Aerosol and Air Quality Research, 15: 1240–1250, 2015

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2014.07.0147

Characterization of Particulate Matter, Ions and OC/EC in a Museum in Shanghai, China

Guangli Xiu[1*], Xin Wu[1], Lina Wang[1], Yuanxiang Chen[1], Ying Yu[1], Fangyuan Xu[2], Laiming Wu[2]

[1] State Environmental Protection Key Laboratory of Risk Assessment and Control on Chemical Process, School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China
[2] Key Scientific Research Base of Museum Environment, State Administration for Cultural Heritage, Shanghai Museum, China

ABSTRACT

The size-fractionated particle number concentrations were monitored continuously in the different exhibition halls of an enclosed museum, in Shanghai. Particles in different size bins were collected to investigate the main chemical compositions. Results indicated that the mass concentrations of coarse particles, fine particles and ultrafine particles were in the range of 20.50–24.38 μg/m^3, 23.39–24.08 μg/m^3 and 16.02–17.48 μg/m^3, respectively. In addition, the activities of cleaning and walking can greatly elevate the number concentration of coarse particles by a factor of about 8–172 times. The decay rates of size-fractionated particle increased with the enlarging particle diameter, ranging from 2×10^{-5} to 8×10^{-4} s^{-1}. The mass concentration of SO_4^{2-}, NO_3^-, NH_4^+ peaked within the particle size range of 0.32–0.56 μm. The ratios of $[NO_3^-]/[SO_4^{2-}]$ on the National Day and working day were 0.08 and 0.12, respectively. Comparatively, the peak concentrations of Na^+, Cl^-, K^+, Mg^{2+} and Ca^{2+} occurred in the various size ranges. Total organic acids distributed uniformly, the acetate ion mass concentration was 1.238 μg/m^3, which was higher than both formate ion and oxalate ion concentrations. The concentrations of OC and EC showed similar trends on both the National Day and working day, and greater OC/EC ratios were found in the particles within the size range less than 0.1 μm and larger than 1 μm.

Keywords: Museum; Particulate matter; Number concentration; Water-soluble ions; Size distribution.

INTRODUCTION

In recent years, the characteristics of particulate matter and its environmental behavior have been identified as important factors for heritage preservation. Pollutants such as sulfur oxides, nitrogen oxides and organic acids which are carried by the particles can cause damage to the cultural relics, once these particles deposit onto the cultural relics (Gysels *et al.*, 2002). In addition, its potentials to serve as location for moisture condensation and adsorbent of gaseous pollutant are also serious (Godoi *et al.*, 2008). Greathouse and Wessel.(1954) pointed out that particles can cling with the corrosive atmospheric pollutants at very early time. Furthermore, the researches of the heritage preservation found that particles not only can mark on paper, cloth, stone carvings, etc., but also can speed up the damage through the surface reactions. Organic compounds or soot in the particle phase can deteriorate surface and behave as the medium for SO_2 capture. And the organic compounds together with the soot were capable of causing visual degradation by soiling the surface as well (Camuffo *et al.*, 2002; Spolnik *et al.*, 2004); Alkaline particles with the diameter less than 0.1 μm can change the color and luster of the pigment and animal glue; Sulfur particles can cause oil painting fading when they were oxidized to form into sulfuric acid. The oxidation process can also be accelerated by iron rich and manganese rich particles (Gysels *et al.*, 2002, 2004; Ammonium sulphate can induce paint cracking; Iron rich particles can catalytic with sulfur-containing compounds to form into sulfuric acid or sulfate to enhance the corrosion of the cultural relics (Thomson, 1965; Toishi and Kenjo, 1975; Brimblecombe, 1990; De Santis *et al.*, 1992).

European and American countries have conducted measurements of particulate matters inside enclosed museums in the 1990s. Nazaroff *et al.*(1990) investigated three museums in California, and they found that when particle size was less than 2 μm, the particle and its element carbon composition could cause great damage to the cultural relics in these museums. In China, the similar studies on museum environment mainly conducted in the Emperor Qin's Terra-Cotta Warriors and Horses Museum with an open situation (Cao *et al.*, 2005a). Morphological and elemental analyses of

* Corresponding author.
Tel.: 021-64251927; Fax: 021-64251927
E-mail address: xiugl@ecust.edu.cn

particles were performed with a scanning electron microscopy and an energy dispersive X-ray spectrometry (SEM/EDX) to observe their composition. The reaction between sulfur dioxide and pigment material or deposited particles was found through the crystals of calcium sulfur which were adjacent to the interconnected pits and cracks on the outer surface of pigment flack (Hu *et al.*, 2006). The influence of visitor numbers on the size distributions and particle types were also found in the Exhibition hall (Hu *et al.*, 2006, 2009, 2010).

In addition, the increasing of mass tourism can disturb the microclimatic significantly and thus elevate the indoor pollution via the fast particle transportation through tourists' movement. Visitors also can increase water vapor level, CO_2 concentration and the extent of heat indoors (Camuffo *et al.*, 1999; Camuffo *et al.*, 2001). The National Day is an important holiday in China, which lasted for seven days from October 1st to October 7th. The other days mentioned were defined as working day including weekend. Museums in Shanghai always attract large amount of visitors every year during this holiday. Aiming to study the characteristics of particulate matter in the enclosed museums, and to explore the impact of mass tourism on the particles, on-site measurements of particulate pollutant during the National day and the working days were conducted in a museum in Shanghai, China. The composition of the particles and size-fractionated particle number concentration in each display hall were also investigated. In addition, the particle decay rates with respect to various size bins were obtained.

METHODOLOGIES

On-Site Sampling

The experiment was conducted in a museum in Shanghai, China, which had 4 floors and 12 exhibition halls. The museum covers the area of 39, 200 m^2 in total, among of which the display area accounts for 12,000 m^2. The top of the lobby was sealed by the glass in the museum, so the sunshine can penetrate from the glass into the lobby of museum. The temperature and humidity were kept constant in the museum by an air-conditioning system, which were T = 20 ± 0.5°C, RH = 45 ± 2%, respectively. The air-conditioning system was switched on all the time every day. Prior to the sampling, all the equipments were calibrated using standard methodologies. The sampling locations (Table 1) were set on all floors. The sampling locations we chosen were far from the entrances, inside the exhibition halls. So it could minimize the factors that came from outside of the exhibition hall. The monitoring was initiated at 9:00 in the morning and completed till midnight. The entire sampling period continued from September 21, 2009 to October 24, 2009.

A NanoMoudi (Model 125A) was used to sample particles within different size intervals, which was located in the middle of the hall on the first floor, and it was 1.2 m high above the ground. This sampling was conducted from 9:00 in the morning to 14:30 in the afternoon. Quartz filters (φ 47 mm) and PTFE filters (d = 0.45 μm, φ 47 mm) were adopted for particle collections in this study. The monitoring of particle number concentration was performed using a laser particle counter (LASAIR II 310B) with a flow rate of 28.3 L/pm. Its cut sizes are 0.3, 0.5, 1.0, 3.0, 5.0, 10.0 μm, respectively.

Particle Decay Rate

Indoor particle concentration can be obtained according to the Eq. (1), expressed as follows (Koutrakis *et al.*, 1992; Chen *et al.*, 2000; Chen and Zhao, 2011):

$$\frac{dC_{in}}{dt} = PaC_{out} + (G/V) - (a+k)C_{in} \quad (1)$$

in which, C_{in} and C_{out} are the particle concentrations of indoors and outdoors, respectively. P is the penetration factor. a is the air exchange rate and k is the removal rate of particles. The value of (a + k) means the particle decay rate inside the museum in this study. G is the generating rate of particles inside the museum. V is the volume of the museum. All the parameters are the function of both time and particle size except the constants of V and a (Li and Chen, 2003).

The decay rates were investigated within the time period from the moment that the museum closed to the moment before the cleaning activities began. Therefore there were no indoor sources to impact on the calculation. The peak values of particle number concentrations in the museum in this study were much higher than the background particle number concentrations monitored outside. Hence we ignored the impact of outside particle on the calculations of decay rates. Under this circumstance, the Eq. (1) can be simplified into Eq. (2):

$$\ln(C_t) = -(a+k)t + \ln C_0 \quad (2)$$

Regarding to the above equation, the slope of the regression line was the decay rate discussed in this study.

Table 1. Sampling locations.

floor	Sampling locations
1	Lobby, Ancient Chinese Sculpture hall (SC), Ancient Chinese Bronze hall (BR), the first temporary exhibition hall (FT)
2	Ancient Chinese Ceramics hall (CE), the second temporary exhibition hall (ST)
3	Ancient Chinese Painting Gallery (PA), Chinese Calligraphy Archive (CA), Ancient Chinese Imperial Seal hall (SE)
4	Chinese Ming and Qing Furniture hall (FU), Ancient Chinese Coin hall (CO), Ancient Chinese Jade hall (JA), the third temporary exhibition hall (TT)

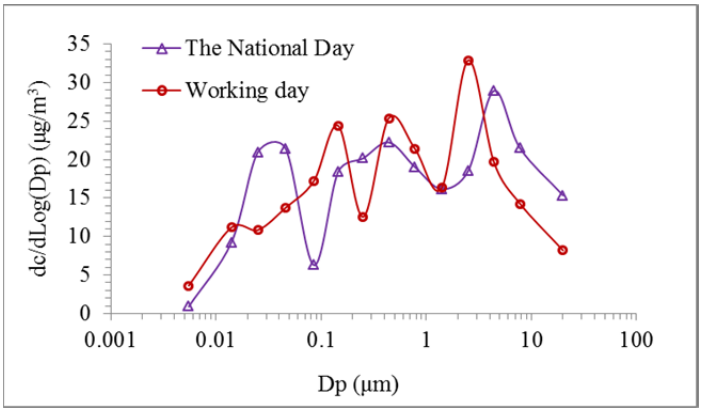

Fig. 1. Size-fractionated mass concentration of particles on working days and the National Day, respectively.

Quality Analysis

Particle mass concentration was analyzed by the weighing methodology. The BT25S type electronic balance (Sartorius Company, Germany) was adopted to weigh the filters. The sensitivity of the electronic balance was about 0.01 mg. The filters were preserved over 24 h in a chamber with constant temperature and humidity (T = 25°C and RH = 40 ± 2%) over a period of 24 h before each measurement. Membranes were weighed more than 3 times before and after samplings, and the weighing error must be controlled in the range of 0.01mg or less. This study adopted the average membrane weight as the membrane weight.

Water Soluble Ion Analysis

Dionex DX-120 Ion Chromatograph and Dionex IC 3000 Ion Chromatograph were used to analyze the concentration of Na^+, NH^+, Mg^{2+}, K^+, Ca^{2+} and F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^-, $HCOO^-$, CH_3COO^-, the oxalic acid and the methyl sulfonic acid, respectively. For the Dionex DX-120, the analytical columns were CG16 and CS16, the suppressor was Diane CSRS300, and the inhibition of current was 100 mA. 40 mmol/L methyl sulfonic acid solution was used as the elution. The operation was conducted at the speed of 1.0 mL/min. The analysis lasted for 13.5 min. For the Dionex IC3000, the analytical columns were AG18 and AS18, the suppressor was Diane CSRS300, and the inhibition of current was 68 mA. 12–27 mmol/L KOH solution was used as the elution. The operation was conducted at the speed of 1.0 mL/min. The analysis lasted for 13 min. The filter was cut into two parts. 1/2 quartz membrane filter was put in a clean centrifugal tube, adding 15ml ultrapure water, then using ultrasonic to extract, lasting for 20 min. The extracting solution was filtrated by a 0.45 μm PTFE filter head. Aiming to ensure the reliability of the sample analysis, the results were calibrated using blank correction methodology. The correlation coefficient of the standard curve was over 0.998. The blank test was repeated on the same day when the sample was analyzed. The analysis was continued only when the error peak value of ion was within 5 %.

RESULTS

Particle Size Distribution

Airborne particulates can be divided into three categories according to the particle size bins: coarse particles (diameter is larger than 2.5 μm), fine particles (diameter is between 0.1 μm and 2.5 μm) and ultrafine particles (diameter is of 0.1 μm or less). MOUDI sampler did not have 2.5 μm cutting head, therefore in this study, particles in the range of 1.8 μm and 10 μm were called coarse particles, particles with diameter ranged between 0.11 μm and 1.8 μm were defined as fine particles, particles with diameter less than 0.11 μm were classified as ultrafine particles (Yao *et al.*, 2003; Worobiec *et al.*, 2008; Zhuang *et al.*, 1999).

Fig. 1 showed the size-fractionated mass concentration of particulate matters on the working day and the National Day, respectively. It could be observed that the concentration of coarse particulate matter was greater on the National Day compared to the working days, account for 38.29% and 33.03% of the total particle mass, respectively. On the contrary, the concentration of fine particulate matter was close to each other during the two periods, with the percentage value of nearly 24% for each. It should be noted that the ultrafine particulate matter, ranging from 20 nm to 60 nm, was higher on the National Day. The flow rate of visitors during the National Day was 1.6 times greater compared to the working day. Therefore, the increase of the coarse particulate matter concentration may relate to the larger tourist flow occurred on the National Day. Visitors could bring the outside particles into the museum and then the particles re-suspended in air when visitors walked around inside the museum.

Particle Number Concentration

Table 2 showed the size-fractionated particle number concentrations monitored inside 12 exhibition halls and the middle hall, respectively. The results indicated that the fraction of particle number concentration was similar for all 13 monitoring sites. The diameters of particles were nearly less than 0.3 μm at all monitoring locations, and fine particles less than 1 μm accounted for over 97% of the total particle number.

Aiming to get better understanding of the relationship between human activities and the size fractionated particle number concentration inside museum, we selected one of the representative set of data to analyze, as shown in Fig. 2.

Table 2. Average percentage of size-fractionated particle number concentration monitored in different exhibition halls on working day.

	< 0.3 μm	0.3–0.5 μm	0.5–1 μm	1–10 μm
Lobby	87.22%	10.16%	1.88%	0.73%
SC	80.11%	17.63%	2.08%	0.18%
BR	78.76%	18.72%	2.09%	0.44%
FT	91.82%	7.68%	0.36%	0.14%
CE	88.64%	9.88%	1.11%	0.38%
ST	88.63%	10.84%	0.49%	0.04%
PA	77.59%	21.80%	0.58%	0.04%
CA	89.09%	9.58%	1.13%	0.21%
SE	87.85%	10.79%	1.22%	0.14%
CO	78.76%	18.72%	2.09%	0.44%
FU	87.48%	11.85%	0.58%	0.09%
JA	82.11%	10.63%	5.14%	2.12%
TT	79.63%	13.53%	4.78%	2.06%

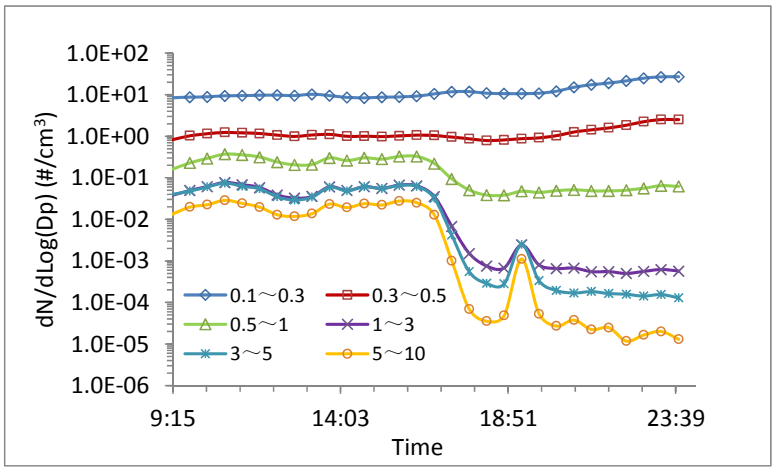

Fig. 2. Diurnal variation of size fractionated particle number concentration in the Gallery of Ceramics hall on October 1st.

The monitoring was from the moment of the museum was opened until 00:00 in the morning. It can be found that the particle number concentrations in all size bins remained at high levels during the museum open time. After the museum closed, almost all size fractionated particle number concentrations decreased sharply except particles in the range of 0.1–0.3 and 0.3–0.5 μm. The particles in these size ranges were mostly influenced by ambient particles, which could penetrate to indoors via air-conditioning system. It almost remained stable throughout the day. However, when cleaning activities were conducted inside museum at 19:00, the reduced number concentrations rose again and reached up to relatively higher peaks, but they started to reduce quickly in half an hour afterwards. In conclusion, human activities had great impact on the particles in the range of 1–10 μm.

The decay rates of particles within various size bins were investigated in this study, as shown in Fig. 3. The decay rates were used to obtain the information about particle depositions. There are numbers of relics placed without any protections in the museum, and exposed in the air. The decay rates can show us which type of and how long the particles can deposited on the surface of relics, and we can also learn which ion or other chemical compositions were deposited on the relics. The decay rate of particles in the range of 0.1–0.3 μm was not calculated because of the concentration of these particles increased again after the museum closed. This may be due to the influence of outdoor sources. It could be concluded from Fig. 3 that particles with large diameters feature the higher decay rates. Particles in the range of 5–10 μm had the highest decay rate, reached up to 0.0008 s^{-1}. It was 40 times higher than particles in the range of 0.3–0.5 μm. The similar result was obtained by (Howard-Reed *et al.*, 2003), and their deposition rates varied from 0.3 h^{-1} for the smallest particle range (0.3–0.5 μm) to 5.2 h^{-1} for particles greater than 10 μm.

Aiming to explore the relationship between the number concentration of coarse particles and visitor flow rate, a statistics analysis was conducted in the Ancient Chinese Ceramics hall using the data of particle number concentration in every half an hour, as shown in Fig. 4.

Two peaks of tourist numbers were observed in Fig. 4. The number of tourists started to increase immediately after the opening time, and the first peak occurred at 12:00, then it began to decrease. The minimum tourist number was found at 14:00 in the afternoon, which can be interpreted as

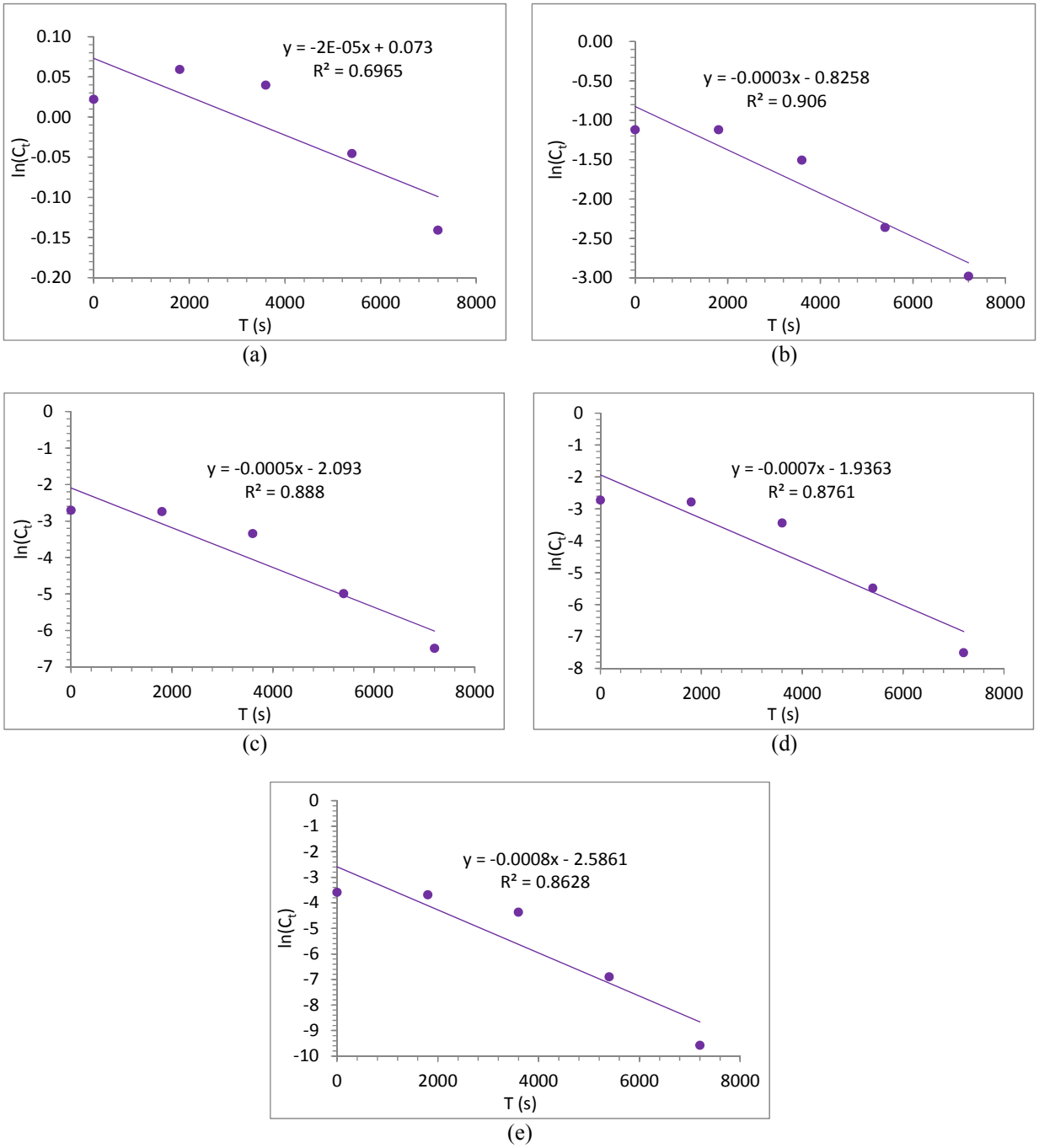

Fig. 3. The particle decay rates in the ranges of 0.3–0.5 μm (a), 0.5–1 μm (b), 1–3 μm (c), 3–5 μm (d) and 5–10 μm (e).

visitors went to lunch during this time period. The second peak appeared at 15:00 in the afternoon. The time-dependent variation of coarse particles in the range of 1–3 μm, 3–5 μm and 5–10 μm were almost coincident with the variation of visitor flow, especially the particles within the size range of 1–3 μm and 3–5 μm. Worobiec *et al.* (2008) also found that particles were significantly influenced by visitors. Their findings indicated that intensive visiting during spring and autumn could generate higher concentrations (130 μg/m^3 and 49 μg/m^3) compared to winter and summer (73 μg/m^3 and 22 μg/m^3), which have relatively less visitors. The decorative materials adopted in the hall may also impact on the distribution of particles. For example, the ground of Ceramic pavilion was covered by a thick carpet. The carpet has a negative influence on the particles as it can re-suspended the retained particles when people walk on it (Camuffo *et al.*, 1999).

The museum opened at 7:00 and closed at 17:00. Cleaners began to clean the museum at 19:00. In this study, we monitored the particle number concentrations during three different time periods, the opening time: 9:00–17:00, the cleaning time: 18:30–19:30 and no human activities time: 21:00–24:00. Fig. 5 indicated that visitors' walking and cleaning activities mostly impacted on coarse particles.

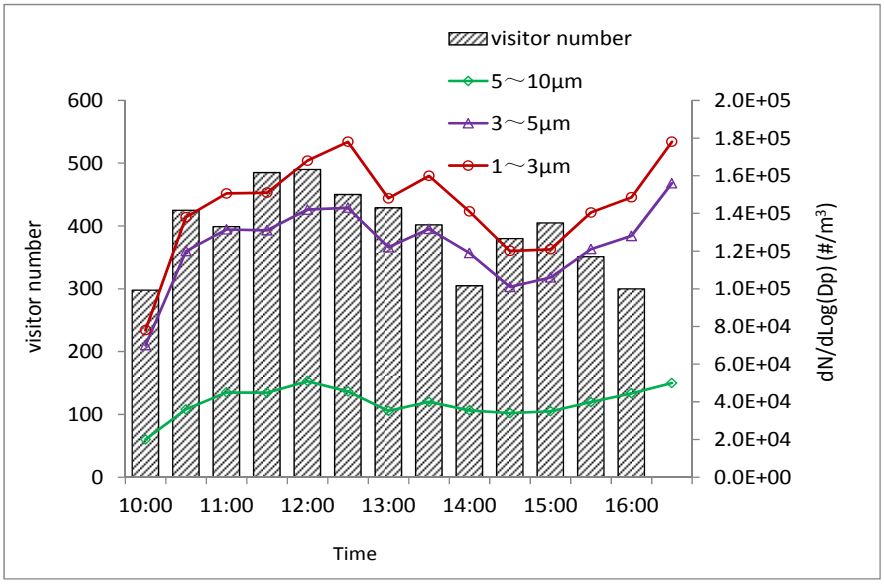

Fig. 4. Visitor flow rate and particle number concentration in different time periods in the Ancient Chinese Ceramics hall on October 1st.

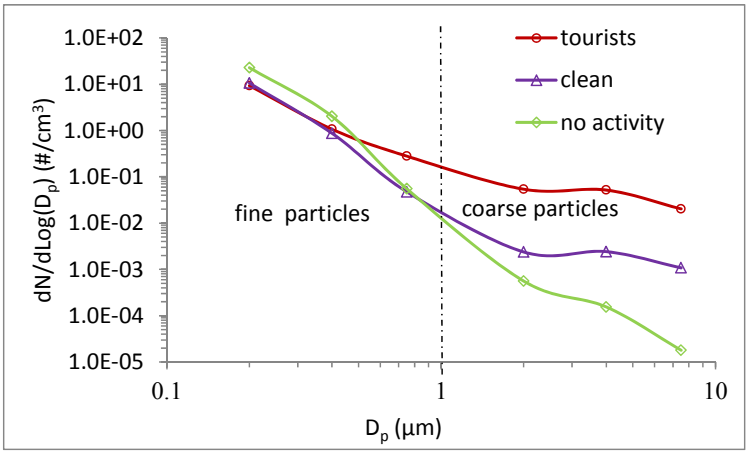

Fig. 5. Particle number size distributions during the open time, cleanup time and night in the museum.

When visitors' walking and cleaning activities occurred in the museum, the particle number concentration increased to 5874 #/m^3 and 126030 #/m^3, respectively. They were 8 and 172 times greater than the condition of no human activities.

Particle Water-Soluble Ion Concentration

11 types of water-soluble inorganic ions were monitored, but only 10 of them were detected. F^- was only found in some individual samples, and the rest were lower than the detection limit, so that F^- was not discussed here. Fig. 6 showed the sampled size-fractionated particle concentration and the total water soluble ion. The percentage of the water soluble ion concentration contributed 50.4%, 60.2% and 54.5% to the total mass concentration of the coarse particle, fine particle and ultrafine particle, respectively. Water soluble ion concentration accounted for 41.1% of the total ion concentration in fine particles.

Fig. 7 showed size-fractionated mass concentrations of SO_4^{2-}, NO_3^- and NH_4^+. All concentrations attained to the maximum values in the size range of 0.32–0.56 μm. SO_4^{2-}, NO_3^- and NH_4^+ accounted for 69 %, 62 % and 94 % of the fine particle mass, respectively. The high values of the above ions were also found by Cao *et al.* (2005a), in which, they found that the peak values appeared in the range of 1.1–3.3 μm. The observation of a high SO_4^{2-} concentration was consistent with the study of Gysels *et al.* (2002). SO_4^{2-}, NO_3^- and NH_4^+ were secondary ions which could combine with each other to form new corrosive salts. These salts could stick on the surface of the fine particles or ultrafine particles which can easily penetrate through the showcase reaching to the surface of cultural relics. The temperature and humidity in this museum remained constant throughout the entire year, and secondary ions took up over 50%, so that the fine particles and ultrafine particles may be originated from the secondary ions. The dominance of the NH_4^+ concentration and the high concentration of SO_4^{2-}, NO_3^- showed that these ions were mainly produced by the photochemical reaction.

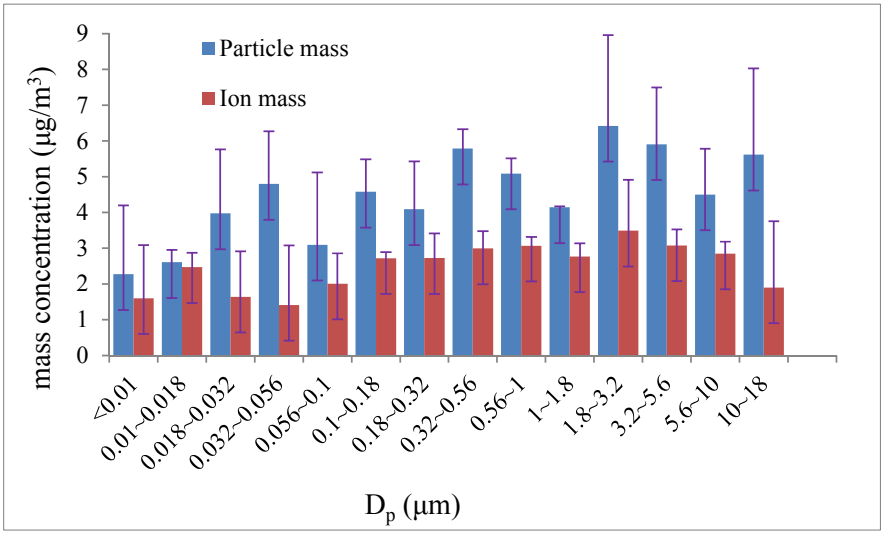

Fig. 6. Size-fractionated particle mass concentrations and total ions during the whole sampling time.

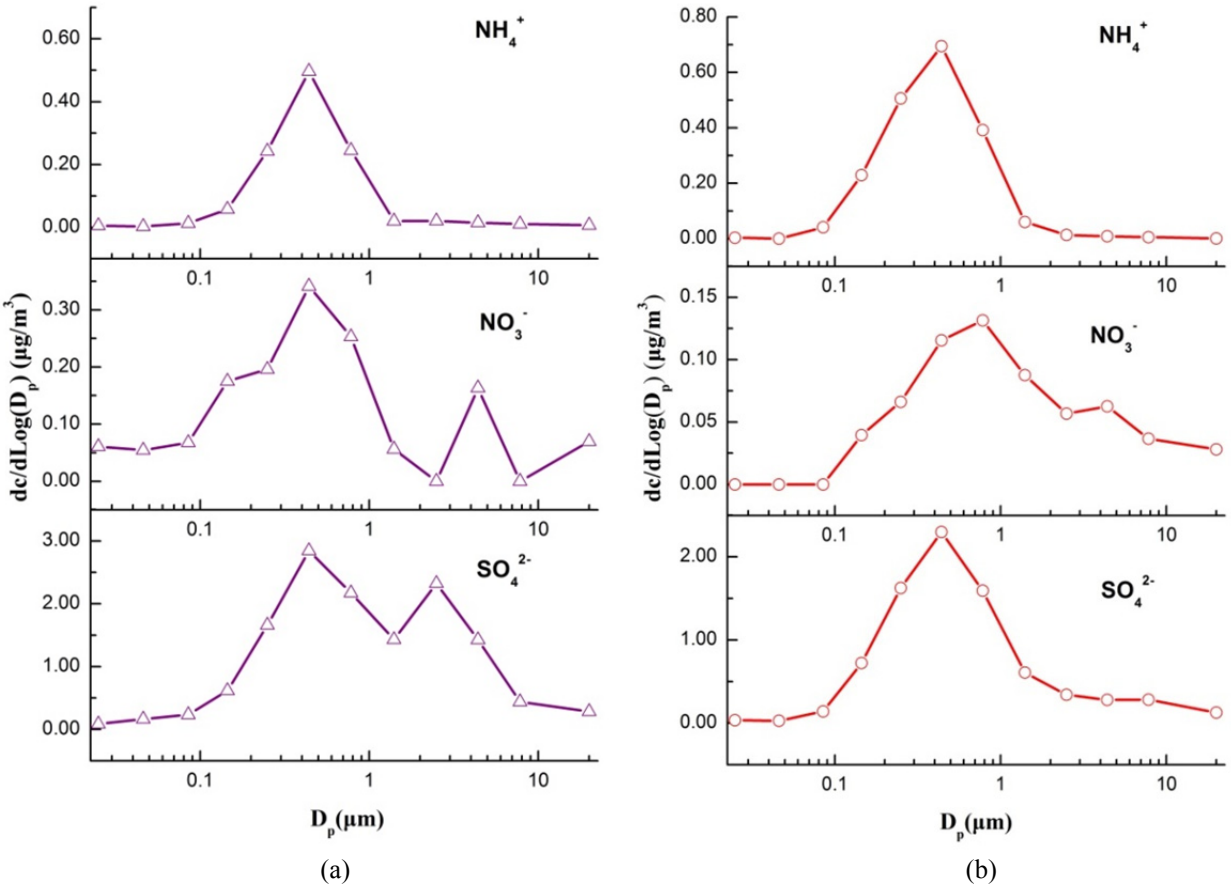

Fig. 7. Size-fractionated mass concentration of SO_4^{2-}, NO_3^-, NH_4^+ on working day (a) and the National Day (b), respectively.

During the National day, the concentration of SO_4^{2-} was lower than that on the working day. This phenomenon was due to the lower temperature during the National day outdoors. The concentration of SO_4^{2-} in museum was mostly formed by the chemical reaction and the higher temperature contributed to more strong generations of SO_4^{2-} on working days. Since the gas phase oxidation of SO_2 to sulfate by OH radical can be improved by higher temperature (Seinfeld, 1986). The similar result was obtained by Canha *et al.* (2014), They found that the highest sulfate concentration occurred during the summer owing this phenomenon to the higher temperature causing more photochemical activity

and higher ozone concentration, then enhance the oxidation of SO_2 and its conversion rate to sulfate (Khoder, 2002). So it can be penetrated into museum as the component of ultrafine particles. Also the higher traffic flow rate on the working days can be another reason for the higher concentration of SO_4^{2-}. The concentration of NO_3^- existing in the fine particles and the ultrafine particles were much lower during National days compared to the working days. The majority of NO_3^- was generated by the photochemical reaction from NO_x. There were no NO_x sources inside the museum, so it was possible that the source originated from outdoors. The higher traffic flow rate on working days was a significant contributor for the higher NO_3^- component in fine particles and ultrafine particles.

The mass ratio of $[NO_3^-]/[SO_4^{2-}]$ has been used as an indicator of weighing the factor of mobile vs. stationary sources of sulfur and nitrogen in the atmosphere (Arimoto *et al.*, 1996; Yao *et al.*, 2002; Xiao and Liu, 2004). Arimoto *et al.* (1996) ascribed high $[NO_3^-]/[SO_4^{2-}]$ mass ratios to the predominance of mobile source over stationary. In this study, the ratios obtained on the National Day and working day were 0.08 and 0.12, respectively. These values were lower than the ratios obtained by Huebert *et al.* (1988). They reported that $[NO_3^-]/[SO_4^{2-}]$ ratios in China were in the range of 0.3–0.5. Zhang *et al.* (2014) found that the indoor and outdoor ratios of $[NO_3^-]$ and $[SO_4^{2-}]$ were closed to 1. Others found that the mass ratios of $[NO_3^-]/[SO_4^{2-}]$ in Shanghai varied between 0.1 and 0.7 with an annual average of 0.4 (Yao *et al.*, 2002; Zhang *et al.*, 2014). In this study, the relatively higher ratio on working days was owing to the heavy traffic occurred. Canha *et al.* (2014) also attributed the higher indoor concentrations of $[NO_3^-]$ and $[SO_4^{2-}]$ in particles to the oxidation from NO_2 and SO_2.

The size-fractionated mass concentrations of Na^+, Mg^{2+}, K^+, Ca^{2+} and Cl^- were shown in Fig. 8. Mg^{2+} mainly concentrated in coarse particles, and peaked in the size range of 3.2–5.6 μm. K^+ distributed in fine and coarse particles, and peaked in the both size bins of 0.32–0.56 μm and 3.2–5.6 μm. Ca^{2+} was mainly found in coarse particles, and peaked in the size range of 1.8–3.2 μm. Na^+ and Cl^- were two typical sea salt compositions, their proportion among the ultrafine particles in this study reached up to 35 and 31%, respectively. The concentrations of Na^+, Mg^{2+} and K^+ in coarse and fine particles during the National Day were very close. Shanghai is a coastal city, so that the sea salt ions may come from the offshore. And the sweat evaporated from visitors was another added factor. Higher temperature could enhance the air exchange between the land and sea. So more sea salts can be brought into the urban atmosphere by the air exchange process. The concentrations of Na^+ and Cl^- were higher on the working day, indicating the influence of sea salt was dominant.

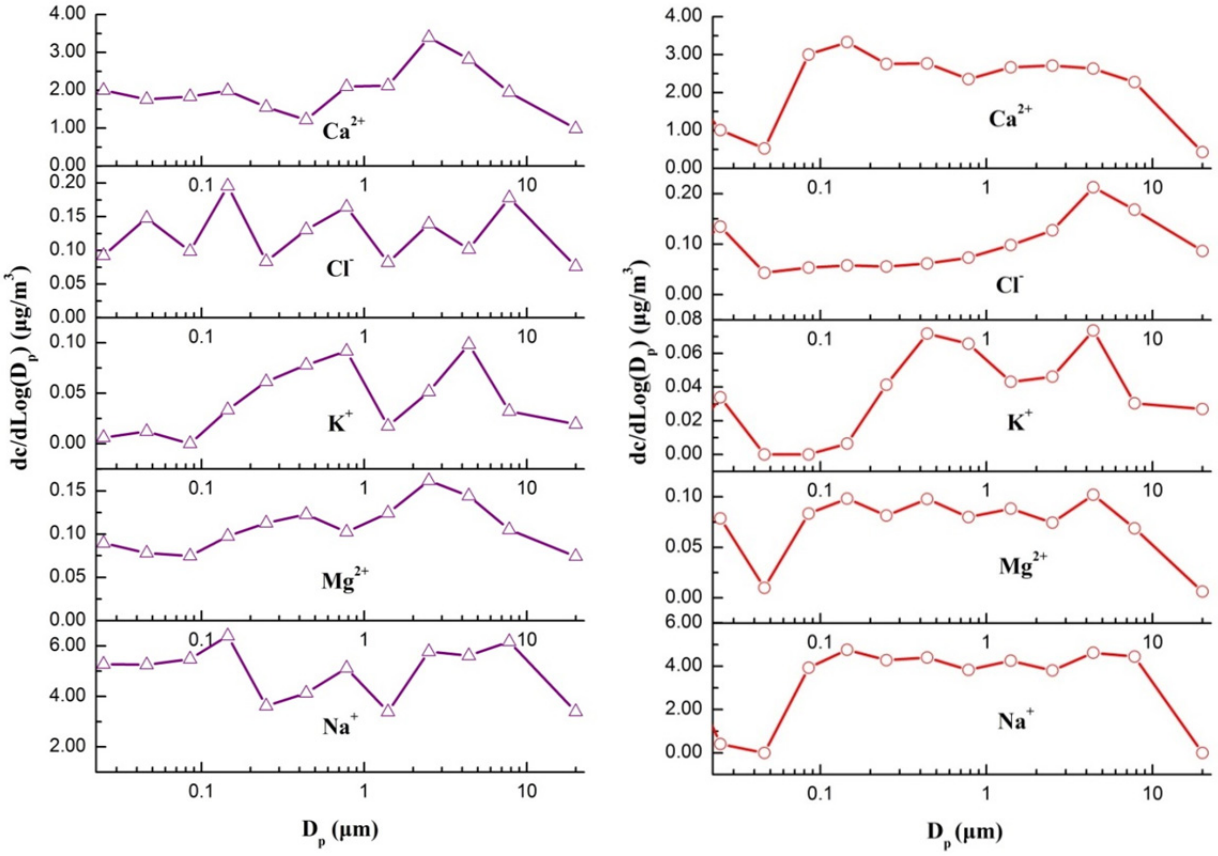

Fig. 8. Size-fractionated mass concentration of Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^- on working day (a) and the National Day (b), respectively.

This study also detected the average mass concentration of $HCOO^-$, CH_3COO^- and $C_2O_4^{2-}$, which were 0.619, 1.238 and 0.066 μg/m^3, respectively. The percentages of mass concentrations of $HCOO^-$, CH_3COO^- and $C_2O_4^{2-}$ in three particle categories were listed in Table 3.

Table 3 indicated that the majority of CH_3COO^- was observed in coarse particles and $C_2O_4^{2-}$ mainly existed in fine particles. The organic acid inside museum was not only affected by the release of wood, but also impacted by the release of green plants indoors. The influence of motor vehicle outdoors also could be one possible interpretation.

Organic and Elemental Carbon

Size-fractionated elemental carbon and organic carbon concentrations were showed in Fig. 9. Average OC and EC concentrations were 26.5 μg/m^3 and 1.42 μg/m^3, 26.68 μg/m^3 and 1.68 μg/m^3 on the National Day and working day, respectively. EC accounted for about 2.22% of the total particle mass on the National Day, while the value on the working day was 2.85%. The similar result was obtained by Cao *et al.* (2011) when they analyzed the particle chemical composition in Emperor Qin's Terra-cotta Museum. It should be noted that EC also had negative influence on culture relics. It had been found that the perceptible soiling in three southern California museums was caused by EC accumulated on vertical surface (Nazaroff *et al.*, 1990). The concentrations of OC or EC presented the same trend on both the National Day and working day. The highest OC and EC concentrations occurred in the fine particles. Fig. 10. gave the ratios of OC and EC. Lower ratios were found in fine particles with the values of 15.51 and 12.61 on the National Day and working day, respectively. Compared to fine particles, the values of OC/EC obtained by ultrafine particles and coarse particles were 1.59 and 1.31 times higher on the National Day, and 1.95 and 1.69 times greater on the working day. The values were much higher than that obtained by Cao *et al.* (2011) in their study, while their OC/EC ratios were 4.5, 4.4 and 4.1 for indoor $PM_{2.5}$, indoor TSP and outdoor TSP in summer, respectively. Higher ratio of OC/EC was found during the episodes of heavy industrial emission (Ho *et al.*, 2004) and the episodes of heavy coal combustion (Cao *et al.*, 2005b). Harley *et al.* (2005) attributed

Table 3. The percentage of $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$ on the National Day.

	Coarse particle	Fine particle	Ultrafine particle
$HCOO^-$	19.2%	36.9%	43.9%
CH_3COO^-	53.1%	21.5%	25.4%
$C_2O_4^{2-}$	27.1%	50.3%	22.6%

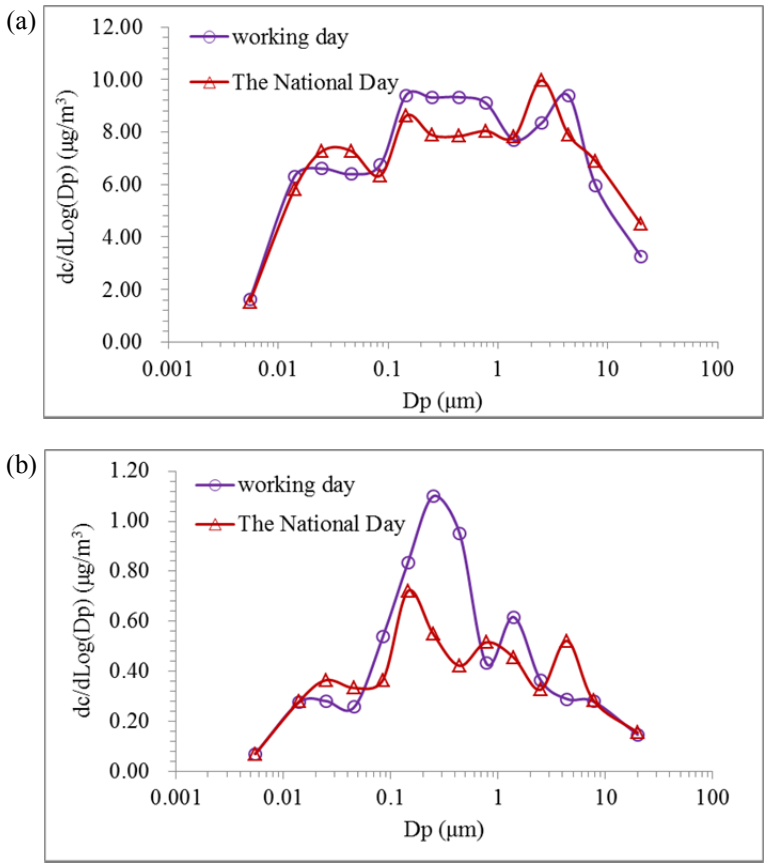

Fig. 9. Size-fractionated elemental carbon (a) and organic carbon (b) concentrations on working day and the National Day.

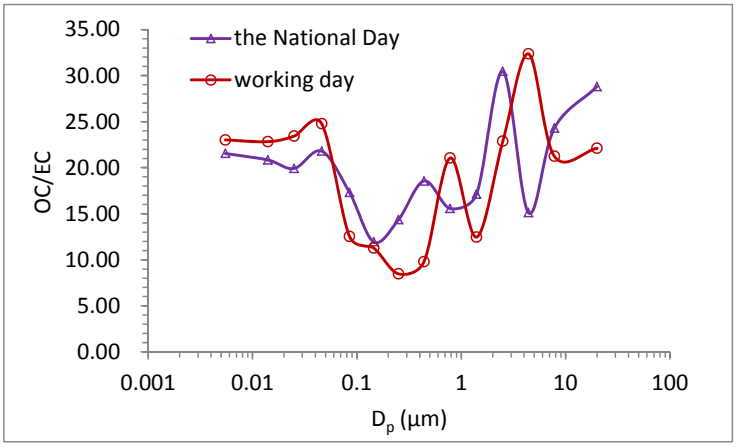

Fig. 10. Ratios of size-fractionated elemental carbon and organic carbon on the National Day and working day.

the increases of OC/EC ratio to the diesel truck traffic and accompanying EC emissions decline precipitously on the weekend and during weekday afternoon rush hour period. In this study, the interpretation of higher OC/EC ratios was that ultrafine and coarse particles in the museum were affected by outside source. Ultrafine particles can penetrated through the ventilation system and the coarse particles can be brought into the museum via the visitors.

CONCLUSIONS

This study aimed to investigate the characteristics of particulate pollutant in a museum in Shanghai. The results showed that particles mainly concentrated at the size less than 0.3 μm. Particles which were less than 1 μm accounted for more than 97% of the total particle number. The influences of the visitors' walking and cleaning activities indoors cannot be ignored when tracing the origin of particles. Hence aiming to preserve the heritage, it would be better to remind visitors to keep the museum clean. Restricting the numbers of hourly entering visitors is another feasible solution. In addition, the result showed that the water-soluble ions in the museum were affected by the human disturbance. The OC/EC ratios of particles with sizes in the ranges less than 0.1 μm and lager than 1 μm were much higher than the ones in the range of 0.1–1 μm. It is necessary for the museums to be equipped with a high efficiency filter system. In addition, a dust-cleaning apparatus could be used at the museum entrance to reduce the total particulate matter brought in by the visitors.

ACKNOWLEDGEMENT

This study was sponsored by the grants of the national science and technology support program2014BAC16B04, 13PJD013 of Shanghai Pujiang Plan, B200-2-13043 of Shanghai Natural Science fund, Innovation Program of Shanghai Municipal Education Commission 12ZZ054, Government of Bilateral Cooperation projects between China and Serbia, WB1113005 and WB1314017 from East China University of Science and Technology. The author would like to thank our colleague and staff from the museum for their contribution to this work.

REFERENCE

Arimoto, R., Duce, R., Savoie, D., Prospero, J., Talbot, R., Cullen, J., Tomza, U., Lewis, N. and Ray, B. (1996). Relationships Among Aerosol Constituents from Asia and the North Pacific during PEM-West A. *J. Geophys. Res.* 101: 2011–2023.

Brimblecombe, P. (1990). The Composition of Museum Atmospheres. *Atmos. Environ. Part B* 24: 1–8.

Camuffo, D., Brimblecombe, P., Van Grieken, R., Busse, H.J., Sturaro, G., Valentino, A., Bernardi, A., Blades, N., Shooter, D. and De Bock, L. (1999). Indoor Air Quality at the Correr Museum, Venice, Italy. *Sci. Total Environ.* 236: 135–152.

Camuffo, D., Van Grieken, R., Busse, H.J., Sturaro, G., Valentino, A., Bernardi, A., Blades, N., Shooter, D., Gysels, K. and Deutsch, F. (2001). Environmental Monitoring in Four European Museums. *Atmos. Environ.* 35: S127–S140.

Camuffo, D., Bernardi, A., Sturaro, G. and Valentino, A. (2002). The Microclimate Inside the Pollaiolo and Botticelli Rooms in the Uffizi Gallery, Florence. *J. Cult. Herit.* 3: 155–161.

Canha, N., Almeida, S.M., Freitas, M.d.C., Trancoso, M., Sousa, A., Mouro, F. and Wolterbeek, H.T. (2014). Particulate Matter Analysis in Indoor Environments of Urban and Rural Primary Schools Using Passive Sampling Methodology. *Atmos. Environ.* 83: 21–34.

Cao, J., Rong, B., Lee, S., Chow, J.C., Ho, K., Liu, S. and Zhu, C. (2005a). Composition of Indoor Aerosols at Emperor Qin's Terra-cotta Museum, Xi'an, China, during Summer, 2004. *China Particuology* 3: 170–175.

Cao, J., Wu, F., Chow, J., Lee, S., Li, Y., Chen, S., An, Z., Fung, K., Watson, J. and Zhu, C. (2005b). Characterization and Source Apportionment of Atmospheric Organic and Elemental Carbon during Fall and Winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.* 5: 3127–3137.

Cao, J., Li, H., Chow, J.C., Watson, J.G., Lee, S., Rong,

B., Dong, J. and Ho, K. (2011). Chemical Composition of Indoor and Outdoor Atmospheric Particles at Emperor Qin's Terra-cotta Museum, Xi'an, China. *Aerosol Air Qual. Res.* 11: 70–79.

Chen, C. and Zhao, B. (2011). Review of Relationship between Indoor and Outdoor Particles: I/O Ratio, Infiltration Factor and Penetration Factor. *Atmos. Environ.* 45: 275–288.

Chen, Y.C., Yuanhui, Z. and Barber, E.M. (2000). A Dynamic Method to Estimate Indoor Dust Sink and Source. *Build. Environ.* 35: 215–221.

De Santis, F., Di Palo, V. and Allegrini, I. (1992). Determination of Some Atmospheric Pollutants Inside a Museum: Relationship with the Concentration Outside. *Sci. Total Environ.* 127: 211–223.

Godoi, R.H.M., Potgieter-Vermaak, S., Godoi, A.F.L., Stranger, M. and Van Grieken, R. (2008). Assessment of Aerosol Particles within the Rubens' House Museum in Antwerp, Belgium. *X-Ray Spectrom.* 37: 298–303.

Greathouse, G.A. and Wessel, C.J. (1954). Deterioration of Materials. Causes and Preventive Techniques. Deterioration of Materials. Causes and Preventive Techniques.

Gysels, K., Deutsch, F. and Grieken, R.V. (2002). Characterisation of Particulate Matter in the Royal Museum of Fine Arts, Antwerp, Belgium. *Atmos. Environ.* 36: 4103–4113.

Gysels, K., Delalieux, F., Deutsch, F., Van Grieken, R., Camuffo, D., Bernardi, A., Sturaro, G., Busse, H.J. and Wieser, M. (2004). Indoor Environment and Conservation in the Royal Museum of Fine Arts, Antwerp, Belgium. *J. Cult. Herit.* 5: 221–230.

Harley, R.A., Marr, L.C., Lehner, J.K. and Giddings, S.N. (2005). Changes in Motor Vehicle Emissions on Diurnal to Decadal Time Scales and Effects on atmospheric Composition. *Environ. Sci. Technol.* 39: 5356–5362.

Ho, K., Cao, J., Harrison, R.M., Lee, S. and Bau, K. (2004). Indoor/Outdoor Relationships of Organic Carbon (OC) and Elemental Carbon (EC) in $PM_{2.5}$ in Roadside Environment of Hong Kong. *Atmos. Environ.* 38: 6327–6335.

Howard-Reed, C., Wallace, L.A. and Emmerich, S.J. (2003). Effect of Ventilation Systems and Air Filters on Decay Rates of Particles Produced by Indoor Sources in an Occupied Townhouse. *Atmos. Environ.* 37: 5295–5306.

Hu, T., Li, X., Dong, J., Rong, B., Shen, Z., Cao, J., Lee, S.C., Chow, J.C. and Watson, J.G. (2006). Morphology and Elemental Composition of Dustfall Particles Inside Emperor Qin's Terra-cotta Warriors and Horses Museum. *China Particuology* 4: 346–351.

Hu, T., Lee, S., Cao, J., Chow, J.C., Watson, J.G., Ho, K., Ho, W., Rong, B. and An, Z. (2009). Characterization of Winter Airborne Particles at Emperor Qin's Terra-cotta Museum, China. *Sci. Total Environ.* 407: 5319–5327.

Hu, T., Cao, J., Lee, S., Li, X., Shen, Z., Rong, B. and An, Z. (2010). Microanalysis of Dust Deposition inside Emperor Qin's Terra-Cotta Warriors and Horses Museum. *Aerosol Air Qual. Res.* 10: 59–66.

Huebert, B.J., Wang, M.X. and Lü, W.X. (1988). Atmospheric Nitrate, Sulfate, Ammonium and Calcium Concentrations in China. *Tellus Ser. B* 40: 260–269.

Khoder, M.I. (2002). Atmospheric Conversion of Sulfur Dioxide to Particulate Sulfate and Nitrogen Dioxide to Particulate Nitrate and Gaseous Nitric Acid in an Urban Area. *Chemosphere* 49: 675–684.

Koutrakis, P., Briggs, S.L. and Leaderer, B.P. (1992). Source Apportionment of Indoor Aerosols in Suffolk and Onondaga Counties, New York. *Environ. Sci. Technol.* 26: 521–527.

Li, Y. and Chen, Z. (2003). A Balance-point Method for Assessing the Effect of Natural Ventilation on Indoor Particle Concentrations. *Atmos. Environ.* 37: 4277–4285.

Nazaroff, W.W., Salmon, L.G. and Cass, G.R. (1990). Concentration and Fate of Airborne Particles in Museums. *Environ. Sci. Technol.* 24: 66–77.

Seinfeld, J.H. (1986). *Atmospheric Chemistry and Physics of Air Pollution.* Wiley, New York, p. 863–863.

Spolnik, Z., Worobiec, A., Injuk, J., Neilen, D., Schellen, H. and Van Grieken, R. (2004). Chemical Characterization of Airborne Particles in St. Martinus Cathedral in Weert, The Netherlands. *Microchim. Acta* 145: 223–227.

Thomson, G. (1965). Air Pollution: A Review for Conservation Chemists. *Stud. Conserv.* 10: 147–167.

Toishi, K. and Kenjo, T. (1975). Some Aspects of the Conservation of Works of Art in Buildings of New Concrete. *Stud. Conserv.* 20: 118–122.

Worobiec, A., Samek, L., Karaszkiewicz, P., Kontozova-Deutsch, V., Stefaniak, E.A., Van Meel, K., Krata, A., Bencs, L. and Van Grieken, R. (2008). A Seasonal Study of Atmospheric Conditions Influenced by the Intensive Tourist Flow in the Royal Museum of Wawel Castle in Cracow, Poland. *Microchem. J.* 90: 99–106.

Xiao, H.Y. and Liu, C.Q. (2004). Chemical Characteristics of Water-soluble Components in TSP over Guiyang, SW China, 2003. *Atmos. Environ.* 38: 6297–6306.

Yao, X., Chan, C.K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K. and Ye, B. (2002). The Water-soluble Ionic Composition of $PM_{2.5}$ in Shanghai and Beijing, China. *Atmos. Environ.* 36: 4223–4234.

Yao, X., Lau, A.P., Fang, M., Chan, C.K. and Hu, M. (2003). Size Distributions and Formation of Ionic Species in Atmospheric Particulate Pollutants in Beijing, China: 1—Inorganic Ions. *Atmos. Environ.* 37: 2991–3000.

Zhang, J., Chen, J., Yang, L., Sui, X., Yao, L., Zheng, L., Wen, L., Xu, C. and Wang, W. (2014). Indoor $PM_{2.5}$ and Its Chemical Composition during a Heavy Haze–Fog Episode at Jinan, China. *Atmos. Environ.* 99: 641–649.

Zhuang, H., Chan, C.K., Fang, M. and Wexler, A.S. (1999). Size Distributions of Particulate Sulfate, Nitrate, and Ammonium at a Coastal Site in Hong Kong. *Atmos. Environ.* 33: 843–853.

Received for review, November 14, 2014
Revised, January 11, 2015
Accepted, February 14, 2015