing of air masses, e.g., its transformation/aging 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, indoor conditions in the Mu.ZEE at Ostende, also located close to the sea, differ from that of the Tile Museum by the presence of a climate control system, which efficiently reduces the influence of sea salt 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

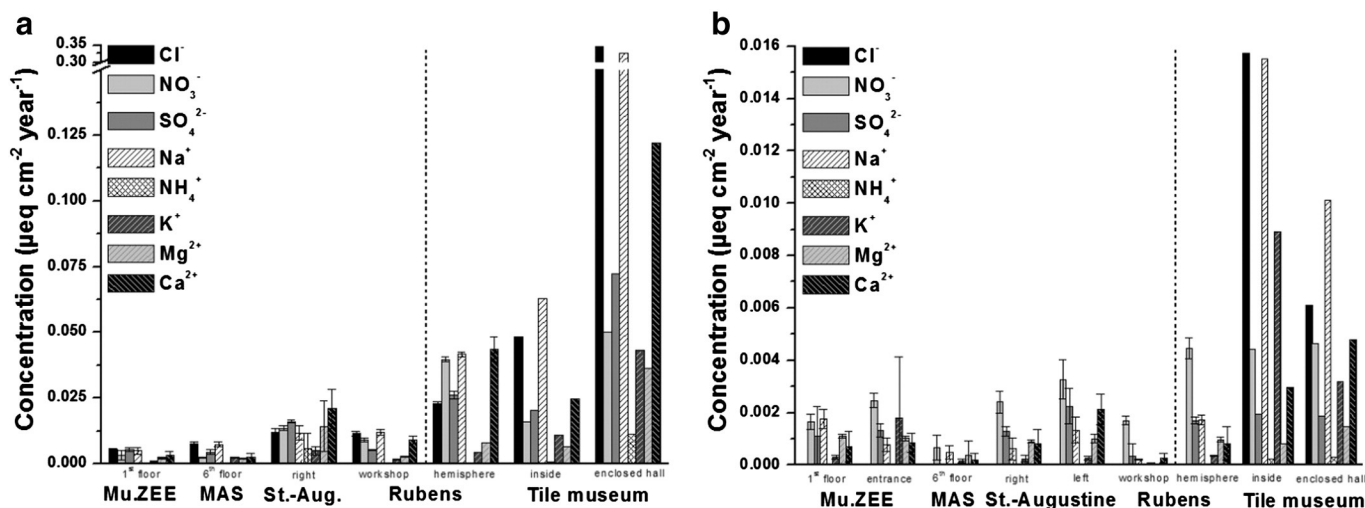
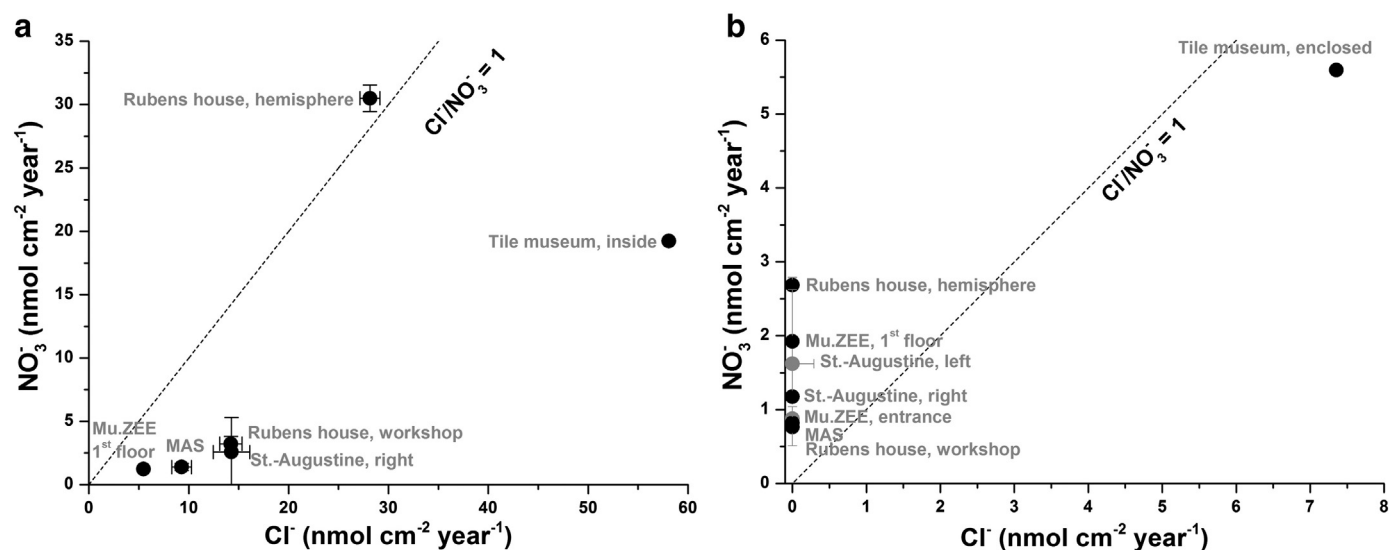


Fig. 5. Total anion and cation concentrations deposited on horizontal (a) and vertical (b) filters in heritage buildings with controlled and uncontrolled indoor climates, on the left and right sides of the dashed lines, respectively.



**Fig. 6.** Experimentally determined  $\text{Cl}^-$ -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.

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 LOD, whereas on horizontal surfaces, high  $\text{Cl}^-$  deposition rates were noticed (Ligocki et al., 1990).

The degree of  $\text{Mg}^{2+}$  deposition correlates well with that of  $\text{Na}^+$  ( $R = 0.98$ ). 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-to-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 LOD of the applied IC method. This may have several reasons. Ammonium-rich particles are mainly present in the particle fraction with fine and intermediate size (0.1–1  $\mu\text{m}$ ), for which the deposition rate is found to be minimal (Seinfeld, 1986a). Moreover,  $\text{NH}_4^+$ -rich particles, certainly nitrates and chlorides, are sensitive towards temperature and humidity gradients (Hu et al., 2011; Lunden et al., 2003). Thus, even once deposited, dissociation can occur.

Sulfates were detected in each sample, except for the vertical filters in the MAS. 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 the main mineral deposition is expected. For the same reason, no significant correlation was observed for the vertical filters.

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

**Table 1**

Deliquescence and crystallization relative humidity at 20–25 °C for some inorganic salts present in atmospheric aerosols.

Salt	DRH (%)	CRH <sup>a</sup> (%)	Reference(s)
NaCl	75–78 <sup>b</sup>	45–48	(Chang and Lee, 2002; Ebert et al., 2002; Hu et al., 2010; Möller, 2010; Tang and Munkelwitz, 1994; Wise et al., 2005)
NaNO <sub>3</sub>	76–80 <sup>c</sup>	– <sup>d</sup>	(Möller, 2010; Tang and Munkelwitz, 1994)
Na <sub>2</sub> SO <sub>4</sub>	82–83 <sup>e</sup>	58	(Chang and Lee, 2002; Ebert et al., 2002; Hu et al., 2010; Tang and Munkelwitz, 1994)
MgCl <sub>2</sub>	33	–	(Möller, 2010)
NH <sub>4</sub> NO <sub>3</sub>	61–62 <sup>c</sup>	<20–30	(Chang and Lee, 2002; Ebert et al., 2002; Frankenthal et al., 1993; Möller, 2010; Sanjurjo-Sánchez and Alves, 2011)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	80–81	31–48	(Ciobanu et al., 2010; Ebert et al., 2002; Frankenthal et al., 1993; Hu et al., 2010; Lobnig et al., 2003; Möller, 2010; Wise et al., 2005)
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>a</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>b</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>c</sup> Abrupt deliquescence behavior is only present in the first hydration cycle (Liu et al., 2008).

<sup>d</sup> Not found in literature.

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

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. However, 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 behaviors. 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 compounds, present in sea salt particles, already show deliquescence behavior at 30–40% RH, 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 (Hu et al., 2011; Hu et al., 2010; Liu et al., 2008). 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.

#### 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, since it delivers 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 for indoor environments. In the current study, a correlation was found between the covering area and the reduction in lightness L\*. The 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 items are useful to evaluate the degradation potential of airborne particles. Particle deposition depends on many factors such as the indoor air composition, indoor climate, air turbulence, indoor–outdoor ventilation rates and the number of visitors. Nevertheless, the chemical analysis of the inorganic water-soluble deposition of suspended particulate matter indicates some interesting trends: (1) The water-soluble fraction in the total deposited PM mass is smaller in controlled environments. This can be 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, while on horizontal surfaces considerable amounts of chlorides were also present. The difference in deposition of Cl<sup>-</sup> on horizontal and vertical surfaces 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.

Regarding preventive conservation, PM-deposition on artworks has to be reduced as much as possible. The deposition/soiling rate depends on many factors, such as the airborne PM concentration, the PM size distribution, the roughness and orientation of the deposition surface, and the number of visitors. Indoor–outdoor ventilation rates and central climate systems influence the indoor airborne PM concentration and its size distribution. The arrangement of the heritage objects and their protection/shielding influences the deposition and the visitors' influence. Objects should not be placed near doors, windows or mechanical ventilation registers, since local air velocities are usually higher in such locations (Nazaroff and Cass, 1991; Nazaroff et al., 1993). Moreover, control of the visitors flow and the distance between a visitor and an object can reduce the extent of deposition (Yoon and Brimblecombe, 2001).

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