Airborne Particles in the Miyagi Museum of Art in Sendai, Japan, Studied by Electron Probe X-ray Microanalysis and Energy Dispersive X-ray Fluorescence Analysis

Jasna INJUK,*† János OSÁN,* René Van GRIEKEN,* and Kouichi TSUJI**

**Department of Chemistry, University of Antwerp, B-2610 Antwerp, Belgium*
***Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-0812, Japan*

The presented work provides baseline data on the existing airborne conditions in the Miyagi Museum of Art in Sendai, Japan, during the summer of 2000. The chemical composition, size and indoor and outdoor origin of the suspended particulate matter were identified using a number of advanced X-ray techniques, such as Electron Probe X-Ray Microanalysis (EPXMA) and Energy Dispersive X-Ray Fluorescence Analysis (EDXRF). Our results, to the best of our knowledge, represent the first detailed study of the chemical nature of the indoor particulate matter in a Japanese museum and, as such, may contribute to future improvements of the air quality inside museums and to the lasting conservation of works of art.

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Introduction

The conservation of works of art displayed in museums can be seriously influenced by indoor air pollution. The potential damage to museum collections from gaseous air pollutants is well documented.[1-4] However, airborne particles have been largely ignored until now, although it is well recognized that the soiling of works of art due to the deposition of airborne particulate matter poses a hazard to museum collections.[5-7] Over long periods of time, dark deposits build up on the surfaces of paintings, sculptures, textiles and tapestries, necessitating expensive and risky cleaning procedures. Besides soiling, deposited airborne material can attack the collections chemically. Alkaline particles released indoors, such as dust from concrete in new buildings, have been reported to have caused problems in Japan.[8] Also, some pigments and colors are pH sensitive. They are vulnerable to gases that are acid precursors, such as sulfur dioxide or nitrogen dioxide. The effect of prolonged contact with sulfate, nitrate and ammonium compounds has not yet been examined. Additionally, metal corrosion could be accelerated by the deposition of acidic particles present in photochemical smog.[4]

In view of the above issues, the purpose of this research effort was to establish the ranges of chemical composition, concentration, size distributions and sources of the airborne particulate matter found in the indoor atmosphere of the Miyagi Museum of Art in Sendai, Japan.

Experimental

During the summer of 2000, airborne particulate matter was collected at different locations inside and outside of the Miyagi Museum of Art in Sendai, Japan. The Miyagi Museum of Art was opened in November, 1981. It is a modern-structure building (steel-reinforced concrete) equipped with HVAC (heating-ventilation-air condition) systems that include double filters (pre-filter and micro-filter) for particle removal. Lying in rolling hills some 6 km distance from the center of Sendai, the museum is surrounded by main city avenues. The relative number of visitors is approximately 200 per day.

Aerosol samples were collected at three different positions inside the museum: restaurant (near the entrance), Gallery 1 (inside) and Sato Gallery (most distant from the entrance) and outside the museum. Ambient up to 24-h samples of both size segregated and total airborne particulate matter were collected at each site.

For bulk aerosol collection, Nuclepore filters of 0.4 μm pore-size and 47 mm diameter were used within a Millipore filter unit connected to a low-volume vacuum pump. For collecting size-segregated aerosol samples, a May cascade impactor with cut-off diameters of 16, 8, 4, 1 and 0.5 μm and Nuclepore filters as a collection substrate were used. The height of the sampling

Table 1 Sampling strategy

Total aerosol mass/ng m^{-3}	Size segregated aerosols (% abundance)
Nuclepore filter (47 mm, 0.4 μm pore size)	Nuclepore filter (0.1 μm pore size)
Millipore filter unit	May impactor (cut-off diameter: 0.5; 1, 2, 4, 8, 16 μm)
Sampling time: 24 h	Sampling time: 30 – 180 min
Flow rate: 20 l min^{-1}	Flow rate: 22 l min^{-1}
Technique: Energy Dispersive X-Ray Fluorescence (EDXRF)	Technique: Electron Probe X-Ray Micro Analysis (EPXMA)

† To whom correspondence should be addressed.
E-mail: injuk@uia.ua.ac.be

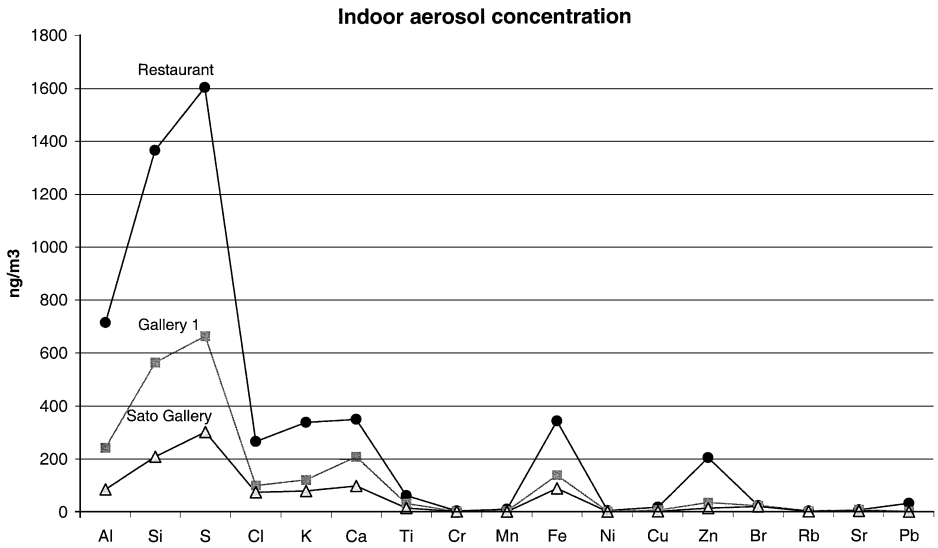

Fig. 1 Elemental aerosol concentrations at the three different places inside the Miyagi Museum of Art.

Table 2 Bulk aerosol concentrations (ng m^{-3}) measured in some European museums (comparison with this work)

Element	Correr Museum, Venice (Italy)	Sainsbury Centre for Visual Arts, Norwich (UK)	Kunsthistorische Museum, Vienna (Austria)	Koninklijk Museum voor Schone Kunsten, Antwerp (Belgium)	The Miyagi Museum of Art-Gallery 1 Sendai (Japan)
Al	890	n.d.	40	n.d.	244
Si	3100	30	110	8	565
S	1200	600	530	50	665
Cl	2700	500	50	9	101
K	1300	20	70	5	123
Ca	15200	30	190	16	211
Ti	150	1	4	n.d.	33
Cr	n.d.	n.d.	n.d.	n.d.	4
Mn	27	n.d.	1	n.d.	4
Fe	1000	52	43	16	139
Ni	n.d.	n.d.	n.d.	2	2
Cu	29	n.d.	9	n.d.	7
Zn	120	7	18	4	36
Br	n.d.	n.d.	n.d.	n.d.	24
Rb	n.d.	n.d.	n.d.	n.d.	2
Sr	n.d.	n.d.	n.d.	n.d.	8
Pb	140	n.d.	13	1	n.d.
Values from	Aug-96	Aug-97	Aug-97	Aug-99	Aug-00

n.d. = not detected.

points was everywhere 1 m.

Energy Dispersive X-Ray Fluorescence (EDXRF) on a Tracor Spectrace 5000 EDXRF instrument was applied for the bulk analysis of the total suspended aerosol samples. The Spectrace-5000 uses a lower power Rh-anode X-ray tube (17.5 Watts). In our measurements, the whole white spectrum by the tube was used to excite the samples under vacuum conditions. For determining high-Z elements, an accelerating voltage of 35 kV and a current of 0.35 mA were used. The acquisition time was set at 10000 s. Low-Z elements were determined at 10 kV and 0.35 mA with an acquisition time of 4000 s. The acquired X-ray spectra were deconvoluted with a non-linear least-squares fitting procedure (QXAS). The measured intensities were converted into elemental concentrations using sensitivity factors obtained from the Micromatter standards (Micromatter, Seattle, WA, USA).

Next to the bulk aerosol samples, size-segregated aerosol samples were analyzed automatically by a JEOL JSM 6300 Scanning Electron Microscope (EPXMA). This instrument is equipped with a PGT energy-dispersive X-ray detector. An accelerating voltage of 20 kV, a beam current of 1 nA and an acquisition time of 20 s per particle were used. The minimal detection limit for elemental concentration was around 1000 ppm, whereas the minimum detectable particle size was 0.2 μm. EPXMA permits one to obtain morphological parameters, such as the diameter and shape factor of a particle, while the chemical composition is derived from an energy-dispersive X-ray spectrum. The relatively large amounts of particles analyzed in each sample (1800 particles from each impactor sample set) generate a huge data matrix. Therefore, a multivariate technique, such as Hierarchical Clustering (HC) is required. This leads to the identification of the different particle types present in the sample, along with their relative abundances. The analyzed particles are divided into different

Table 3 Outdoor museum elemental aerosol concentrations and st. dev. on average (ng m^{-3})

Element	Outdoor	
	begin-August 2000	end-August 2000
Al	1460 ± 70	1940 ± 120
Si	4180 ± 80	5310 ± 90
S	5320 ± 90	4180 ± 60
Cl	165 ± 20	215 ± 18
K	480 ± 20	804 ± 27
Ca	1770 ± 60	2110 ± 65
Ti	150 ± 6	146 ± 6
Cr	6 ± 2	12 ± 2
Mn	51 ± 2	56 ± 3
Fe	1610 ± 50	1870 ± 60
Ni	10 ± 2	8 ± 2
Cu	27 ± 2	37 ± 2
Zn	82 ± 3	142 ± 5
Br	70 ± 2	48 ± 3
Rb	6 ± 2	7 ± 2
Sr	18 ± 2	17 ± 2
Pb	30 ± 2	81 ± 7

Table 4 Comparison of the outdoor elemental aerosol concentrations at different locations in Sendai (mean value ± st. dev. on average, ng m^{-3})

Element	Museum[a]	Institute for Materials Research-7 floor[a]	Sendai[b] Ref. Var *et al*., 2000
Al	1700 ± 120	430 ± 43	626 ± 375
Si	4750 ± 80	930 ± 40	n.d.
S	4850 ± 80	1860 ± 24	n.d.
Cl	190 ± 20	4980 ± 90	n.d.
K	640 ± 20	320 ± 12	n.d.
Ca	1940 ± 60	610 ± 20	570 ± 290
Ti	150 ± 6	32 ± 2	42 ± 24
Cr	9 ± 2	4 ± 1	4 ± 3
Mn	53 ± 2	15 ± 1	19 ± 10
Fe	1740 ± 50	430 ± 6	514 ± 360
Ni	9 ± 2	4 ± 1	3 ± 2
Cu	32 ± 2	19 ± 1	11 ± 3
Zn	112 ± 4	52 ± 2	182 ± 100
Br	59 ± 2	27 ± 1	n.d.
Rb	7 ± 2	3 ± 1	n.d.
Sr	17 ± 2	9 ± 1	n.d.
Pb	56 ± 4	20 ± 3	40 ± 26

a. August 2000.
b. Between 1974 – 1996.
n.d.: not detected.

clusters, based on their compositional similarity. The absolute concentrations of the detected particle types cannot be obtained with this technique. A detailed review of single-particle techniques applied to aerosol samples can be found in Ref 9. An overview of the sampling and analytical procedures is given in Table 1.

Results and Discussion

Total aerosol mass concentrations

Indoor. Figure 1 gives the results of the total aerosol mass concentrations obtained at three different locations inside the museum. The numbers are the arithmetic mean concentrations of 17 elements measured. It is clear that the elemental

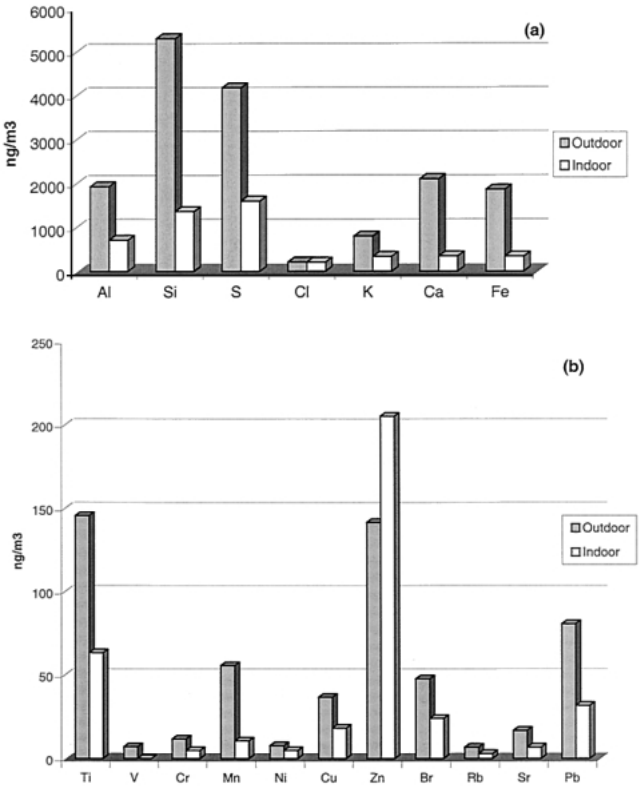

Fig. 2 Comparison of the outdoor and indoor elemental aerosol concentrations.

concentrations inside the restaurant, located at the ground level of the museum, are significantly higher than those in Gallery 1 (immediately adjacent to the entrance and the restaurant) and at Sato Gallery (first floor). The same trend, observed for all of the elements, unfortunately indicates a good exchange with the indoor environment. The combustion products from the restaurant and cafeteria certainly penetrate into galleries, and are expected to end up in the exhibition areas, and then possibly damaging the works of art.

Table 2 gives the results for bulk aerosol samples during this campaign, which are represented along with those for several European museums.[10] The different architecture and environment of the selected museums are clearly reflected in the composition and concentrations of the indoor aerosols. The comparison reveals the highest values to be found in the Correr Museum in Venice (Italy) followed by those in the Miyagi Museum of Art. The influence of visitors (both museums are on the average daily visited by 200 people) and the presence of carpets (both museums) are clearly reflected in the concentrations of soil-derived elements, like Al, Si and Ti. These values are more than ten-fold higher than those in the other three museums. When the absolute concentrations of S and Fe are considered, the situation in both the Correr Museum and the Miyagi Museum cannot be regarded as ideal.

Outdoor. The outdoor elemental aerosol concentrations, measured in the backyard of the museum, are given in Table 3. The values refer to two different periods: the beginning and the end of August, 2000. A comparison with the values obtained during the same period, but some 6 km downtown (at the Institute for Materials Research) and with the literature values mentioned earlier[11] reveals a high degree of variations (Table 4). The composition of the outdoor samples is clearly influenced by the meteorological parameters (*e.g.* weather conditions, like

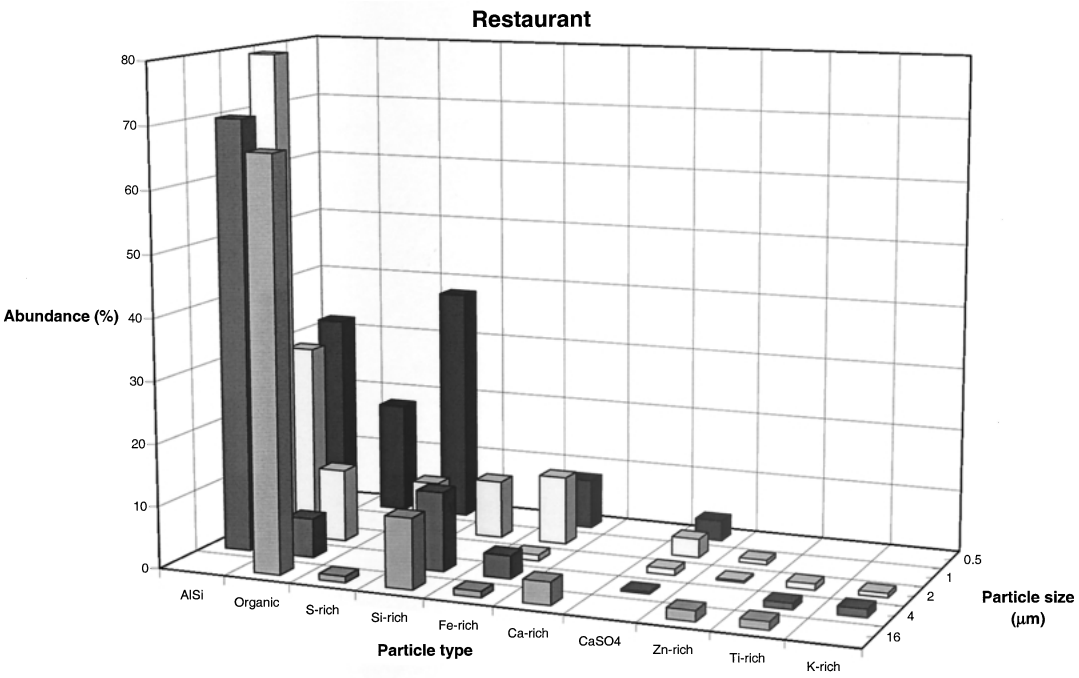

Fig. 3 Identified major particle types and their size inside the restaurant.

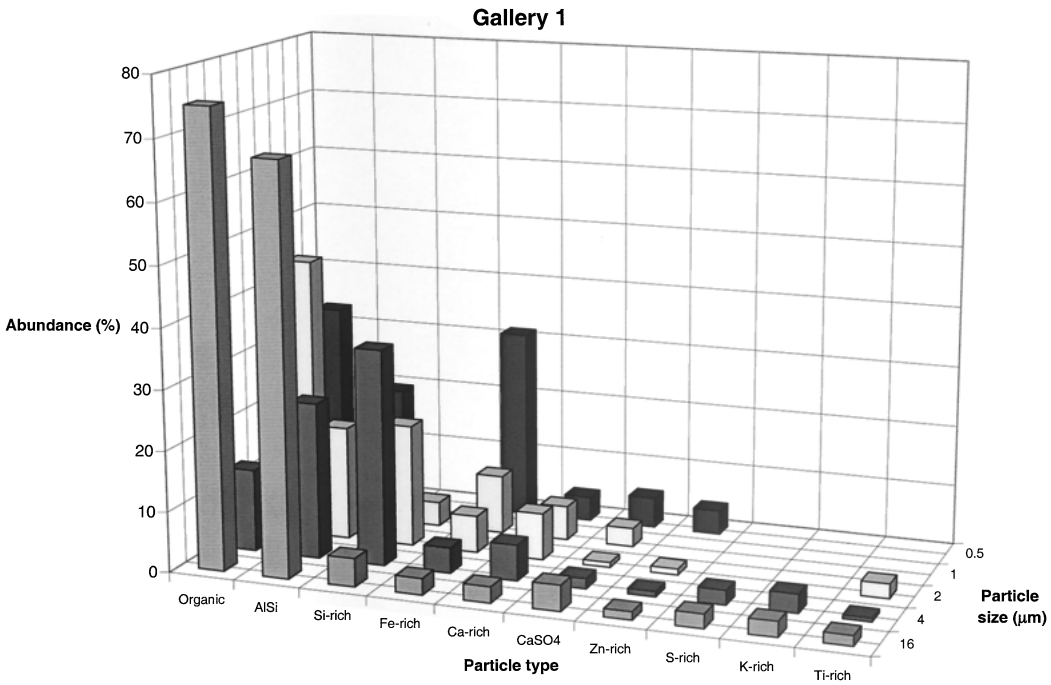

Fig. 4 Identified major particle types and their size inside the Gallery 1.

wind speed, temperature and precipitation).

Comparison indoor/outdoor. Figures 2(a) and (b) verify that the indoor elemental aerosol concentrations are substantially below those measured outdoors. According to Wallace,[12] in the absence of indoor sources, the indoor/outdoor ratio would be between 0.43 to 0.65, depending on the size of the particulate matter. A comparison of our results leads to the conclusion that for almost all of the measured elements, the indoor/outdoor ratios range from 0.2 (Ca) to 0.6 (Ni). This indicates that a direct exchange with the outdoor environment does not occur. The air exchanges between the outdoor and indoor air are entirely due to filtration and because of opening doors. In the case of Cl, no difference was observed, while for Zn the indoor/outdoor ratio exceeded 1.5. This was mainly due to exceptionally high Zn values determined inside the restaurant. Clearly, an extra indoor source of Zn must be present in the restaurant, very likely due to combustion and maintenance operations, such as floor waxing and vacuuming. Based on this study, it cannot be stated that this source poses a significant soiling hazard in the museum, but it is highly advisable to adopt

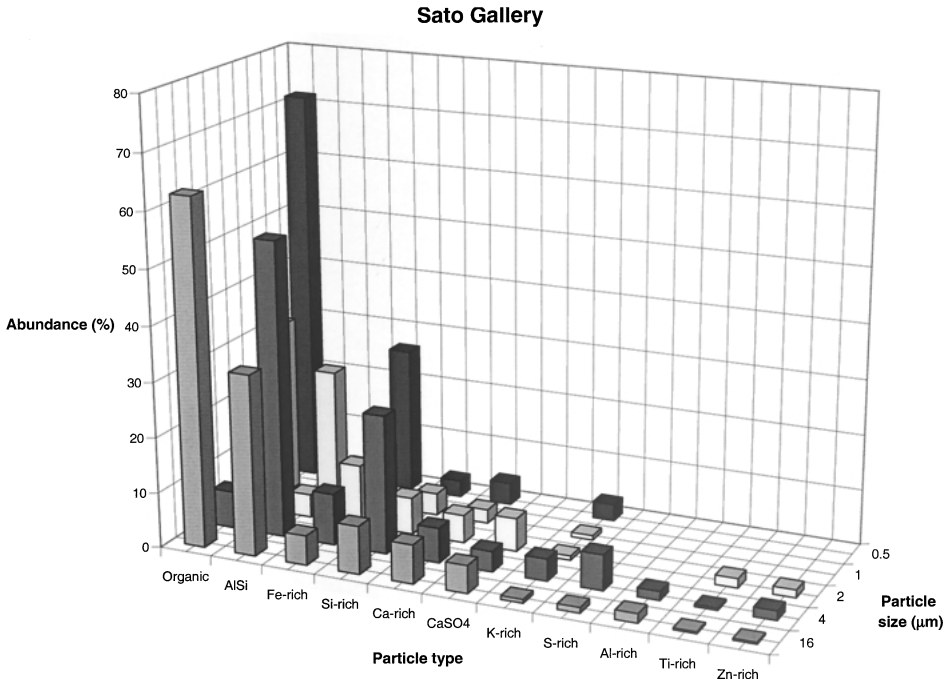

Fig. 5 Identified major particle types and their size inside the Sato Gallery.

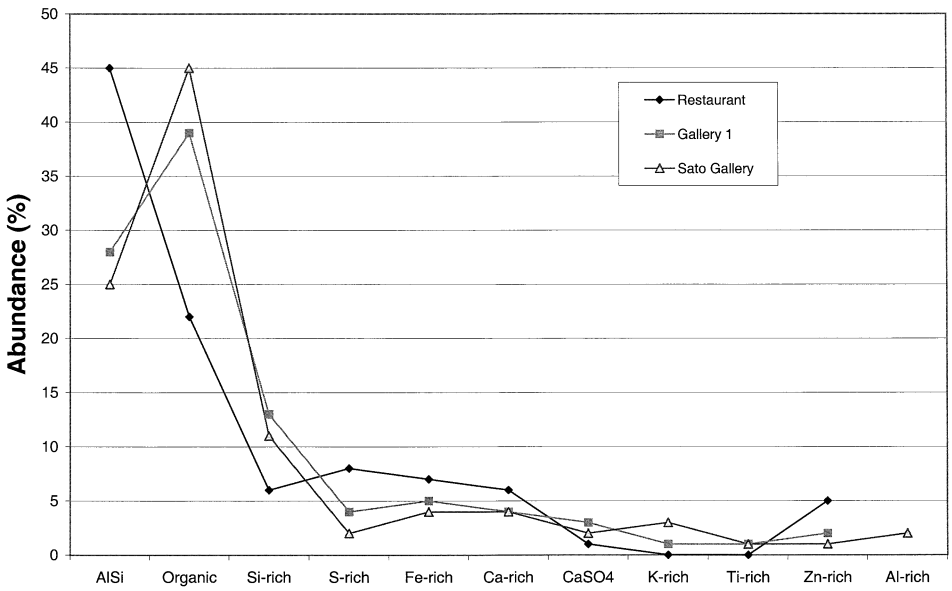

Fig. 6 Overview of the most important particle types inside the museum.

measures to control indoor particle generation inside the restaurant.

Single particle analysis

Figures 3, 4 and 5 show that airborne particles cluster into distinctly different size ranges with different chemical properties. Coarse particles (with diameters of about 2 μm and larger) consist largely of aluminosilicates (soil dust and fly ash) and organic material. Fine particles (smaller than 2 μm in diameter) consist mainly of organic particles, soot, acidic material and Fe- and Ca-rich particles. Special attention should be drawn to the composition of the particles in a size range of around 0.5 μm, since they are especially important regarding conservation. According to Camuffo *et al.*,[13] the estimated deposition flux is maximum in this size range.

An overall analysis of the most important particle types in the museum is given in Fig. 6. By far, the most abundant particles in the museum are organic and aluminosilicates. Aluminosilicates dominate in the restaurant (comprising about 45%), while organic particles are most prominent in the galleries (comprising about 40%). Soil dust particles (AlSi, Ti) are mostly introduced by visitors, and can later be resuspended. A large number of visitors can increase the soil dust concentrations by a factor of 10 to 100. This process is even

more efficient in the presence of carpets (enhancement by a factor of 10), that are present in both galleries. Unfortunately, the composition of organic particles was beyond of this work.

In accordance with a bulk aerosol analysis, the concentrations of potentially damaging S-rich and Fe-rich particles were found to be considerable. S-rich organic material is dangerous because it can be oxidized to H_2SO_4. This leads to a fading of pigments; paper and textiles can be damaged, and the corrosion of metals is accelerated. Fe-rich particles have a negative effect because they act as catalysts for the oxidation of SO_2 to H_2SO_4. Moreover, significant soiling could be caused by the numerous Ca- and Si-rich particles found in the museum, although they are not chemically damaging. Ca- and Si-rich particles have their origin in building materials. The presence of K-rich particles is attributed to cigarette smoking and combustion processes. Zn-rich particles, having their source in the restaurant, were found to be strongly accumulated through-out the museum. The presence of $CaSO_4$ particles should be recognized as well, since they constitute a medium for blackening by the adsorption of soot.

Overall, based on EPXMA, it can be stated that all of the investigated (deposited) particles might be considered to be harmful because they cause soiling and visual degradation. In that respect, our results clearly stress the importance of improving of the indoor air quality inside the museum.

Conclusions

The results from this study serve several purposes. Firstly, they provide considerable information, beyond that previously available, about the indoor airborne particulate concentrations and chemical composition, their sizes and possible indoor sources in the Miyagi Museum of Art in Sendai, Japan. Secondly, they should help to explore the options available to museum conservators to reduce the soiling rates due to the presence and the deposition of airborne particles within the museum. The potential effectiveness of several control options, like reducing the ventilation rates, improving particle filtration with filters of higher collection efficiency, especially for small particles, and limiting indoor aerosol sources, should be re-examined. Thirdly, they provide perspectives from a wide-ranging context of protecting museum collections.

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