Science of the Total Environment 506–507 (2015) 361–368

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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.

ARTICLE INFO

Article history:
Received 20 August 2014
Received in revised form 5 November 2014
Accepted 5 November 2014
Available online 24 November 2014

Editor: Pavlos Kassomenos

Keywords:
Indoor air quality
Particulate matter
Deposition
Museum
Preventive conservation

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.

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_2 to H_2SO_4 (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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http://dx.doi.org/10.1016/j.scitotenv.2014.11.018
0048-9697/

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 Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, mainly originating from sea salts (e.g., NaCl, $NaNO_3$, Na_2SO_4), secondary inorganic aerosols (e.g., NH_4NO_3, $(NH_4)_2SO_4$), and mineral dust (e.g., $(Ca,Mg)CO_3$, $CaSO_4$) (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_{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^2 (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^2, respectively. For the IC-analysis, first the filters were leached in 5 ml of deionized water for 15 min using a Model Bransonic 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^{-1} $NaHCO_3$ and 3.5 mmol l^{-1} Na_2CO_3 for anion analysis, and a 17 mmol l^{-1} aqueous H_2SO_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^{-1} (anions) or 1.2 ml min^{-1} (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 Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and 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^{-3} 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_{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