Environ Earth Sci (2011) 63:1433–1445
DOI 10.1007/s12665-010-0657-5

SPECIAL ISSUE

Characterization of indoor and outdoor atmospheric pollutants impacting architectural monuments: the case of San Jerónimo Monastery (Granada, Spain)

Velichka Kontozova-Deutsch · Carolina Cardell · Maja Urosevic · Encarnación Ruiz-Agudo · Felix Deutsch · René Van Grieken

Received: 15 April 2010 / Accepted: 5 July 2010 / Published online: 20 July 2010

Abstract Indoor and outdoor concentrations of atmospheric gaseous pollutants as well as composition, size, and morphology of particulate matter have been investigated at the monastery of San Jerónimo in Granada (Southern Spain). Complementary micro- and nano-analytical techniques were applied; elemental and mineralogical composition and morphological characteristics of particulate matter were investigated combining electron probe microanalysis at the single particle level, and bulk aerosol samples were analyzed using energy-dispersive X-ray fluorescence, X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray analyzer and transmission electron microscopy (TEM). Microclimatic conditions at the monastery were monitored, and gas concentrations were assessed by means of diffusion tubes subsequently analyzed with ion chromatography. Results revealed high abundances of soil dust particles (aluminosilicates, calcite, dolomite, quartz), salt aerosols (chlorides, sulfates and ammonium-rich salts), and NO_2 and SO_2 both outdoors and indoors. Amorphous black carbon particles had surprisingly high abundances for Granada, a non-industrialized city. The composition of indoor particles corresponds to severe weathering affecting the construction materials and artworks inside the church; moreover their composition promotes a feedback process that intensifies the deterioration. Chemical reactions between chloride-rich salts and pigments from paintings were confirmed by TEM analyses. Indoors, blackening of surface decorative materials is fostered by particle re-suspension due to cleaning habits in the monastery (i.e. dusting). This is the first air quality study performed in a monument in the city of Granada with the aim of developing a strategy for preventive conservation.

Keywords Atmospheric aerosols · Architectural monument · SEM–EDX · EPMA · TEM · Preventive conservation

V. Kontozova-Deutsch · R. Van Grieken
Micro and Trace Analysis Centre, Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Belgium

C. Cardell (✉) · M. Urosevic · E. Ruiz-Agudo
Department of Mineralogy and Petrology, University of Granada, Av/Fuentenueva s/n, 18071 Granada, Spain
e-mail: cardell@ugr.es

F. Deutsch
Environmental Modeling Unit, Flemish Institute for Technological Research (VITO), Boeretang 200, 2400 Mol, Belgium

Introduction

Most buildings of cultural interest are located in urban environments, where pollution caused by road traffic, residential heating systems, and industry has harmful consequences for outdoor and indoor construction and decorative materials (Pérez-Rodríguez et al. 1998; Van Grieken et al. 2000; Esbert et al. 2001; Moropoulou et al. 2001; Jordan et al. 2009). On the exterior of buildings, black crusts are formed and dust is deposited due to impact of gases and particles, leading to undesirable aesthetic effects and also compromising the integrity of the materials (Pérez-Rodríguez et al. 1998; Esbert et al. 2001; Moropoulou et al. 2001; Bonazza et al. 2005; Sanjurjo Sánchez et al. 2009; Xu et al. 2010). The aggressiveness of particles depends on their composition, size, hygroscopicity, and solubility; for example, deposition of acids such as sulfuric and nitric acid

can lead to local corrosion processes on certain stones, glass, paintings, and metals (Nazaroff et al. 1993; Sabbioni et al. 2003; Tétreault 2003). On the other hand, indoor air pollution, a result of both indoor and outdoor phenomena, can cause soiling and chemical weathering of decorative materials via adsorption of gases or particulate matter (Sánchez-Moral et al. 1999; Gysels et al. 2004; Worobiec et al. 2006; Spolnik et al. 2007; Kontozova-Deutsch 2007; Jordan et al. 2009).

Currently, preventive conservation measures are acknowledged as important for safeguarding cultural heritage (CH), both in terms of preserving CH and also reducing the cost of future conservation measures. Preventive conservation requires knowledge of a variety of parameters connected to a specific CH site, including microclimatic conditions, concentration, and character of caustic gases and particles in the surrounding air, as well as management of the CH site (Cataldo et al. 2005; Kontozova-Deutsch et al. 2008a; Worobiec et al. 2008; Brimblecombe et al. 2009). Hence, monitoring and sampling campaigns for air pollutants and microclimatic parameters have to be performed to identify possible threats and thereby remedies (Delalieux et al. 2001; Esbert et al. 2001; Camuffo et al. 2002; La Gennusa et al. 2005; Corgnati et al. 2009; García-Diego and Zarzo 2010).

There is a vast body of literature tackling the impact of outdoor and indoor air composition and microclimate on damaging our CH, in which diverse analytical techniques are applied to characterize and quantify atmospheric aerosols, such as, e.g., electron probe microanalysis (EPMA), X-ray fluorescence (EDXRF), scanning electron microscopy (SEM), ion chromatography (IC), gas chromatography–mass spectrometry (GC–MS), transmission electron microscopy (TEM), and X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and recently Raman spectroscopy (RS) (Weinbruch et al. 1997; Van Grieken et al. 2000; Delalieux et al. 2001; Ro et al. 2001; Murr and Bang 2003; Liu et al. 2005; De Hoog et al. 2005; Simão et al. 2006; Ivleva et al. 2007).

Most of these studies have been carried out in well-protected buildings like museums (Camuffo et al. 2002; Gysels et al. 2004; La Gennusa et al. 2005: Corgnati et al. 2009), which differ from numerous churches that are required to be open for congregation and which commonly use incense and candles in liturgical practices (Worobiec et al. 2006, 2008; Spolnik et al. 2007; Kontozova-Deutsch et al. 2008b; García-Diego and Zarzo 2010). This is the case of the church of the monastery of San Jerónimo (Granada, Spain). The purpose of this work was to characterize at micro and nano-scale, outdoor and indoor air composition at the monastery of San Jerónimo in Granada (Southern Spain). To this end qualitative and quantitative analyses of atmospheric particulates and gases were performed by combining complementary mineralogical and elemental analytical techniques to typify the levels, composition, and also size and morphology of particulates. The origin of the outdoor and indoor aerosols and their contribution to damaging the artworks exposed inside the church of the monastery are assessed.

Experimental

Sampling location

The city of Granada in Southern Spain has a population of around 300,000 (agglomeration 600,000). It is about 50 km from the Mediterranean Sea and approximately 200 km from the African continent. The city is situated in a natural basin surrounded by mountains with altitudes up to 3,500 m. Due to this topography and the prevailing low wind speeds, in combination with traffic emissions, pollution-derived particulate matter often accumulates in the urban air of Granada (Lyamani et al. 2010). The city has a near-continental climate with cool winters, hot summers, and high diurnal temperature variability. Most rainfall occurs during winter and spring seasons, leading to re-suspension of dust particles predominantly in the dry seasons.

The investigated monastery of San Jerónimo is located in the city center of Granada, surrounded by busy streets. Its construction started in 1496 and was directed by two famous architects: Jacobo Florentino until 1526 and later by Diego de Siloé, the most famous Spanish architect at that moment. It is a splendid Renaissance temple with an extraordinary church, one of the best representative works of the Spanish Baroque with a spectacular altar piece and choir, considered one of the masterpieces of Spanish sculpture. The interior of the temple is entirely covered with polychromes. The monastery was plundered during Napoleon's invasion and converted into cavalry barracks. Numerous restorations of the remains have been undertaken, most recently in 1998. At present, the monastery of San Jerónimo constitutes a historic building where numerous scientific investigations have been realized, as for example salt weathering characterization and investigations on salt inhibitors (Cardell 1998; Laiz et al. 2000; Cardell and Rodríguez-Gordillo 2003; Ruiz-Agudo 2007). However, prior to this study no research on air quality in the framework of a CH study had been carried out in this or other monuments in the city of Granada.

The sampling campaign was carried out in the period of February–March 2008. Samples of gaseous (NO_2, SO_2, O_3) and particulate pollutants (bulk and single particles) were taken indoors and outside the monastery. The sampling locations are shown in Fig. 1. Outdoor samples were taken

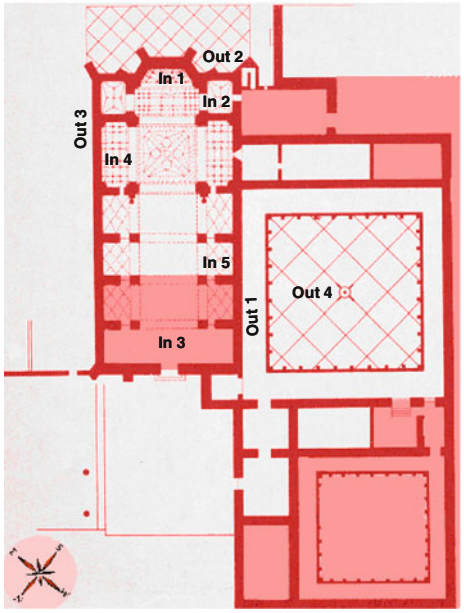

Fig. 1 Sampling locations and outline ground-plan of the monastery of San Jerónimo (Granada, Spain). Map reproduced with permission (Cardell 1998)

Sample	Sample location	Type of sample
In 1	Altar, h=1m	gases
In 2	Lateral room, W altar h=1m	gases
In 3	Organ, h~5m	gases, bulk and single particles
In 4	Side chapel E, h=1m	gases, bulk and single particles
In 5	Side chapel W, h=1m	gases
Out 1	Cloister, 1st floor h~5m	gases, bulk and single particles
Out 2	Apse, h~20m	gases
Out 3	Roof, h~20m	gases, bulk particles
Out 4	Cloister, garden h=1m	gases

at two different heights at the church and the major cloister. Inside the church sampling sites were selected considering orientation and height in order to establish possible differences in both quantity and composition of particles. The altar and lateral rooms are the most distant from the entrance, which is situated in the NW of the church connected to the major cloister. Hence, less deposition of outdoor-derived particulate matter can be expected at those locations. The organ is found on the first floor above the entrance at approximately 5 m above ground level (a.g.l.). Some of the stained glass windows of the church are broken and the main entrance remains open during visiting hours (in winter from 1000 to 1830 and in summer from 1000 to 1930). Hence, pigeons can fly inside and the indoor–outdoor air exchange can be expected to be quite large. In addition, in this work a PM10 sample (AER-GR) was taken at the roof of the Andalusian Centre for Environmental Studies (CEAMA), located in Granada.

Analysis of gaseous pollutants

SO_2, NO_2, and O_3 were collected by means of radiello® (Fondazione Salvatore Maugeri, Padova, Italy) diffusive samplers, exposed in parallel for 1 week, both indoors and outdoors. The radiello® sampler consists of a chemically adsorbing cartridge, surrounded by a cylindrical microporous diffusive body (5.8 mm diameter, 60 mm height) coated with triethanolamine (TEA) and was mounted on a supporting plate.

NO_2 and SO_2 were chemically adsorbed onto TEA, respectively, as nitrite (NO_2^-) and sulfite (SO_3^{2-}), or sulfate (SO_4^{2-}). They were quantitatively recovered from the cartridges by means of extraction in 5 mL of Milli-Q water (Millipore, Haverhill, USA). Nitrite and sulfite contents were determined by means of IC. Analysis of aqueous extracts was performed on a dual-column Dionex DX-120 ion chromatograph (Dionex, Sunnyvale, USA) equipped with a Dionex AS50 auto sampler. Suppression of background conductivity was achieved with a Dionex self-regenerating suppressor model ASRS-ULTRA (anions) with neutralization of the eluent by exchanging its counter ions with H^+ (generated by the electrolysis of H_2O). The separation of the anions was attained on an AG14 guard column, preceded by an AS14 analytical column. The eluent was composed of 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$ at 1.2 mL min^{-1} flow rate. Calibration was performed using certified standard multi-ion solutions (Combined Seven Anion Standard II, Dionex, USA), diluted to obtain effective concentrations of 20, 10, 5, 2.5, and 1 ppm standard solutions. Data acquisition, calibration curve, and peak integration were done using the Peaknet software package, version 6.11.

The diffusion tubes for O_3 sampling consisted of a polyethylene tube, filled with 4,4′-dipyridylethylene-coated silica gel and closed, at one end, by a PTFE cap. During exposure, the 4,4′-dipyridylethylene was transformed into 4-pyridylaldehyde through ozonolysis. A silica gel ensured the presence of H_2O inside the pores, necessary to complete the ozonolysis reaction. During sample preparation, 4-pyridylaldehyde was recovered from the silica gel by adding 3-methyl-2-benzothiazolinone hydrazone (MBTH). Subsequently, 4-pyridylaldehyde was converted into the corresponding yellow-colored azide, analyzed by means of UV–Vis spectrophotometry (UVIKON 930, Kontron Instruments) at 430 nm.

Analysis of single particles

For the collection of size-segregated aerosol samples, a 9-stage May cascade impactor was applied with aerodynamic cut-off diameters of 8, 4, 2, 1, and 0.5 μm for stages 3, 4, 5, 6, and 7. As collection substrates Si wafers and Ag foils were chosen. The size-segregated samples were analyzed by an electron probe microanalyser (EPMA, JEOL 733, Tokyo, Japan) equipped with an ultra-thin window Si(Li) detector (Oxford). To avoid beam damage of the analyzed particles, cooling of the sample holder by liquid nitrogen was applied, which is especially important for low-Z elements. Approximately 300 particles were measured on each stage, so almost 1,500 individual aerosol particles were analyzed in one sample set. The X-ray spectra were processed using the *AXIL* software for both EDXRF and EPMA (Van Espen et al. 1986). For EPMA, quantitative calculations of the particle composition (including light elements such as C, N and O) were performed using a method based on iterative Monte Carlo simulations using the in-house program *Elementary* (Ro et al. 2003). The large data set from the single-particle analysis was treated by statistical methods. To compare the different aerosol sample sets, all particles were classified by non-hierarchical clustering analysis based on the Forgy algorithm (Massart and Kaufmann 1983). The initial centroids were selected by a sequence of hierarchical cluster analyses using the homemade software *IDAS* (Bondarenko et al. 1996). The results for the five stages were divided into three representative and main fractions: the fine fraction, which contains average results of particles with cut-off diameter of 0.5 and 1 μm (and thus suitable to be characterized at nanoscale by TEM), the middle-sized fraction, which contains average results of particles with cut-off diameter of 2 and 4 μm, and the coarse fraction comprising the average results of particles with cut-off diameter of 8 m. These last two fractions were suitable to be analyzed by micro (SEM–EDX) and mineralogical (XRD) analytical techniques as well.

Bulk aerosol particles

For the collection of bulk aerosol samples from the monument, Nuclepore® filters of 0.4 μm pore-size and 47 mm diameter were used in a Millipore filter-unit connected to a low-volume vacuum pump. The average sampling time was 24 h and the flow rate about 30 L min^{-1}. Bulk concentrations were analyzed for up to 20 elements by energy-dispersive X-ray fluorescence (EDXRF) analysis. The measurements were carried out with a Tracor Spectrace-5000 instrument employing a low-power Rh-anode X-ray tube (17.5 W). For the determination of high-Z elements (starting from K) a tube voltage of 35 kV, a current of 0.35 mA, and an acquisition time of 10,000 s were selected. For low-Z elements (from Al to Cl), the tube voltage was adjusted to 10 kV; a current of 0.35 mA, and an acquisition time of 4,000 s were used. The detection limits were between 5 and 10 ng cm^{-2} on the filters. The measured intensities were converted into elemental concentrations by the application of the *AXIL* program code (Van Espen et al. 1986).

Conventional powder XRD was used to determine the mineral composition of the bulk aerosol samples taken from the monastery (indoors and outdoors), as well as the PM10 (AER-GR) sample collected from the CEAMA. The PM10 (AER-GR) sample was collected during 12 h by means of a high-volume sampler MCV-CAV with DIGITEL DH-80 and with a flow rate of 30 m^3 h^{-1}, using circular glass fiber filters (15 cm, QF20 Schleicher and Schuell, Dassel, Germany). To perform the XRD analyses, a Philips PW-1710 diffractometer was used with the Bragg–Brentano focusing geometry, a graphite secondary monochromator, CuKα radiation ($\lambda = 1.5405$), and automatic divergence 1° slit. The voltage was 40 kV and the tube current 40 mA. Diffraction patterns for the total suspended aerosols were obtained using continuous scan mode exploring an area over 3°–64° 2θ, with 0.05 scan rate, and 0.80 integration time. XRD was applied directly to the Nuclepore® filter surface (no sample preparation was required). Automatic acquisition, evaluation, and identification of minerals were carried out with the *Xpowder* software (Martín-Ramos 2004).

To study the chemical composition and micro-morphology of the bulk aerosol samples taken from the monastery and the PM10 sample (AER-GR), a scanning electron microscope (SEM Leo 1430VP, VP-SEM) coupled with an EDX microanalyzer (Inca 350 version 17, Oxford Instruments) was used. Analyses were carried out in secondary electron (SE) and backscattered electron (BSE) mode. Both operating modes are complementary, as SE-mode provides information on texture and structure and BSE-mode on elementary composition. The SEM–EDX working conditions were 500 pA filament current, 20 keV beam energy, 10 eV/ch resolution, and an acquisition time of 50 s for pinpoint analyses. Samples requiring no preparation were mounted on a tee and coated with carbon for microanalysis purposes, and with gold to better visualize the morphology.

Transmission electron microscopy (Philips CM20) equipped with an EDAX solid-state ultrathin-window energy dispersive X-ray (EDX) detector was used to investigate the composition and morphology at nanoscale of the indoor and outdoor samples from the monastery and the PM10 sample (AER-GR). The acceleration voltage of the microscope was 200 kV, and a lens aperture of 40 μm was used as a compromise between amplitude and phase

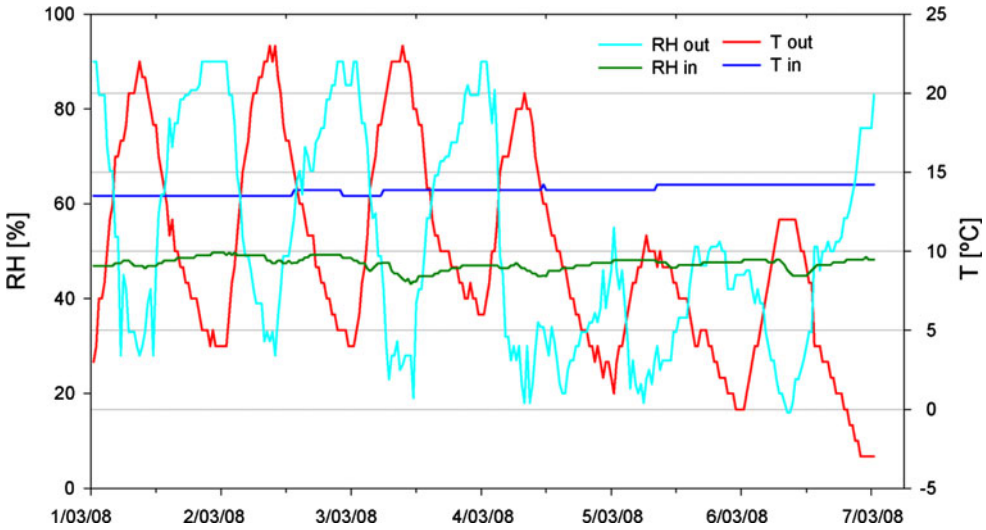

Fig. 2 Temperature and relative humidity at the monastery of San Jerónimo (Granada, Spain)

contrast for the images. The identification of phases was facilitated by collecting selected area electron diffraction (SAED) patterns. Quantitative analytical electron microscopy analyses were performed in scanning TEM mode using a 10-nm diameter beam and a 20 × 100 nm scanning area. A low-background condenser aperture and an analytical Be sample holder were employed to improve spectrum quality. Prior to TEM analysis samples were dispersed in ethyl alcohol and deposited on Formvar© and carbon-film coated Cu grids.

Microclimatic parameters, namely temperature (*T*) and relative humidity (RH) were monitored during the sampling period by means of Signatrol SL502 (Signatrol Ltd, Gloucestershire, UK) sensor. The data were collected every 20 min indoors (altar, In 1) and outdoors (major cloister, Out 1).

Results and discussion

Microclimatic parameters

Figure 2 shows the trend of *T* and RH recorded outside and inside the monastery during the sampling campaign. Outdoors, the means of *T* and RH were 10.5 ± 6.6°C and 44.3 ± 22.6%, respectively. It should be recalled that the city of Granada has a near continental climate with large day/night amplitudes of temperature and RH (Cardell 1998; Lyamani et al. 2010). These fluctuations cause high thermal stress to stone materials accelerating their deterioration (Rodríguez-Gordillo and Sáez-Pérez 2006). As result, particles are easily generated and subsequently may enter the studied building and cause soiling and deterioration of artworks exposed indoors. In the interior of the church the mean *T* (13.9 ± 0.3°C) and mean RH (47.5 ± 1.5%) stayed almost constant due to the buffering effect of the high volume of the building. This circumstance is certainly advantageous for the preservation of the artworks in the church.

Gaseous pollutants

The results obtained for concentrations of NO_2, SO_2, and O_3 are shown in Fig. 3. Indoor and outdoor mean concentrations of NO_2 were found to be similar. The average indoor value of NO_2 was 29 μg m^{-3}, whereas a mean outdoor value of 32 μg m^{-3} has been measured. NO_2 is a gas with largely outdoor sources (via NO_x, mainly from road traffic). The comparable NO_2 values could be attributed to the considerable indoor–outdoor air exchange in the church (due to circumstances mentioned above, see sampling location), and the lower deposition velocity compared with that of O_3. However, indoor sources have to be considered as well, such as burning candles and incense, the latter particularly during weekends. Similar trends have been identified in other churches (Spolnik et al. 2005; Worobiec et al. 2006; Kontozova-Deutsch et al. 2008b).

As expected, indoor SO_2 concentrations were lower than outdoors. The average SO_2 value was 1.6 μg m^{-3} for indoors, and 3.6 μg m^{-3} for outdoors. Surprisingly, the SO_2 concentrations in the interior of the church were higher than others reported in the literature, which were near the detection limit (Spolnik et al. 2005; Worobiec et al. 2006; Kontozova-Deutsch et al. 2008b). Again, the considerable indoor–outdoor air exchange in the church likely plays an important role as no significant indoor SO_2 sources have been identified.

The average outdoor O_3 concentrations were much higher than those indoors. The calculated O_3 mean value for outdoors was 12 μg m^{-3}, versus only 0.6 μg m^{-3} indoors. This result has to be attributed to the high-deposition velocity and reactivity of the O_3, and the absence of

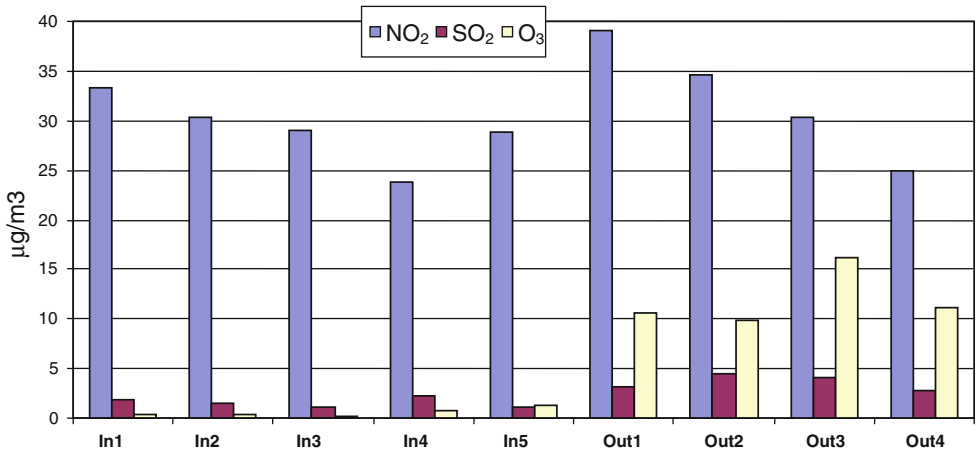

Fig. 3 Indoor and outdoor concentrations of NO_2, SO_2 and O_3 at the monastery of San Jerónimo (Granada, Spain)

an indoor ozone sources. The obtained O_3 values (both indoors and outdoors) are rather low in comparison with indoor O_3 concentrations measured during winter in other churches (Worobiec et al. 2006; Kontozova-Deutsch et al. 2008b). The location of the monastery in the city center of Granada, near busy streets, should be responsible for these low O_3 concentrations since high NO_x (mainly NO) emissions by traffic lead to substantial ozone titration.

The literature reports that NO_2 causes formation of nitric acid (HNO_3) leading to decomposition of lime-containing materials, fading of pigments, and corrosion of metals (Tétreault 2003). On the other hand, SO_2 oxidizes quickly to sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4), which leads to damage of basic construction and decorative materials like limestone, plaster, and frescoes. The interior of the church of San Jerónimo is covered with mural paintings and polychromes (on a substrate of gypsum-based plaster), severely damaged by salt crystallization at particular sites, thus exposing the limestone used to build the church (Cardell 1998; Cardell and Rodríguez-Gordillo 2003). Hence, the high indoor concentrations of NO_2 and SO_2 are a potential threat for the construction and artwork materials contained in the monastery.

Single particles

The results of the size-segregated single particle analysis performed with EPMA are shown in Fig. 4. The samples were divided into three fractions (fine, middle and coarse) according to their aerodynamic cut-off diameters (8, 4, 2, 1 and 0.5 µm for stages 3, 4, 5, 6 and 7). Soil dust particles, i.e., aluminosilicates (AlSi + Fe-oxid) were found in particles of the middle size-fraction and in coarse particles. Aluminosilicates derive from the geological materials present in the vicinity of the city, e.g., limestones and metamorphic rocks (Puga et al. 2007). In addition, sources such as windblown soil dust, road traffic, and fly ash aerosols have to be considered (Lyamani et al. 2010). Aluminosilicates showed higher abundances in indoor versus outdoor samples. This fact has to be attributed to the intense sanding-off of various construction materials used to build the monastery, such as renders, mortars and, to a smaller extent, bricks, all severely altered as described elsewhere (Cardell 1998) (Fig. 5). Additionally, transport of these particles by the shoes of visitors and monastery nuns may also contribute to the observed high indoor abundances. Inside the building, re-suspension of particles plays an important role as inferred from the cleaning habits (dusting instead of vacuum cleaning or moist wiping) and the high amounts of dust deposited at unreachable places. The high abundance of soil dust particle type certainly represents a threat to the indoor environment, since these particles can accelerate the soiling of material surfaces, although they are not considered to be chemically aggressive. Dust accumulation is an important management and conservation problem in monuments (Brimblecombe et al. 2009).

Calcite ($CaCO_3$) was the most abundant mineral found in particles of the fine and middle size-fractions, while dolomite ($CaMg(CO_3)_2$) was detected only in the fine size-fraction. Calcite particles of the fine and coarse fractions showed slightly higher abundances indoors. Limestone (calcite-bearing rock) and dolostone (dolomite-bearing rock) are abundant near the city of Granada and have been used profusely as construction materials in ancient and modern buildings such as the monastery of San Jerónimo (Cardell 1998). However, the high abundance of these minerals inside the church suggests a source from deterioration of construction materials (limestone and mortars; already visible to the naked eye), in addition to mineral particles originating from outdoor sources entering by the indoor–outdoor air exchange.

Ammonium sulfate ($(NH_4)_2SO_4$) particles clustered with carbon (C) were found only in the fine fraction and predominantly in the smallest particles. Abundances were slightly higher for outdoor versus indoor samples. This

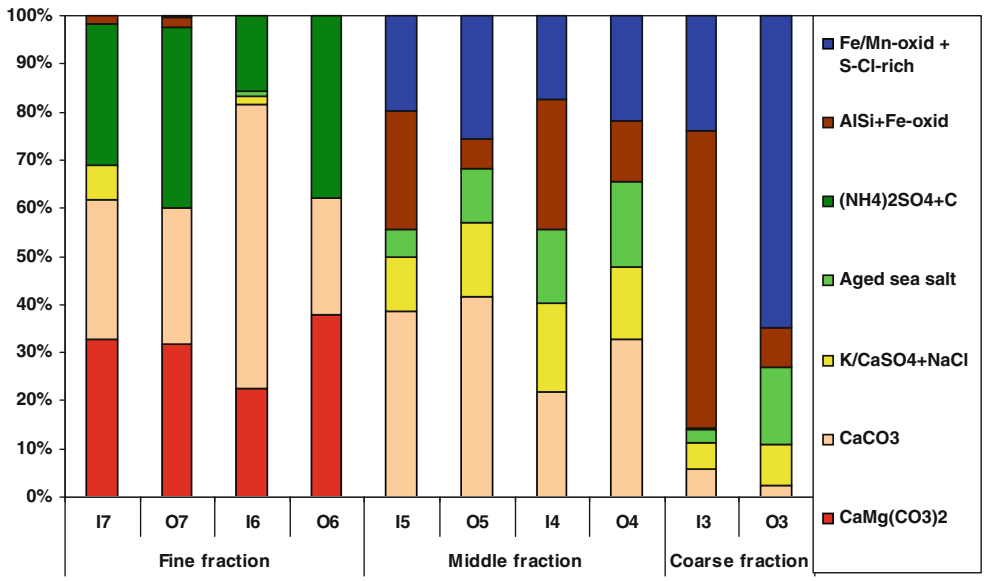

Fig. 4 Relative abundances of particle types in indoor and outdoor samples of the fine, middle-sized, and coarse size fraction in the monastery of San Jerónimo (Granada, Spain)

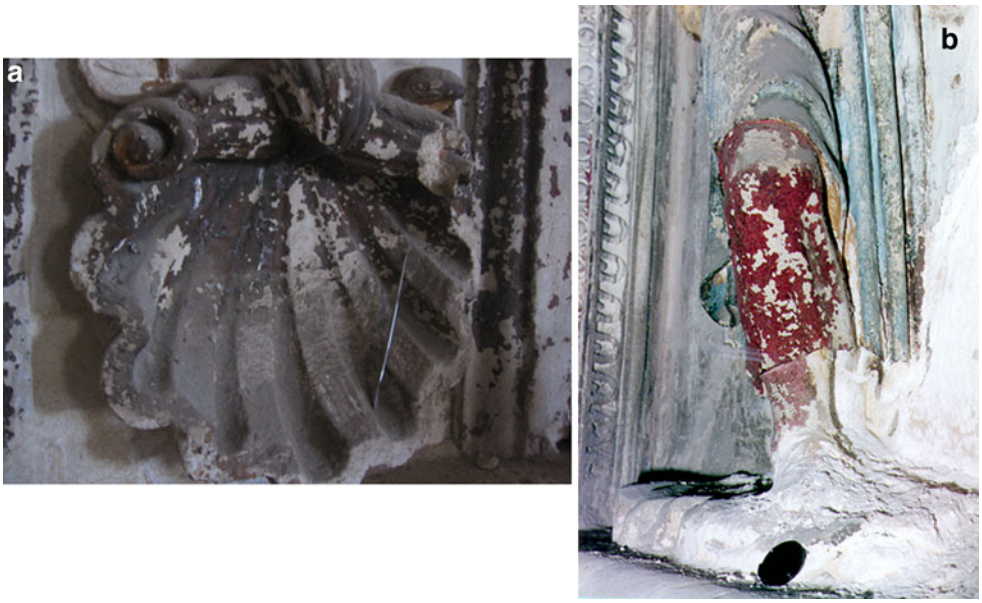

Fig. 5 **a** Photograph of a weathered, polychromed ornament covered with a thin layer of dust. **b** Photograph of polychromed sculpture intensively deteriorated showing massive formation of sulfate-rich salts (epsomite and gypsum) and detachment of the paintings. Both ornaments are placed in the church of San Jerónimo at ~15 m a.g.l

particle type is potentially threatening for the decorative materials of the monastery due to its hygroscopicity. Aged sea salt (a mixture of sodium chloride, sodium nitrate and sodium sulfate) had rather higher abundances in the middle and coarse-sized fractions, being slightly more predominant in outdoor samples. Clusters of calcium sulfate with potassium and sodium chloride were also found in most of the samples. In the middle- and coarse-sized fractions abundances were comparable indoors and outdoors, though in the fine fraction this cluster was only found in the indoor samples. Indoor sources for these sulfate/nitrate/chloride-containing particles also must be considered. This is supported by the results of previous studies in the church of San Jerónimo (Cardell 1998; Ruiz-Agudo 2007) showing intense weathering of the limestone used in walls, windowsills, vaults, and carved figures as a result of the massive presence of salts. Gypsum ($CaSO_4 \cdot H_2O$), halite (NaCl), Mg/Na-rich sulfate efflorescences (mostly epsomite), and minor amounts of nitrates (niter, KNO_3, and nitratine, $NaNO_3$) were found in the building in these studies, mainly in the outer layer of the walls (Fig. 5b). As Mg-sulfates were not detected in outdoor aerosol samples,

Table 1 Elemental concentrations of bulk particles at the monastery of San Jerónimo (Granada, Spain)

	In 1 ng m^{-3}	Out 1 ng m^{-3}	In 2 ng m^{-3}	Out 2 ng m^{-3}
Al	166	304	111	231
Si	400	742	271	578
S	469	339	352	179
Cl	4.1	24	1.8	82
K	233	358	311	335
Ca	388	1790	310	2004
Ti	15	30	9.1	24
V	5.1	7.7	8.3	4.2
Mn	2.2	5.7	1.9	5.2
Fe	108	283	92	215
Ni	2.9	2.6	5.1	1.5
Cu	3.1	7.2	2.8	4.8
Zn	8.5	18	6.7	8.2
Pb	4.0	2.1	5.3	1.8

they most probably originate from indoor sources, such as infiltration of ground water and subsequent interaction with building materials in the walls (joining mortars, stone and paintings), which contain significant amounts of Mg. Regarding other sulfates, nitrates, and chlorides, both aerosols and indoor sources may contribute to their presence inside the church.

Finally, a cluster containing particles comprised of iron (Fe), manganese (Mn), sulfur (S), and chlorine (Cl) was found predominantly in the outdoor samples of the middle-sized and coarse fraction. The origin of this particle type can be attributed to soil dust sources (aluminosilicates), and a marine source for Cl.

Bulk particles

The bulk aerosol concentrations obtained indoors and outdoors at the monastery of San Jerónimo by EDXRF analysis are presented in Table 1. The concentrations of all elements, except for S and Pb, were observed to be significantly higher outside the building. This suggests that these two elements have an indoor source. As stated above, the higher level of S indoors can be attributed to the high amount of sulfate-rich salts such as epsomite, hexahydrite, and gypsum present in the interior of the church, as found in earlier studies (Cardell 1998; Ruiz-Agudo 2007), while the higher amount of Pb should be due to the intense deterioration of the paintings (totally covering the interior of the church) containing Pb-based pigments (Cardell and Rodríguez-Gordillo 2003).

The highest outdoor and indoor concentrations were found for Ca and Si, followed by S, K, and Al. The origin of the outdoor particles can be attributed to geological materials from the vicinity of the city as limestones and metamorphic rocks (Puga et al. 2007). Indoors, lower concentrations of these elements were detected. The sampling period was characterized by dry weather conditions leading to rather high outdoor particulate matter concentrations. The results suggest that there was considerable indoor–outdoor air exchange rate leading to transport of ambient particles into the monastery. However, indoor sources cannot be excluded for these particle types. In fact, the severe weathering of the construction (stone and mortars) and decorative materials (paintings), and the related efflorescence affecting the interior of the church should be one of the major (indoor) sources for S, Ca, Si, and K (Cardell 1998). In addition, K and S can also be connected to the burning candles and incense inside the church (Kontozova-Deutsch et al. 2008b). From a preventive conservation perspective, the high concentration of sulfates in indoor aerosols is a threatening factor for pigments, metals, and other acid-sensitive artworks. Thus, the results obtained in this work confirm a feedback process inside the church that enhances further weathering of the indoor construction and decorative materials.

The analysis of the samples with XRD revealed a broad hump in the diffractograms due to the presence of amorphous black carbon particles (~9%), in agreement with previous studies (Rodriguez-Navarro and Sebastian 1996; Lyamani et al. 2010). The basin-like geography of the Granada basin favors weak wind speeds that, in combination with pollutant emissions, mainly from traffic, lead to heavy accumulations of particles. Moreover, the monastery of San Jerónimo and the CEAMA are located in the southern part of the city near the highway that rings it. Considering that Granada is a non-industrialized city, local aerosol sources are mainly heavy traffic (mostly diesel vehicles) together with re-suspension of material available on the ground. In addition, during winter domestic heating (typically oil burning central heating) represents an additional important source of anthropogenic aerosols. These aerosols contain significant amounts of carbonaceous particles, in agreement with our results of XRD analysis. As a consequence a dark haze can be observed frequently above the city, especially during morning hours, indicating the presence of soot particles as important pollutant in the basin.

The identified crystalline phase consists largely of calcite ($CaCO_3$, ~28%), muscovite (~27%), i.e., a phyllosilicate mineral known as common mica with formula $KAl_2(AlSi_3O_{10})(F,OH)_2$, and dolomite ($CaMg(CO_3)_2$, ~12%). Minor phases include Na-feldspar ($Na(AlSi_3O_8$, ~9%), gypsum ($CaSO_4{\cdot}2H_2O$, ~8%), paragonite (~5%) which is a phyllosilicate with empirical formula $NaAl_2(Si_3Al)O_{10}(OH)_2$, and quartz ($SiO_2$, ~3%). This composition is consistent with the results obtained elsewhere

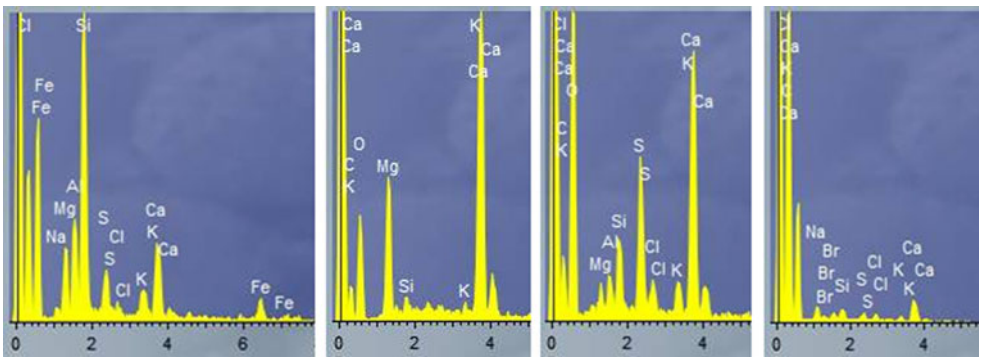

Fig. 6 SEM–EDX spectra representative for the composition of the outdoor PM10 sample (AER-GR)

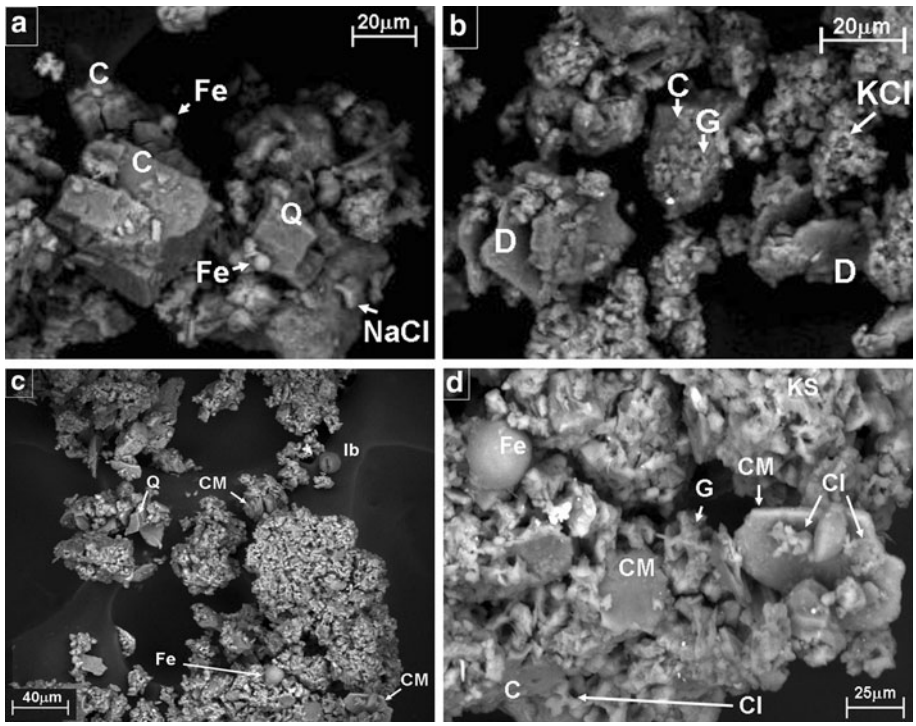

Fig. 7 SEM images of outdoor samples showing different particles. Sample Out-3 (**a**, **b**, outside the monastery) and sample AER-GR (**c**, **d**). Clay mineral (*CM*), calcite (*C*), dolomite (*DO*), quartz (*Q*), gypsum (*G*), Fe-rich particle (*Fe*); iberulite (*Ib*), chloride-based salts (*Cl*) and K-based sulfates (*KS*)

(Rodriguez-Navarro and Sebastian 1996), as well as with the mineralogy of the geological materials in the vicinity of Granada, namely limestones, dolostones, gypsum, and metamorphic rocks (e.g. micaschists) proceeding from the Sierra Nevada mountains and the surrounding basins (Puga et al. 2007).

The microanalysis of the samples (with particle size above 2 μm) performed with SEM–EDX showed that the major constituents were O, Si, Ca, Mg, and Al; the K content was also noteworthy. Minor constituents were Na, S, Cl, and Fe in decreasing order of abundance, and more rarely Br and P in sample AER-GR (Fig. 6). The spectra suggest the presence of clay minerals (phyllosilicates) accompanied by calcite, dolomite, and gypsum in a lower amount, in agreement with the mineralogical results obtained with XRD. In addition, minor amounts of chlorine-based salts such as KCl and NaCl, Fe oxides, K-based sulfates and Fe-rich, and aluminosilicate-rich (Si and Al) particles can be inferred from the spectra, in accordance with the EPMA results. This composition is consistent with results published elsewhere for the city of Granada (Rodriguez-Navarro and Sebastian 1996) and results of airborne particulate matter deposited on the exterior of other monuments (Esbert et al. 2001). Iron (Fe) can be related to diesel exhaust, mainly composed of soot and metallic particles bearing Fe and Fe–S as major elements, while Br can be ascribed to emissions from gasoline engines composed of minor amounts of soot and Br-rich particles (Simão et al. 2006). Figure 7 shows several SEM images of the outdoor samples. In the outdoor samples taken at the monastery (Fig. 7a, b), soil erosion particles were observed, composed of calcite, dolomite, and quartz, as well as minor amount of Fe-rich particles and salts made of NaCl, KCl, and gypsum. Figure 7c, d corresponds to

AER-GR sample revealing the presence of Fe-rich spherical particles, clay minerals, calcite, quartz, gypsum, chlorine, and sulfate-based salts as well as the so-called iberulite particle. This is a new type of spherical aerosol particle with a vortex, detected in Southern Spain, made of a complex mineral assemblage that also contains biological remains (Díaz-Hernández and Párraga 2008). The most likely source areas based on inherent mineral components are the Sahara and Sahel, while other minerals are the results of atmospheric neoformation. The appearance of iberulites is a discontinuous phenomenon, occurring mainly during summer and in dry periods corresponding to the highest total suspended particle (TSP) contents. Thus a correlation between amounts of dust and iberulites can be established; indeed, often their presence coincides with red dust rains and periods with no heavy rains. The sampling period of our study was characterized by dry weather conditions that lead to high outdoor particulate matter concentration.

Outdoor and indoor particles below 1 μm in size from the monument and the PM10 sample (AER-GR) were studied by TEM (Fig. 8). The main particles found in the aerosols sampled outside the church were salts, in particular chlorides and sulfate-rich salts. Also ammonium chloride (i.e. sal-ammoniac) was a common component; its origin may be related to the existence of guano deposits in the upper part of the church (Cardell 1998). Ammonium-rich salts were also identified by EPMA in the smallest particles of the fine fraction inside and outside the church. It should be noted that pigeon feathers and excrement are abundant not only in the exterior of the church in the upper parts at around 15 m a.g.l., but also in the interior due to open doors and broken stained-glass windows. Particles of Ca–K–S and Ca–Na–K–S were also frequently detected, in agreement with the aged salts analyzed with EPMA inside and outside the monastery, as well as in the AER-GR sample. Their presence may be attributed to transport of marine aerosols to the city, although in-cloud processes cannot be neglected as a possible source (Liu et al. 2005). Oxidation of atmospheric SO_2 in the presence of water leads ultimately to the formation of sulfates. Aluminosilicates were also found in the fine fraction of these samples as revealed by EPMA,

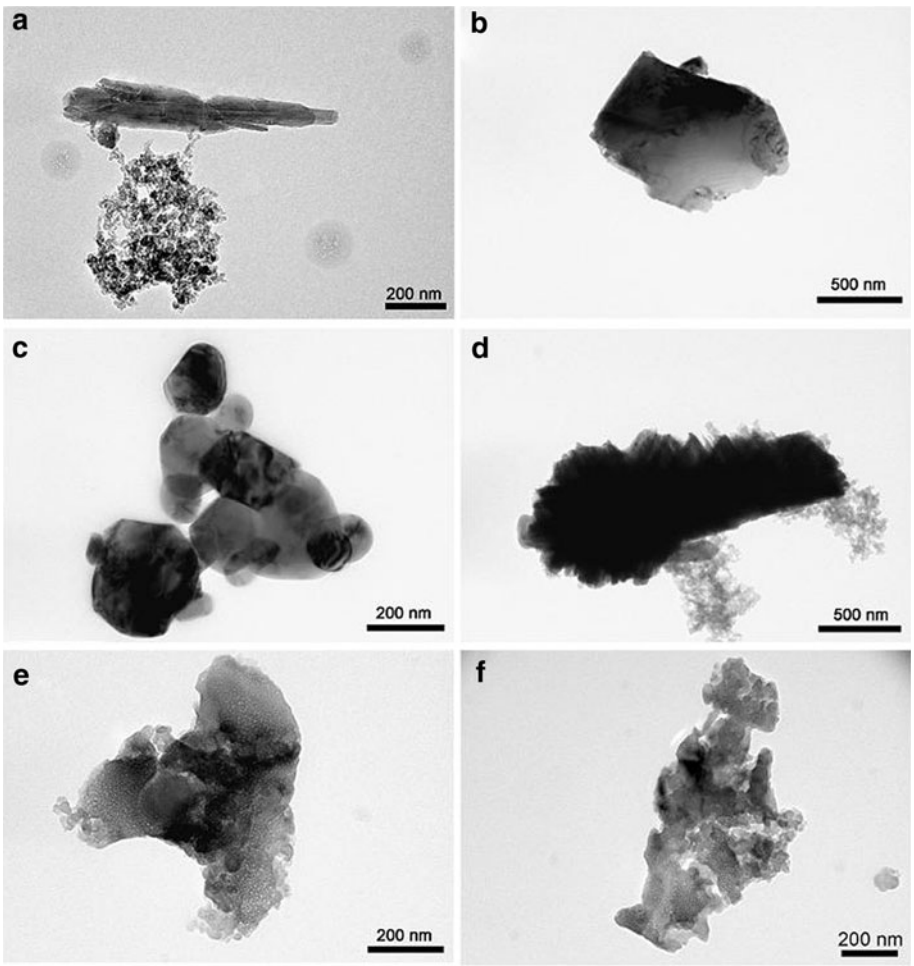

Fig. 8 Representative TEM images of particles found in aerosols. Sample AER-GR: **a** phyllosilicate particle and aggregate of amorphous carbon particles and **b** calcite; sample Out-3: **c** rutile, **d** iron oxide; sample In-4: **e** NaCl and **f** calcium–potassium double sulfate particles

XRD, and SEM–EDX in the coarser fractions. In particular, fibrous paragonite was detected with TEM which corroborated the XRD results. The presence of calcite, as well as the detected silicates could originate from windblown dust released during natural erosion of limestone rocks and clay formations surrounding the city of Granada. Aggregates of amorphous carbon particles and particles of amorphous SiO_2 were also identified with TEM in outdoors samples. These aggregates, randomly oriented and poorly crystalline, are composed of graphite particles, typically present in particulate matter from diesel motor vehicles exhaust emissions (Simão et al. 2006).

Regarding the indoor particles, again the main particles found were chlorides and sulfates, essentially ammonium chloride and Ca–K–S-rich particles (Fig. 8e, f). The composition of the indoor samples obtained with TEM can be related to that of the outdoor aerosols, in accordance with the EPMA results. However, as stated above, indoors sources such as the sanding-off of salt-containing building stone may also contribute to some extent to the presence of these particles in indoors aerosols. The identification of iron chloride particles inside the church reveals interaction between chloride-based particles (e.g. salt-rich particles) and Fe-rich pigments and clay-based pigments present in the wall paintings (Cardell and Rodríguez-Gordillo 2003). However, interaction with iron-rich particles from diesel motor vehicle exhaust emissions present in outdoor aerosols (entering the church by air exchange) cannot be neglected, although it is highly unlikely as these particles were not observed in outdoor samples, which also contain Cl-rich particles. Finally, silicates such as talc ($H_2Mg_3(SiO_3)_4$), carbonates like calcite and dolomite, and rutile (TiO_2) were also found (Fig. 9). As mentioned earlier, the indoor origin of these minerals can be attributed to the debris released during the sanding-off process that affects the construction materials (limestone, renders and mortars).

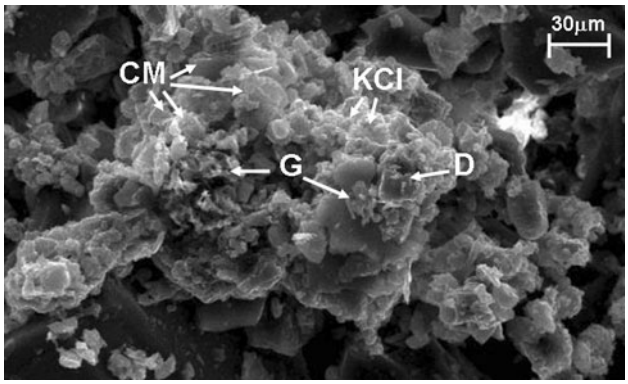

Fig. 9 SEM image of indoor samples showing dolomite (*D*), clay minerals (*CM*), gypsum (*G*), and KCl salt (*KCL*)

Conclusions

An outdoor and indoor air quality study was carried out at the monastery of San Jerónimo (Southern Spain) allowing characterization of atmospheric aerosols at nano- and microscale. Detected outdoor atmospheric aerosols are related to the geographical characteristics and climate of the city. Severe day/night temperature fluctuations contribute to soil dust generation. In addition, the basin-like shape of Granada surrounded by high mountains, in combination with heavy traffic, enhances the accumulation of soot particles. Also, an influx of marine particles can be expected when the wind direction is southerly (S and SW are the prevailing wind patterns).

In accordance with these characteristics, abundant soil dust particles (aluminosilicates, calcite, dolomite, quartz and clay minerals) and ca. 9% of black carbon particles (soot particles) were detected outside the monument. Other abundant particle types such as $(NH_4)_2SO_4$ clustered with C, and Fe/Mn oxides plus S–Cl rich particles were identified, as well as minor amounts of Br and Fe-rich rounded particles (related to traffic) and iberulites (a new type of spherical aerosol particle identified in Southern Spain). TEM analyses identified salt aerosols (chloride, sulfate and ammonium-rich salts) and aggregates of both amorphous C and SiO_2 particles.

Inside the church of San Jerónimo, high NO_2 and SO_2 concentrations were detected, implying both indoor sources and an indoor–outdoor air exchange. The impact of both gases in the murals of the church is particularly aggressive. Abundances of C and soil dust particles, and ammonium and calcium sulfate and chloride-rich aerosols were found to be similarly high indoors and outdoors. In addition, high levels of S, Pb, and chloride- and sulfate-rich aerosols further showed that the source of these particles was related to the intense weathering of the construction and decorative materials, and to the copious efflorescences inside the church. Chemical reactions between Fe-rich pigments from paintings and chloride-rich salts were identified through the recognition of iron chloride particles. All of these particles promote a feedback process that triggers further weathering of the mentioned indoor materials. In addition, although stable indoor microclimatic conditions were registered, the inappropriate cleaning habits foster the re-suspension of particles which play a key role in the darkening of distant and isolated places inside the church.

Acknowledgments Financial support was provided by the University of Antwerp and by the Andalusian Research Group RNM-179. The authors thank the nuns of the Monastery of San Jerónimo in Granada, as well as H. Lyamany and L. Alados-Arboledas from the CEAMA (Granada) for supplying the PM10 sample.

References

Bonazza A, Sabbioni C, Ghedini N (2005) Quantitative data on carbon fractions in interpretation of black crusts and soiling on European built heritage. Atmos Environ 39:2607–2618

Bondarenko I, Treiger B, Van Grieken R, Van Espen P (1996) IDAS: a Windows based software package for cluster analysis. Spectrochim Acta B51:441–456

Brimblecombe P, Thickett D, Hun Yoon Y (2009) The cementation of coarse dust to indoor surfaces. J Cult Herit 10:410–414

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

Cardell C (1998) Salt crystallization in calcarenites: application to the Monastery of Saint Jerome, Granada (Spain). Dissertation, University of Granada (in Spanish)

Cardell C, Rodríguez-Gordillo J (2003) Polychromes in the Church of the Monastery of San Jerónimo in Granada: composition, alteration and applied techniques. Bol Soc Esp Mineral 26:113–121 (in Spanish)

Cataldo R, De Donno A, De Nunzio G, Leucci G, Nuzzo L, Siviero S (2005) Integrated methods for analysis of deterioration of cultural heritage: the Crypt of "Cattedrale di Otranto". J Cult Herit 6:29–38

Corgnati SP, Fabi V, Filippi M (2009) A methodology for microclimatic quality evaluation in museums: application to a temporary exhibit. Build Environ 44:1253–1260

De Hoog J, Osán J, Szalóki I, Eyckmans K, Worobiec A, Ro C-U, Van Grieken R (2005) Thin-window electron probe X-ray microanalysis of individual atmospheric particles above the North Sea. Atmos Environ 39:3231–3242

Delalieux F, Cardell C, Todorov V, Dekov V, Van Grieken R (2001) Environmental conditions controlling the chemical weathering of the Madara Horseman monument, NE Bulgaria. J Cult Herit 2:43–54

Díaz-Hernández JL, Párraga J (2008) The nature and tropospheric formation of iberulites: pinkish mineral microspherulites. Geochim Cosmochim Acta 72:3883–3906

Esbert RM, Díaz-Pache F, Grossi CM, Alonso FJ, Ordaz J (2001) Airborne particulate matter around the Cathedral of Burgos (Castilla y Leon. Spain). Atmos Environ 35:441–452

García-Diego FJ, Zarzo M (2010) Microclimate monitoring by multivariate statistical control: the renaissance frescoes of the Cathedral of Valencia (Spain). J Cult Herit. doi:10.1016/j.culher.2009.06.002

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

Ivleva NP, McKeon U, Niessner R, Pöschl U (2007) Raman microspectroscopic analysis of size-resolved atmospheric aerosol particle samples collected with an ELPI: soot, humic-like substances, and inorganic compounds. Aerosol Sci Technol 41:655–671

Jordan MM, Sanfeliu T, Gómez ET, Pallarés S, Vicente AB (2009) A valuation of the influence of particulate atmospheric aerosol in constructions of the cultural and architecture patrimony of the urban area of Castellon (NE, Spain). Water Air Soil Pollut 200:245–251

Kontozova-Deutsch V (2007) Characterisation of indoor gaseous and particulate pollutants for conservation in museums and churches. Dissertation, University of Antwerp

Kontozova-Deutsch V, Deutsch F, Godoi RHM, Spolnik Z, Wei W, Van Grieken R (2008a) Application of EPMA and XRF for the investigation of particulate pollutants in the field of cultural heritage. Microchim Acta 161:465–469

Kontozova-Deutsch V, Godoi RHM, Worobiec A, Spolnik Z, Krata A, Deutsch F, Van Grieken R (2008b) Investigation of gaseous and particulate air pollutants at the Basilica Saint-Urbain in Troyes, related to the preservation of the medieval stained glasses windows. Microchim Acta 162:425–432

La Gennusa M, Rizzo G, Scaccianoce G, Nicoletti F (2005) Control of indoor environments in heritage buildings: experimental measurements in an old Italian museum and proposal of a methodology. J Cult Herit 6:147–155

Laiz L, Cardell C, Rodríguez-Gordillo JF, Saiz-Jiménez C (2000) Bacteria in the efflorescences of Saint Jerome church, Granada, Spain. In: 5th international symposium on the "The Conservation of Monuments in the Mediterranean Basin", Seville, Spain, 15–16

Liu X, Zhu J, Van Espen P, Adams F, Xiao R, Dong S, Li Y (2005) Single particle characterization of spring and summer aerosols in Beijing: formation of composite sulfate of calcium and potassium. Atmos Environ 39:6909–6918

Lyamani H, Olmo FJ, Alados-Arboledas L (2010) Physical and optical properties of aerosols over an urban location in Spain: seasonal and diurnal variability. Atmos Chem Phys 10:239–254

Martín-Ramos JD (2004) Using XPowder: a software package for powder X-ray diffraction analysis. http://www.xpowder.com. D.L.; 2004. GR 1001/04, ISBN 84-609-1497-6

Massart D, Kaufmann L (1983) The interpretation of analytical chemical data by the use of cluster analysis. Wiley, New York

Moropoulou A, Bisbikou K, Van Grieken R, Torfs K, Polikreti K (2001) Correlation between aerosols, deposits and weathering crusts on ancient marbles. Environ Technol 22:607–618

Murr LE, Bang JJ (2003) Electron microscope comparisons of fine and ultra-fine carbonaceous and non-carbonaceous, airborne particulates. Atmos Environ 37:4795–4806

Nazaroff WW, Ligocki MP, Salmon LG, Cass GR, Fall T, Jones MC, Liu HIH, Ma T (1993) Airborne particles in museums, research in conservation. The Getty Conservation Institute, USA

Pérez-Rodríguez L, Maqueda C, Jiménez de Haro MC, Rodríguez-Rubio P (1998) Effect of pollution on polychromed ceramic statues. Atmos Environ 32:993–998

Puga E, Díaz de Federico A, Nieto JM, Díaz Puga MA (2007) Petrology, geodynamic evolution and georesources of the Natural Space of Sierra Nevada. Est Geol 63:19–40 (in Spanish)

Ro CU, Oh K-Y, Kim H, Kim YP, Lee CB, Kim K-H, Kang CH, Osán J, de Hoog J, Worobiec A, Van Grieken R (2001) Single-particle analysis of aerosols at Cheju Island, Korea, using low-Z electron probe X-ray microanalysis: a direct proof of nitrate formation from sea salts. Environ Sci Technol 35:4487–4494

Ro CU, Osan J, Szaloki I, de Hoog J, Worobiec A, Van Grieken R (2003) A Monte Carlo program for quantitative electron-induced X-ray analysis of individual particles. Anal Chem 75:851–859

Rodríguez-Gordillo J, Sáez-Pérez MP (2006) Effects of thermal changes on Macael marble: experimental study. Constr Build Mater 20:355–365

Rodriguez-Navarro C, Sebastian E (1996) Role of particulate matter from vehicle exhaust on porous building stones (limestone) sulfation. Sci Total Environ 187:79–91

Ruiz-Agudo EM (2007) Prevention of salt damage to the built cultural heritage by the use of crystallization inhibitors. Dissertation, University of Granada (in Spanish)

Sabbioni C, Ghedini N, Bonazza A (2003) Organic anions in damage layers on monuments and buildings. Atmos Environ 37:1261–1269

Sánchez-Moral S, Soler V, Cañaveras JC, Sanz-Rubio E, Van Grieken R, Gysels K (1999) Inorganic deterioration affecting the Altamira Cave, N Spain: quantitative approach to wall-corrosion (solutional etching) processes induced by visitors. Sci Total Environ 243–244:67–84

Sanjurjo Sánchez J, Alves CAS, Vidal Romaní JR, Fernández Mosquera D (2009) Origin of gypsum-rich coatings on historic buildings. Water Air Soil Pollut 204:53–68

Simão J, Ruiz-Agudo E, Rodriguez-Navarro C (2006) Effects of particulate matter from gasoline and diesel vehicle exhaust emissions on silicate stones sulfation. Atmos Environ 40:6905–6917

Spolnik Z, Bencs L, Worobiec A, Kontozova V, Van Grieken R (2005) Application of EDXRF and thin window EPMA for the investigation of the influence of hot air heating on the generation and deposition of particulate matter. Microchim Acta 149:79–85

Spolnik Z, Worobiec A, Samek L, Bencs L, Belikov K, Van Grieken R (2007) Influence of different types of heating systems on particulate air pollutant deposition: the case of churches situated in a cold climate. J Cult Herit 8:7–12

Tétreault J (2003) Airborne pollutants in museums, galleries and archives: risk assessment, control strategies, and preservation management. Canadian Conservation Institute, Ottawa

Van Espen P, Janssens K, Nobels J (1986) AXIL-PC software for the analysis of complex X-ray spectra. Chemom Intell Lab Syst 1:109–114

Van Grieken R, Gysels K, Hoornaert S, Joos P, Osán J, Szalóki I, Worobiec A (2000) Characterisation of individual aerosol particles for atmospheric and cultural heritage studies. Water Air Soil Pollut 123:215–228

Weinbruch S, Wentzel M, Kluckner M, Hoffmann P, Ortner HM (1997) Characterization of individual atmospheric particles by element mapping in electron probe microanalysis. Microchim Acta 125:137–141

Worobiec A, Samek L, Spolnik Z, Kontozova V, Stefaniak E, Van Grieken R (2006) Study of the winter and summer changes of the air composition in the church of Szalowa, Poland, related to conservation. Microchim Acta 156:253–261

Worobiec A, Samek L, Karaszkiewicz P, Kontozova-Deutsch V, Stefaniak EA, Van Meel K, Krata A, Bencs L, 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

Xu F, Tang J, Gao S (2010) Characterization and origin of weathering crusts on Kylin carved-stone, Kylin countryside, Nanjing—a case study. J Cult Herit 11:228–232