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ABSTRACT

Day- and nighttime total suspended particulate matter was collected inside and outside Emperor Qin's Terra-Cotta Museum in winter and summer 2008. The purpose was to characterize the winter and summer differences of indoor airborne particles in two display halls with different architectural and ventilation conditions, namely the Exhibition Hall and Pit No. 1. The morphology and elemental composition of two season samples were investigated using scanning electron microscopy and energy dispersive X-ray spectrometry. It is found that the particle size, particle mass concentration, and particle type were associated with the visitor numbers in the Exhibition Hall and with the natural ventilation in Pit No. 1 in both winter and summer. Evident winter and summer changes in the composition and

physicochemical properties of the indoor suspended particulate matters were related to the source emission and the meteorological conditions. Particle mass concentrations in both halls were higher in winter than in summer. In winter, the size of the most abundant particles at the three sites were all between 0.5 and 1.0 μm , whereas in summer the peaks were all located at less than 0.5 μm . The fraction of sulfur-containing particles was 2–7 times higher in winter than in summer. In addition to the potential soiling hazard, the formation and deposition of sulfur-containing particles in winter may lead to the chemical and physical weathering of the surfaces of the terra-cotta statues.

INTRODUCTION

The conservation of our cultural heritage and its protection against possible damage from air pollution is of increasing concern.¹ Indoor air pollution can cause chemical deterioration or soiling of surfaces due to particle deposition or absorption of gases.² Once particles are deposited, their appearances and chemical interactions with the surface depend on their chemical composition and morphology.³ Nazaroff et al. and Camuffo have discussed in detail the deposition mechanisms of particles on vertical and horizontal surfaces.^{3,4} Investigations of calcareous stone weathering show that physical stress from soluble salt crystallization in pores causes stone breakage.⁵ It is suggested that visitors entering the buildings are responsible for transferring particulate materials inside or for resuspending the deposited dust from the floor and pavement.⁶ Visitor flow is considered as a major contributor to soiling and changes of microclimate.^{7,8} Studies also showed seasonal variations of airborne particles in terms of their mass concentration, elemental composition, and size distribution, due to weather conditions and seasonal sources of air pollution.^{9,10}

IMPLICATIONS

Relatively few microanalyses of indoor airborne particles inside museums in China have been performed. The mass concentrations of winter and summer indoor total suspended particulate (TSP) are presented for the Emperor Qin's Terra-Cotta Museum along with the characterization of individual particles via computerized scanning electron microscopy and an energy dispersive X-ray spectrometry. The results indicate that both the high level of particle mass concentrations in winter and the predominant fine particles in summer were responsible for the soiling of the statues over a long period of time. The irreplaceable statues were also facing with weathering hazards posed by abundant sulfur-containing particles, especially in winter. Data provided in this study suggested that mechanical ventilation, air filtration, and air conditioning systems should be installed in Pit No. 1 display hall and proper display strategy should be adopted in Exhibition Hall.

The discovery of Emperor Qin's terra-cotta warriors in 1974 was one of the most important archeological findings of the 20th century. More than 2 million tourists visit the museum each year to see the fabulous terra-cotta army in full battle array in Pit No. 1 (Pit 1) and the bronze chariots and horses in the Exhibition Hall (EH). Since their excavation, these priceless and irreplaceable statues have undergone changes in their appearance following more than 30 years of exposure in the display halls.¹¹ The Emperor Qin's Terra-Cotta Museum is located 30 km to the east of Xi'an, a city with a population of 8 million, which is experiencing increasing traffic, high coal consumption, and intensive construction. The Museum is in a suburban environment, 17 km from the BaHe Power Plant to the west and 5 km from a highway to the north. The Museum is also surrounded by agricultural fields in which biomass is periodically burned.

In this study, the size, morphology, and elemental composition of approximately 17,000 individual particles were analyzed using scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) to examine their potential soiling and corrosive hazards to the artifacts. Detailed knowledge of the concentration and composition of airborne particles present in this on-site museum could be used to prevent future soiling and deterioration of the artifacts on display.

EXPERIMENTAL METHODS

Sample Collection

Airborne total suspended particulate (TSP) matter samples were collected inside and outside the Museum during winter (from 15 to 22 February 2008) and summer (from 13 to 19 August 2008). The collection of samples was organized at the three separate sampling sites marked with stars in Figure 1. One sampling site was at the western part of Pit 1. Another sampling site was in the EH. The two display halls are different in the building structures and their ventilation. Pit 1 is covered with a hangar-like steel-frame vault to shield the statues from direct solar illumination and rain or snow. All the wide windows in Pit 1 remain open all year long. The EH has no window and is equipped with a mechanical ventilation and air-conditioning system. The system was not operating during the two sampling periods for economic and maintenance reasons. The air mass exchanges in the EH were only through the entrance of the hall and through narrow cracks in the building shell. The outdoor samples were collected on the roof of the Museum's office building, about 10 m above the ground.

Sampling was carried out at the three sites simultaneously in order to obtain comparative results for the measurements. TSP samples were collected on 47-mm polycarbonate Nuclepore filters (0.4 μm in porosity; Whatman International Ltd., Maidstone, UK) using

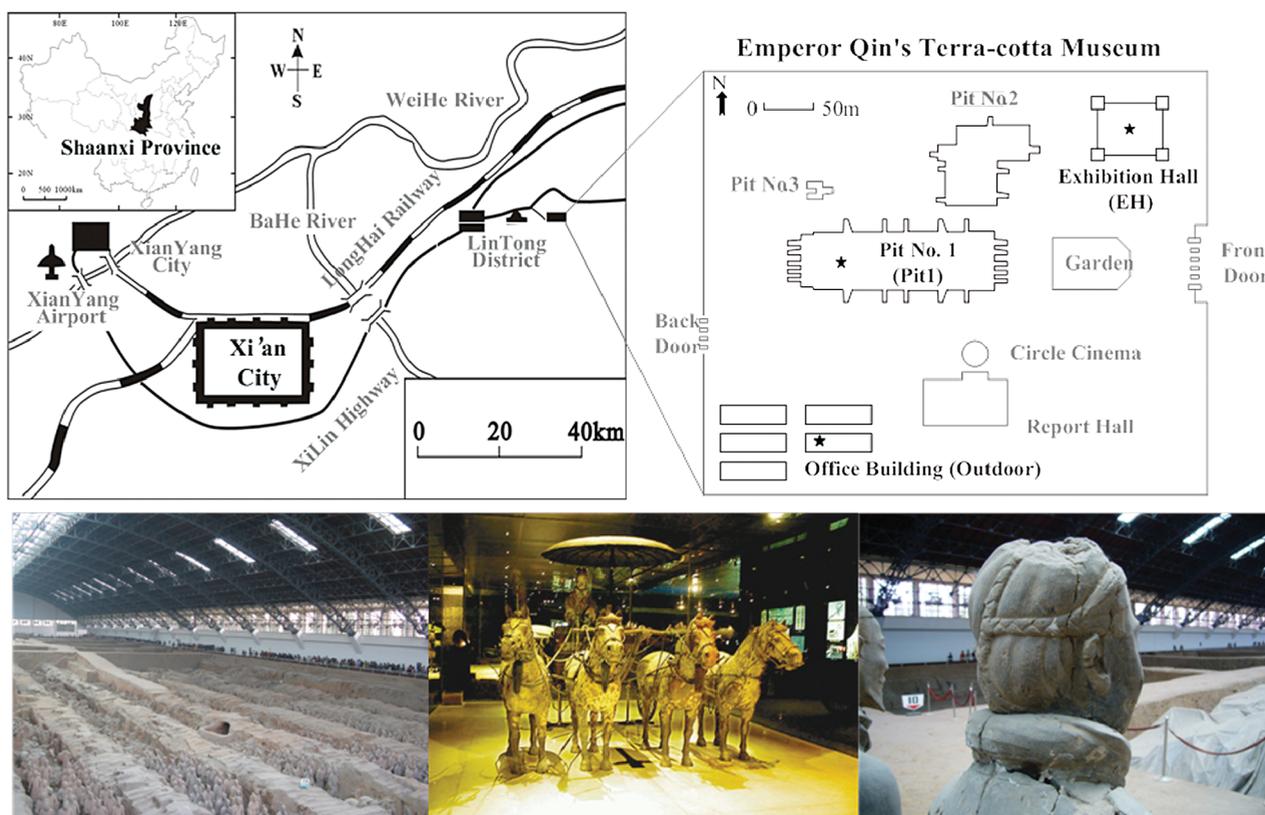


Figure 1. The three sampling sites in the Exhibition Hall, in Pit 1, and on the roof of office building (Outdoor) are marked with stars.

mini-vol air samplers (Airmetrics Corp., Springfield, OR, USA) without PM₁₀ impactors. The operating flow rate was 5 L min⁻¹. The Museum is open to the public from 8:30 a.m. to 5:00 p.m. Day- and nighttime samples were collected separately: the daytime samples (10:00 a.m.~3:00 p.m.) were representative of airborne particles arising from the influence of visitor activities, and the nighttime samples (11:00 p.m.~4:00 a.m.) were representative of airborne particles that were not subject to the influence of visitors. During the preoptimized 5-hr sampling period, particles were collected in a single layer on the filters with minimal particle-to-particle contact. After sampling, the filters were placed in plastic cassettes and stored in a refrigerator at 4°C until they were analyzed. The absence of sample on 17 August was due to the malfunction of samplers.

Sample Measurement

Small rectangular sections (approximately 10 × 10 mm) were cut from the filters and mounted on stubs with conductive adhesive carbon tape. Samples were coated under vacuum with gold and analyzed using a computer-controlled JEOL JSM-6460 LV SEM (Japan Electron Optics Laboratory Co. Ltd., Japan) under 25 kV accelerating voltage at a work distance of 10 mm. For each sample, 10 secondary electron images (SEIs) were acquired with magnifications from 1000× to 5000×, depending on the particle size in respective image views. The diameter of each individual particle was estimated as the average of the longest dimension and its orthogonal width from SEI images using IMAGE PRO PLUS (IPP) 5.0 software (Media Cybernetics, Inc., Silver Spring, MD, USA).¹² All particles with a diameter larger than 0.2 μm in each image were measured to obtain general size distributions. Individual particles larger than 0.5 μm in each sample were selected for elemental analyses manually using a Noran System Six Si-Li EDX detector with an ultrathin window (Thermo Electron Corp., Waltham, MA, USA). The EDX counting time was 30 sec live-time for each particle at magnifications of 1000×, 3000×, and 5000×, according to the particle size in respective images. Nearly 200 particles in each sample were measured. X-ray peak intensities for each element were converted into atomic and weight fractions using the EDX software without atomic number, absorption, and fluorescence (ZAF) correction.

The Nuclepore polycarbonate filters were analyzed gravimetrically for mass concentrations by means of a Sartorius MC5 electronic microbalance with a ±1 μg sensitivity (Sartorius, Göttingen, Germany). Meteorological

conditions were recorded using a Davis Vantage Pro2 weather station (Davis Instruments Corp., Hayward, CA, USA) positioned at the outdoor site. Indoor temperature and relative humidity were recorded by two Testo infrared sensors (175H2 and 177H1; Testo Inc., Lenzkirch, Germany) since 2006. Visitor numbers were obtained from the managers of the Museum.

RESULTS AND DISCUSSION

Microclimate

The site of the Museum has a semiarid and semihumid continental climate, with the lowest temperatures and rare rain or snow in winter, and the highest temperatures and more frequent rain in summer. Most days in the winter sampling period were sunny days. Southwesterly wind predominated and wind speed was 0.2~1.3 m·s⁻¹. The weather in the summer sampling period was mainly cloudy, with northeasterly prevailing wind of 0.3~3.3 m·s⁻¹. It rained on August 16. The temperature and relative humidity (RH) at the three sampling sites during the winter and summer sampling periods are shown in Table 1. Although the air-conditioning system in the EH was not operated during the two sampling periods, the diurnal indoor temperature did not fluctuate more rapidly than in Pit 1 due to the protection by thick walls. The mean RH in summer was higher than that in winter, both indoor and outdoors. In winter, the indoor temperature in Pit 1 was a little lower than that outdoors; however, the indoor RH was much higher. Condensation occurred at night when the temperature of building materials, including steel and glass, reached or dropped below the dew temperature. The condensation and subsequent evaporation of surface water at daytime increased the indoor relative humidity. In the potential deterioration processes affecting the statues, the frequent condensation–evaporation cycles may cause migration of dissolved salts and recrystallization, which are responsible for physical and chemical weathering of terra-cotta and lacquer materials. Surface moisture may also increase the deposition rate of airborne pollutants and favor biological weathering.

When the temperature of the statue dropped below freezing point, freezing-thawing cycles develop, and the pressure produced by the ice crystals may have disruptive effects. As recorded in Pit 1, an indoor temperature below freezing point appeared on more than 20 days in 1989 and in 1992,¹³ and on 33 days in 2007. This aggressive indoor environment in Pit 1 may promote the deterioration of the terra-cotta materials through frequent freezing-thawing

Table 1. Microclimate data during winter and summer sampling periods.

Time	Site	Temperature (°C)			Relative Humidity (%)		
		Max.	Min.	Mean	Max.	Min.	Mean
Winter	Outdoor	18.4	-1.1	5.2	77.7	19.2	54.4
	Pit 1	13.0	-1.2	6.7	98.6	34.0	67.6
	EH	11.4	7.9	9.5	87.1	12.4	59.4
Summer	Outdoor	38.0	18.4	25.2	98.0	35.0	78.4
	Pit 1	31.5	25.0	27.2	83.6	62.8	76.2
	EH	26.8	24.8	25.8	89.7	79.6	85.3

cycles in winter. Visitors can release vapor and heat according to previous observations.⁸ In this study, no significant association between visitor flow and indoor temperature and relative humidity was found.

Mass Concentrations of TSP

In winter, daytime particle mass concentrations in EH, Pit 1, and at outdoor site were 108.1~291.7 (mean and standard deviation: 199.7 ± 73.9), $131.4 \sim 285.4$ (220.6 ± 51.3), and $205.3 \sim 395.4$ (317.7 ± 80.4) $\mu\text{g}\cdot\text{m}^{-3}$, respectively, whereas nighttime mass concentrations were $54.7 \sim 173.2$ (95.2 ± 37.4), $95.3 \sim 260.7$ (166.0 ± 61.2), and $203.3 \sim 341.3$ (271.9 ± 51.5) $\mu\text{g}\cdot\text{m}^{-3}$, respectively. In summer, daytime particle mass concentrations in EH, Pit 1, and at outdoor site were $28.7 \sim 205.9$ (96.4 ± 22.5), $60.1 \sim 124.7$ (125.9 ± 64.3), and $64.7 \sim 274.2$ (169.6 ± 87.7) $\mu\text{g}\cdot\text{m}^{-3}$, respectively, whereas nighttime mass concentrations were $27.0 \sim 142.0$ (80.9 ± 45.3), $72.7 \sim 172.6$ (100.4 ± 35.4), and $46.8 \sim 327.3$ (182.3 ± 84.1) $\mu\text{g}\cdot\text{m}^{-3}$, respectively. The particle mass concentrations were higher in winter than in summer presumably because of the higher emissions arising from coal combustion for heating. In Pit 1, the winter average particle mass concentration of $220.6 \mu\text{g}\cdot\text{m}^{-3}$ in this study was substantially lower than a 5-day average concentration of $360 \mu\text{g}\cdot\text{m}^{-3}$, recorded in January 1994, and the summer average value of $125.9 \mu\text{g}\cdot\text{m}^{-3}$ was also a little lower than a 7-day average value of $172.4 \mu\text{g}\cdot\text{m}^{-3}$ in August 2004.¹¹ Despite the great variability in measurements, the indoor winter and summer values in this study are much higher than the respective values monitored in Royal Museum of Wavel Castle in Poland.¹⁰ Compared with that measured in a museum in London equipped with an air-conditioning system, the highest TSP concentration in the EH is 2.5 times higher, and the highest TSP concentration in Pit 1 is a little lower than the maximum value of $303 \mu\text{g}\cdot\text{m}^{-3}$ in the naturally ventilated Bethnal Green Museum located in a

highly polluted urban environment.⁸ Therefore, the particle mass concentrations in both seasons in the indoor environment had reduced probably owing to the different meteorological conditions.¹⁴ However, compared to other museums with similar ventilation conditions, the mass concentrations of airborne particles in both of the display halls remained at a high level. The soiling due to deposition of airborne particulate matter posed a hazard to statues in the Museum. After more than 30 years of exposure, it was found that gray dust depositions have covered some details of the warriors in Pit 1. Necessitating cleaning procedures of those dark deposits on the surfaces may bring further risk to the statues. In addition to soiling by airborne particles, the deposited acidic particles can attack terra-cotta material chemically.

The ratios of day- to nighttime mass concentrations of the TSP at the three sites and visitor numbers on each sampling day are given in Figure 2. In winter, the ratios in the EH, ranging from 1.30 to 3.12, are higher than those in Pit 1 (0.96~2.59) on most sampling days. In summer, the trend were more obvious, with daytime/nighttime ratios in the EH (0.83~3.80) being much higher than the corresponding ratios in Pit 1 (0.58~1.39), indicating obviously larger contributions of the tourist flow on TSP concentrations inside the EH in both seasons. In the EH, some coarse particles stirred up by visitors in the day were deposited at night by gravitational settling. Compared to the EH site, the TSP in Pit 1 did not synchronize with the visitor fluctuation in both seasons. In Pit 1 those coarse particles were still driven by free air mass exchanged through the open windows at nighttime. There were much more visitors on the summer sampling days than in winter. But most of the daytime/nighttime ratios were lower than those in winter, implying differences in outdoor meteorological conditions, microclimate, and physical properties and chemical compositions of particles between winter and summer.

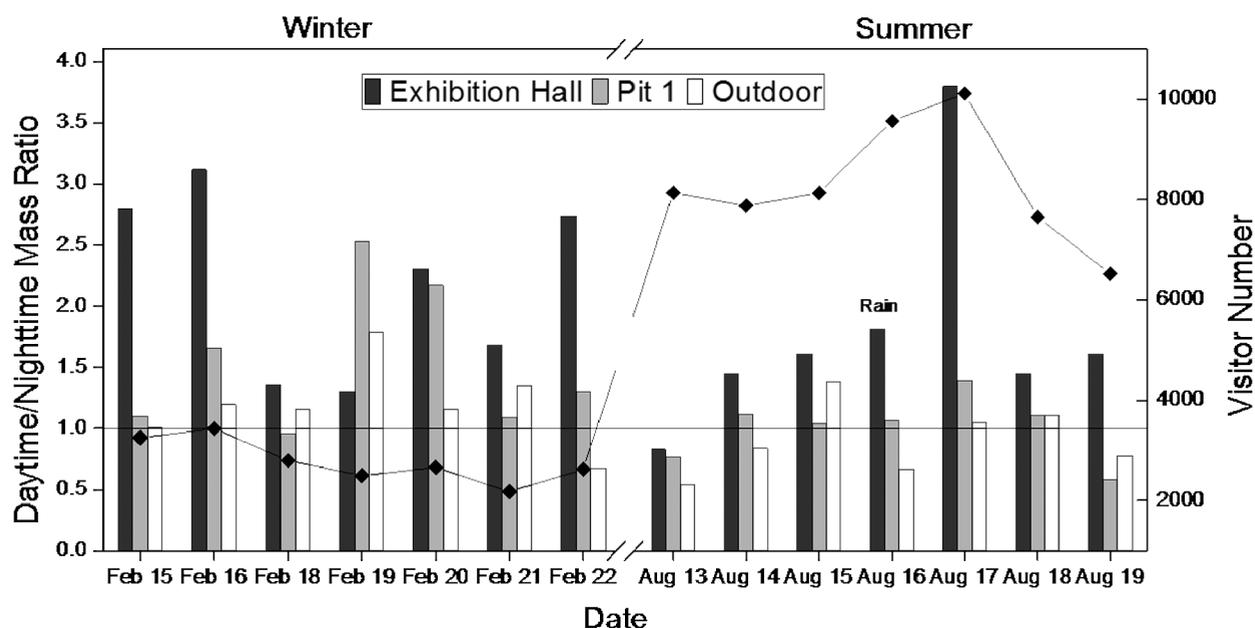


Figure 2. The daytime/nighttime mass concentration ratios of airborne particles collected in the Exhibition Hall, in Pit 1, and outdoors during winter and summer sampling periods. The black diamonds illustrate the number of visitors that entered the Museum on each sampling days.

Table 2. Indoor/outdoor ratios of airborne particle mass concentrations in EH at daytime (EHD) and at nighttime (EHN), in Pit 1 at daytime (P1D) and at nighttime (P1N), and the visitor numbers on the sampling days.

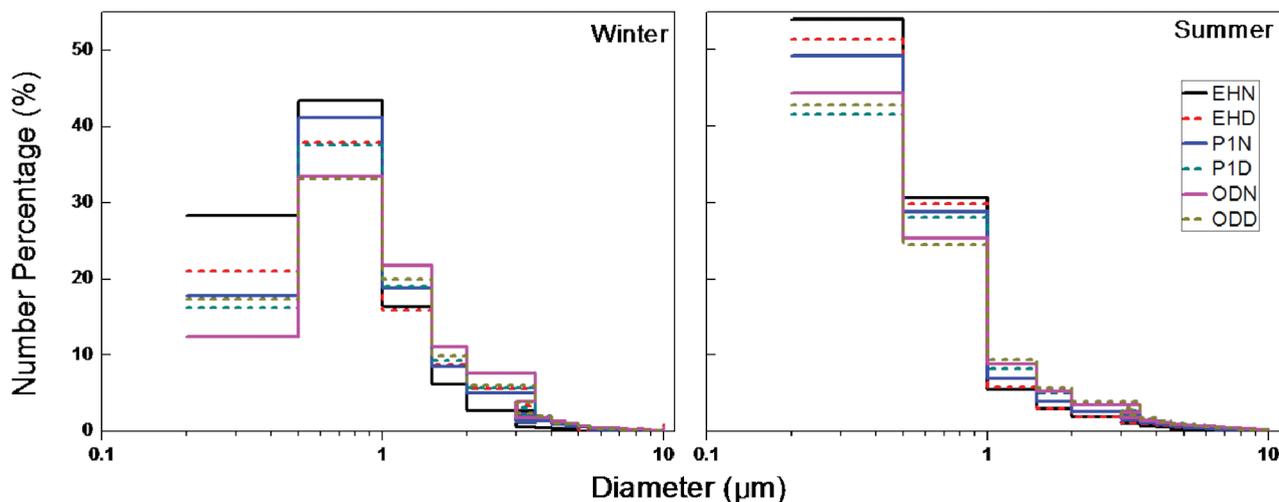
Date	Indoor/Outdoor Ratio of Mass Concentration				Visitor Number
	EHD	EHN	P1D	P1N	
Feb 15	1.22	0.44	0.64	0.58	3255
Feb 16	0.74	0.28	0.81	0.58	3439
Feb 18	0.29	0.25	0.56	0.68	2806
Feb 19	0.30	0.41	0.66	0.47	2501
Feb 20	0.74	0.37	0.83	0.44	2662
Feb 21	0.44	0.35	0.72	0.89	2186
Feb 22	0.71	0.18	1.05	0.55	2626
Aug 13	0.44	0.29	0.93	0.65	8143
Aug 14	0.29	0.17	0.44	0.33	7881
Aug 15	0.97	0.82	0.38	0.51	8135
Aug 16	2.88	1.06	1.87	1.17	9566
Aug 17	0.61	0.17	0.60	0.46	10111
Aug 18	0.81	0.61	0.49	0.48	7656
Aug 19	0.74	0.50	0.76	0.63	6521

As shown in Table 2, only two indoor/outdoor (I/O) ratios are larger than 1 in winter. There were indoor cleaning activities on the two sampling days. The I/O ratios larger than 1 in summer all occurred on a rainy day on August 16, implying visitor activity and clean activity as indoor sources. Although Pit 1 is built in situ directly on the loess soil, most of the I/O ratios are smaller than 1, indicating outdoor penetration was more active than indoor sources. It is also supported by the linear regression analysis of the indoor and outdoor particle mass concentrations after excluding the two cleaning days in winter and one rainy day in summer. The R^2 value in Pit 1 (0.79 at daytime and 0.49 at nighttime) were higher than in EH (0.19 at daytime and 0.01 at nighttime), respectively. Although the amount of data was limited and the correlations were not strong, the result of linear regression analysis is consistent with the building structures of the two display halls and their ventilation. Particle mass concentrations were

associated with infiltration of outdoor particles in Pit 1 and with human activity in EH.

Particle Size

The rate of deposition of particles and their potential hazards to surfaces are governed by the atmospheric mass concentration and by the size distribution of those particles.³ In winter, the maximal diameter of daytime particles in EH, Pit 1, and at outdoor site were 17.5, 26.0, and 26.4 μm , respectively, whereas the maximal diameter of nighttime particles were 14.3, 16.2, and 19.4 μm , respectively. In summer, the maximal diameter of daytime particles in EH, Pit 1, and at outdoor site were 17.4, 19.9, and 26.1 μm , respectively, whereas the maximal diameter of nighttime particles were 11.3, 12.6, and 16.5 μm , respectively. The number percentages of particles in each size ranges at the three sites are shown in Figure 3. The smallest particle size that can be measured by IPP software from the SEM images

**Figure 3.** Number percentages of particles in each size range in samples collected EH at daytime (EHD) and at nighttime (EHN), in Pit 1 at daytime (P1D) and at nighttime (P1N), and at outdoor site at daytime (ODD) and at nighttime (ODN) during winter and summer sampling periods.

is 0.2 μm . Because the pore size of Nuclepore filter was 0.4 μm , the relative number percentages of particles smaller than 0.4 μm in Figure 3 were underestimated. There were more particles of larger diameter suspended inside Pit 1 than inside EH on all the winter and summer sampling days. Those coarse particles were supposed to be resuspended by extra air mass exchange through the open windows in Pit 1. This is consistent with the results of the mass concentration measurement, because particle mass concentrations were controlled dominantly by coarse mode particles. In both seasons, nighttime indoor particles were smaller than daytime particles in the respective buildings because of the rapid settling of coarse particles when all doors were closed at night. The measured particles at all sampling sites were mainly 0.2~2.5 μm in size in both seasons. Particles beyond this range accounted for less than 15% in winter and less than 10% in summer. In winter, the size of the most abundant particles at the three sites were all between 0.5 and 1.0 μm , whereas in summer the peaks were all located at less than 0.5 μm . Those fine airborne particulate matters were mostly soot and acidic materials. The averaged visitor number in summer (8288) during the sampling days was nearly 2 times higher than that in winter (2782), which led to more soot particle emission from traveling vehicles.

The dominant deposition mechanism for indoors coarse particles, mostly soil dust, is gravitational settling onto surfaces with an upward orientation. By contrast, fine particles with diameter less than 1 μm , such as soot, may deposit onto surfaces with any orientation due to convective diffusion and thermophoresis. Soot and acidic materials in fine particulate matter are characteristically black and are difficult to remove by air filtration devices, whereas soil dust components in coarse particles appear brown on a white surface.³ In Pit 1, gray depositions have been observed covering some details of the warriors. When agglomerated with high RH, soil dusts and soot aggregates become more harmful because they appear more adhesive

and are difficult to remove by ordinary brushing. If soiling is to be prevented over long periods, control of both fine and coarse particles must be considered. It should be noted that fine particles were predominant in both display halls of the Museum, especially in summer.

Particle Classification

Once the particles have deposited, their optical appearance and chemical interaction with works of art depend on the details of the chemical composition and morphology of the particles.³ The particles were grouped, according to their morphologies, into four main types: soot aggregate, soil dusts, coal fly ash, and biological particles. The dominant morphologies of soot aggregates were small chain of spherulites or large clusters. Soil dusts were usually larger than 1 μm with irregular shapes. Fly ash particles were normally smooth spheres or spherical aggregates adhering to other particles. Biological particles were with regular surfaces or symmetrical shapes. The most frequently observed indoor particles, including soil dust particles in winter and soot aggregates in summer, may contribute to the color of deposits.

On the basis of the quantitative results of EDX analyses, all particles with diameter larger than 0.5 μm were classified into three main groups, including soil dust, soot, and S-containing particles. The number percentages of each group illustrated in Figure 4 showed distinct winter and summer differences. In both display halls, the soil dusts occupied a higher number percentage in winter (26~45%) than in summer (12~23%). Soot aggregates occupied a range of 10~35% in winter, but dominated the summer samples with percentages higher than 49%. Soil dust appears brown when deposited, whereas soot aggregate can produce black or grey soiling deposits. Once lodged in the pores in surfaces, those soot particles cannot be removed easily due to their small size. Moreover, soot particles from oil combustion were active in forming black crusts when they are wet, because they constitute a

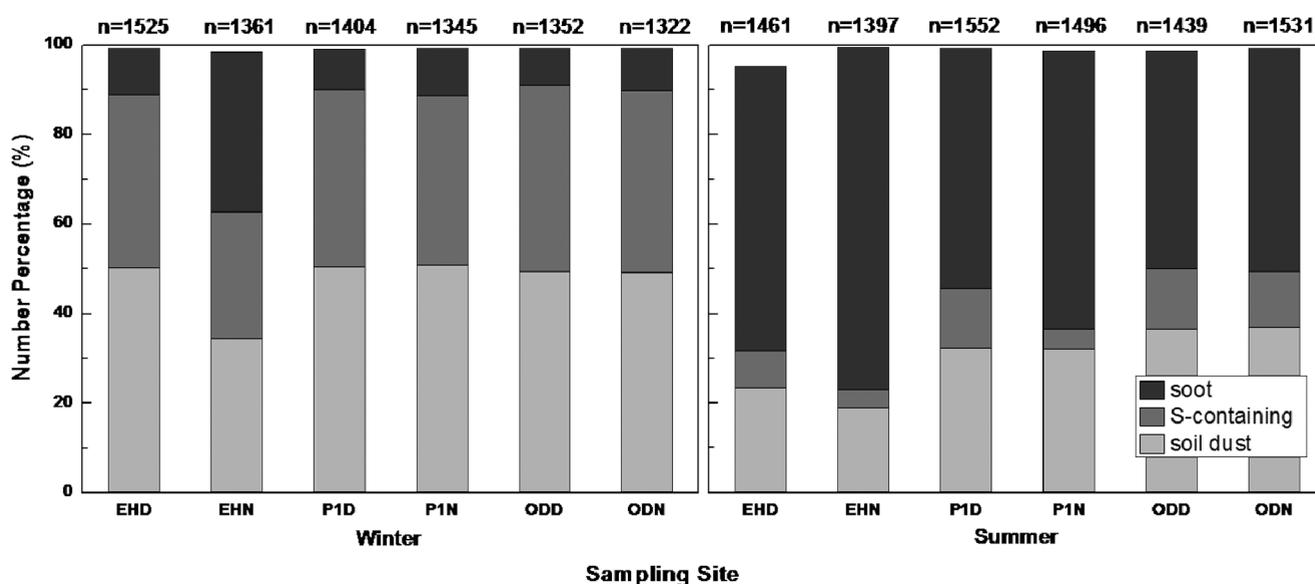


Figure 4. Classification and number percentage of each group in winter and summer airborne particles collected in EH at daytime (EHD) and at nighttime (EHN), in Pit 1 at daytime (P1D) and at nighttime (P1N), and at outdoor site at daytime (ODD) and at nighttime (ODN).

medium for the absorption of atmospheric SO₂ and the nucleation of gypsum crystals.¹⁵

S-Containing Particles

Table 3 shows that S-containing particles were detected at levels that were 2–7 times higher in winter than those in summer, probably due to the high coal consumption for heating systems in winter. Compared to the summer conditions, the increase of SO₂ emission and the decrease of the atmospheric boundary layer high in winter compensated the decrease of photochemical formation rate of sulfates.

Figure 5 shows the typical morphologies of the most abundant S-containing subgroups, “S+Ca”, followed by

“S-rich” and “S+Ca+Si” particles. Those S-containing particles were frequently observed adhering to other particles, including soil dust (Figure 5a, e, f), fly ash (Figure 5b), and soot particle (Figure 5c). “S+Ca” particles of elongated (Figure 5a, e), acicular (Figure 5b), and grain shape were mostly gypsum crystals evidently produced by the interactions between calcium carbonate and atmospheric sulfur dioxide.

Fe-containing particles from natural and anthropogenic emissions can act as the catalyst in sulfation reactions.¹⁴ As shown in EDX elemental X-mapping (Figure 6), an Fe-containing fly ash, probably emitted by coal combustion was found surrounded by several calcium sulfate particles.

Table 3. Number percentage of each subgroup in daytime and nighttime S-containing particles collected in EH at daytime (EHD) and at nighttime (EHN), in Pit 1 at daytime (P1D) and at nighttime (P1N), and at outdoor site at daytime (ODD) and at nighttime (ODN) during winter and summer sampling periods.

Particle Type	Number Percentage (%)											
	Winter						Summer					
	EHD (590)	EHN (385)	P1D (556)	P1N (506)	ODD (563)	ODN (536)	EHD (122)	EHN (57)	P1D (210)	P1N (68)	ODD (195)	ODN (191)
S+Ca	16.07	8.74	17.81	17.55	20.78	22.01	1.03	0.29	2.45	1.00	3.96	4.31
S-rich	9.57	11.17	7.19	8.85	7.03	6.73	0.48	0.50	0.90	0.40	1.32	0.78
S+Ca+Si	7.67	2.94	10.11	6.32	9.10	6.81	6.64	3.22	10.12	3.14	8.13	7.05
S+Na	4.85	4.56	3.63	3.57	4.29	4.61	0.14	0.00	0.00	0.00	0.07	0.00
S+Fe	0.13	0.29	0.50	0.74	0.30	0.30	0.07	0.00	0.06	0.00	0.07	0.20
S+K	0.39	0.59	0.36	0.59	0.15	0.08	0.00	0.07	0.00	0.00	0.00	0.13
Total	38.69	28.29	39.60	37.62	41.64	40.54	8.35	4.08	13.53	4.55	13.55	12.48

Note: Numbers in parentheses are the numbers of S-containing particles being detected.

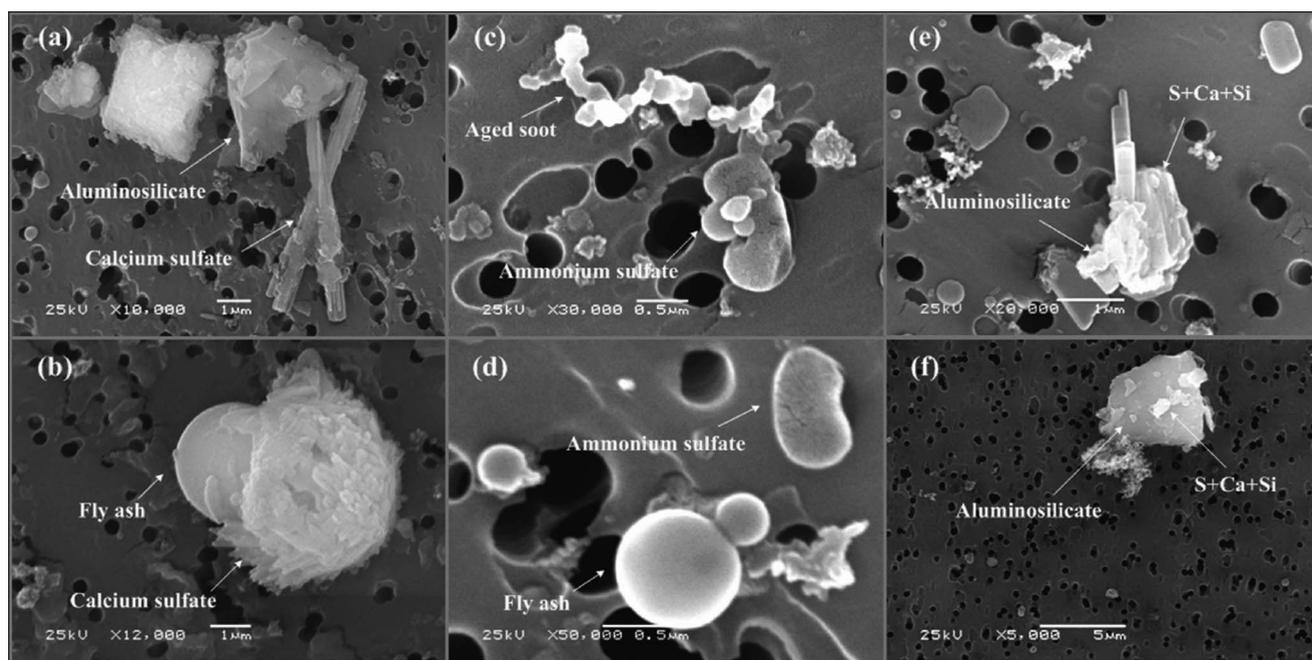


Figure 5. Scanning electron micrograph of typical S-containing particles on Nucleopore filters collected in EH (a, c, d) and Pit 1 (b, e, f).

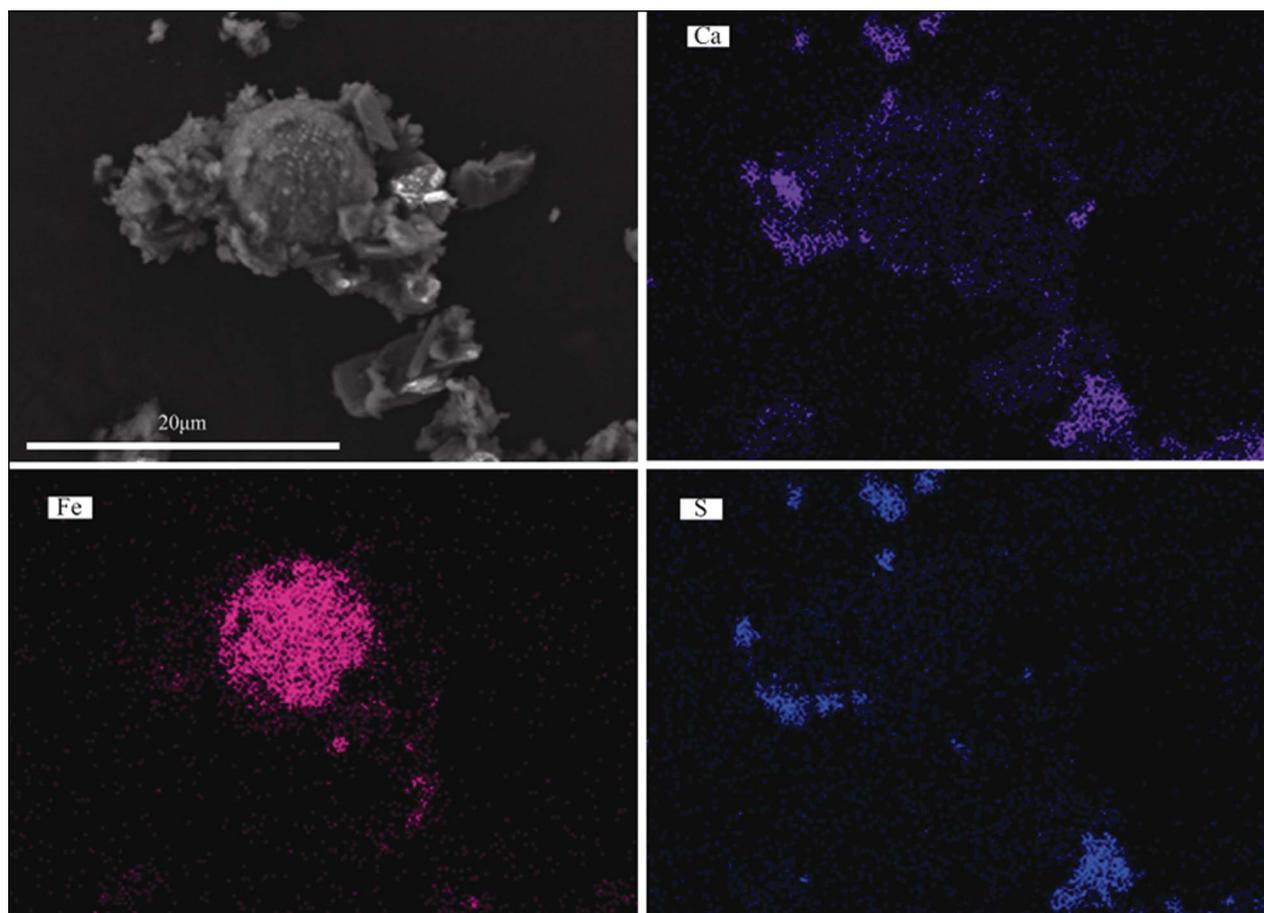


Figure 6. EDX X-mapping image and scanning electron micrograph of a Fe-containing aluminosilicate fly ash surrounded by several calcium sulfate particles.

“S-rich” particles were more frequently observed in winter with near spherical and near cubic shapes, as shown in Figure 5c and d. Those particles were supposed to be ammonium sulfate or ammonium bisulfate formed in a complicated way as secondary particles from homogeneous chemical reactions between ammonia emitted by visitors to the Museum or from surrounding agricultural fields and sulfur dioxide emitted by coal combustion. Simulated experiments have proved that ammonium sulfate can react with calcite during coagulation.¹⁶ A previous study on the mixing state of “S+Ca+Si” particles also showed that soil dust may act as the carriers and/or reactants of sulfate compounds.¹²

Salt weathering is one of the most important and common decay processes that affect materials such as rocks,¹⁷ building stones,⁵ brick,¹⁸ ceramics,¹⁹ and concrete.¹⁹ The harmful effects are mainly associated with chemical reaction and crystallization pressure presented by soluble sulfates on porous calcareous surfaces.²⁰ In a previous study, gypsum crystals were observed near the edge of pits and cracks on the surface of apatite (calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$) lacquer pieces in the Museum.²¹ At higher RH, fine grains of sulfate can dissolve and penetrate into the inner pores of the statues. After evaporation of water, these salts recrystallize and cause stress, which may play an

important role in the formation of pits and cracks on the surfaces of lacquer pieces.

SUMMARY

In a previous study in winter, the mass concentration, type, and size of indoor ambient particles were proved to be associated with visitor activities in the Exhibition Hall and with free air exchange in Pit No. 1. The results of the current study showed that source emissions and the meteorological conditions were responsible for winter and summer changes in the composition and the physicochemical properties of indoor suspended particulate matter. From the point of view of artifact conservation, the artifacts in both display halls face soiling hazard posed by the high level of particle mass concentration in winter and abundance of soot particles in summer. Besides the direct soiling hazard, the formation and transformation of S-containing particles in winter may cause chemical and physical weathering on the surface of terra-cotta and lacquer materials. The urgent matter that should be considered in Pit 1 is to install mechanical ventilation, filtration, and air conditioning systems. As well as in EH, the visitors entered this display hall should be limited to a proper number to decrease the introduction and resuspension of particles. The heating, ventilating, and air conditioning system in EH should

also be operated throughout the year to decrease the soiling hazard from fine particles.

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