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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)

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Abstract The constructions of Cultural and Architecture Patrimony are influenced by pollutants. Many of degenerative processes in the materials which constitute them have their origin in pollutants. That is the reason why a physical–chemical characterisation of the particulate pollutants in the air has been carried out. The deposition and, as a consequence of that, the interaction of the pollutants with the different materials of the monuments depend on the reactivity of the chemical elements that form the atmospheric particulate. Studies of both, bulk dust deposition and total suspended matter, a mineralogical and chemical characterisation of them have been made. Lastly, starting from these data, it can be established that the interactions and degenerative processes are taking place in the monuments of the studied locations. In the present work, the methodology carried out in the study of the particulate atmospheric pollutants, which are capable of accumulating on monuments and buildings with artistic and historical interest in the area of Castellon, is displayed. By means of a network of captors, important samples of sedimentary and suspension atmospheric pollutants, total suspension particles (TSP) were obtained. Firstly, by gravimetric methods, we have obtained the concentration levels of these kinds of pollutants in milligrams per day in busk dust samples and micrograms per cubic meter in TSP. Due to the fact that the corrosivity of these pollutants fundamentally depends on their compositions, the study has been completed with a mineralogical and chemical characterisation. By X-ray diffraction and scanning electron microscopy, we have analysed the particles of the two kinds of samples. The chemical analysis was carried out by inductively coupled plasma-atomic spectroscopy and inductively coupled plasma-mass spectrometry (multielement analysis techniques) in TSP samples and in the soluble fraction of the depositing particulate matter. The results have shown as main compounds: clay minerals, calcite, and carbonaceous matter coming from non-perfect combustion of vehicles. The chemical analysis indicates a high Ca/S ratio and high levels of concentration in chemical elements associated to this representative industrial cluster of ceramics industry in Europe.

Keywords Patrimony · Atmospheric pollutants · Particulate matter · Castellon · Spain

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1 Introduction

The processes that involve the damage of the stone are certainly complex. Damage on monuments has increased by the high levels of air pollution. The removal of dry and humid deposits on the surface of the monuments is a degrading agent, which is determined by several external agents. The European climate helps humid deposits in the North and dry deposits in the South (Monn et al. 1995a, b; Querol et al. 2002). Atmospheric precipitations do not happen frequently in the southern basin of the Mediterranean Sea, so most of the deposits happen during the humid period, especially in urban environment (Artiñano et al. 2001).

The type of damage and its effects on marble and calcareous rocks have been classified according to three types of terms: white zones, grey zones and black crusts. Both water and atmospheric particles have contributed in its formation (Camuffo et al. 1982, 1983, 1987).

The white spots are found where the water goes through the surface, removing dry deposits. In case of calcareous rocks, for example, water current causes dissolution of calcium carbonated, and for this reason, the erosion of the stone is accelerated. The conversion of carbonated sandstone into gypsum is very strong after sulphate action. Gypsum dissolution produces surface erosion that fluctuates among 20–100 μm/year. The critical period happens when the dry deposit is humid due to a drizzle (Aires-Barros 1990)

Products of combustion of urban transport contain carbonaceus particles and other organic compounds (Marcazzan et al. 2001; Manoli et al. 2002). Deposition of these particles operates in the erosion process when they are humid. As a final result, the interaction produces black crusts. The grey crusts are characteristic of Mediterranean cities with few precipitations. Their dark/white coloration results from the deposit of the sedimentary atmospheric particulate accumulated during a long period of time on the surface of the monument. This makes a cover of dust and particles, which does not react with the underlying surface and preserves it perfectly. These damages have been identified in region of Castellon. The effects on the gothic door at the Cathedral of Santa Maria (Castellon) are shown in Fig. 1.

2 Materials and Methods

2.1 Sampling

Different types of samples have been collected according to the captor system, which has been used. The location of bulk dust captors of the firm MCV S. A., British standard model PS, in several areas of Castellon has supplied us with monthly samples of particulate matter and water during the sampling period. The samples of dust have been collected by washing along the particles deposited on the surface of the collecting funnel using distilled water, removing solids in suspension by filtrate (0.45 μm) and saving the liquid samples in suitably conditioned containers in order to analyse leachates and the chemical composition of rain water (Jordan et al. 2002).

The samples of total suspension particulate (TSP) have been obtained by high volume equipment type CAV-A/A and CAV/HF, with sampling periods of 24 h. We have used membrane filters of the firm MF-Millipore (HAWP 142 50)—mixed esters of cellulose—and

Fig. 1 Gothic door at the Cathedral of Santa María (Castellon). Detail on columns indicates "stone's harm"

fibreglass filters (Jordan et al. 2006). The level of suspension particles is determined from the intake volume by the captors and the weight of the filters in controlled conditions of temperature and humidity (Pallarés et al. 2007; Fig. 2).

2.2 Mineralogical Analysis

Bulk dust samples Whole samples of solid particles were subjected to a process of separation according to particle size (Fukasawa et al. 1983; Jordan et al. 2002). Each of these fractions, called whether enriched in high-, medium- or fine-size fraction, was separately analysed by XRD (Harrison et al. 1997; Allen et al. 2001). The separation of the different size distribution fractions by fractional deposition allows an important improvement in the quality and resolution of the diffraction patterns corresponding to both the enriched in high-size and the enriched in medium-size fractions. This fact causes an increase of the intensity of the peaks associated to materials of non-clay nature (quartz, feldspar, carbonate) in the high-size fraction, separating clay minerals in the fine fraction. The content of organic and inorganic matter of low crystallinity grade (amorphous of small particle size) decreases and concentrates in fine-size fraction, hindering the obtainment of quality diffraction patterns for this fraction (Gómez et al. 2002, 2005).

Total suspended particle Filters with the retained matter were divided into four parts. A section of 2× 2 cm^2 belonging to one of these parts was separated and kept in order to make chemical analyses by inductively coupled plasma-mass spectrometry (ICP-MS) later on. Before applying this technique, the sections of the filters were digested by means of an acid treatment in PTFE reactors. The particulate matter was mechanically extracted from two of the parts (9×9 cm^2) by means of a spatula. The extracted dry dust was placed on suitable supports to carry out the mineralogical analyses. As we have done before, part of the matter belonging to some samples was dispersed in aqueous solution. Later on, it was concentrated by centrifugation, and new diffraction tests were taking place. The fourth part was kept in *petri* boxes, saved from sunlight, and in a refrigerator for future analyses (Gómez et al. 2004).

In both cases, the equipment used for mineralogical characterisation was a Siemens D5000 diffractometer, with Bragg Brentano geometry. The spectra were taken with Cu Kα radiation at 40 kV and 30 mA. The diffraction patterns were recorded between 3° and 65°, steps of 0.04–0.05° and time of

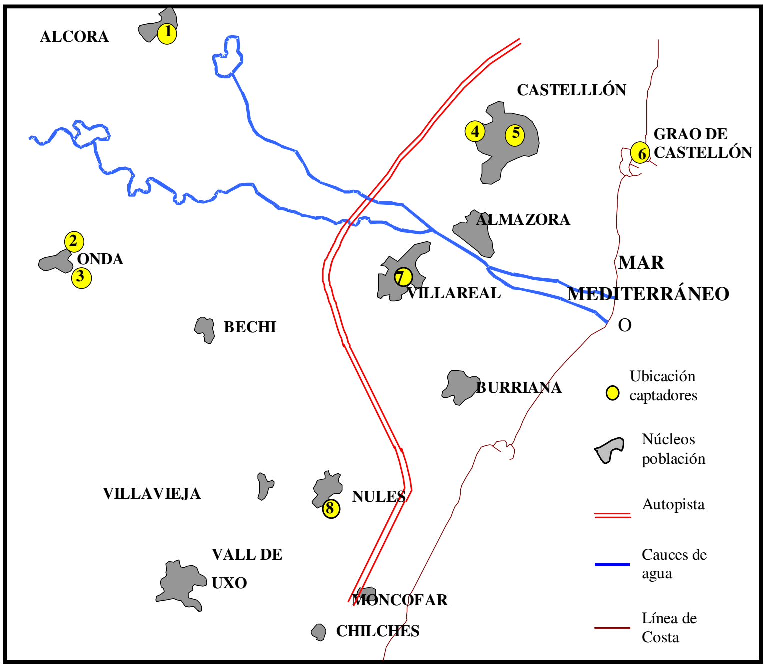


Fig. 2 Distribution of the captors and location of the population centres

2–3 s (Davis 1984; Gómez et al. 2002, 2005). Some samples were also analysed by scanning electronic microscope with an equipment 440 LEO SEM and an EDX LINK-OXFORD micro-analysis equipment (Jordán et al. 2002, 2006).

2.3 Chemical Analysis

In the present research, the inductively coupled plasma-atomic spectroscopy (ICP-AES) and ICP-MS methods have been complementary used in order to gain a good capability for the multielemental analysis. A section of 2×2 cm of a filter was used for the chemical analysis. The filters digestion needed for the analysis of samples through ICP-MS and ICP-AES was carried out with the help of an acid attack (HNO_3, HF and $HC1O_4$) in PFA reactors (Maenhaut and Cornille 1989; Monn et al. 1995a, b; Kubilay and Saydam 1995; Laitinen et al. 1996). The digestion of a whole filter has been carried out for the preparation of the white. For the standard preparation, a whole filter together with a flying ash standard NBS 1633B has been digested.

A Yobin-Yubon JY-38 VHR inductive coupling plasma spectrometer has been used for the chemical analysis of samples through ICP-AES. It is equipped with two monochromators (main monochromator and auxiliary monochromator), which are lined up against the main force of excitation. The former, with a holographic net of 3,600 strokes/mm, has been used in direct determination. The latter (1,200 strokes/mm) has been used simultaneously with the previous one to take measurements with inner pattern. The generator of radio frequency works at 56 MHz. The torch is Durr-JY/Plasmather, dismountable, and the nebulizer used has been glass pneumatic Meinhard type C(TR-C2-30). A mass spectrometer Fisons VG Plasma Quad ICP 20P was used in the sample analysis through ICP-MS.

3 Results and Discussion

3.1 Mineralogical Characterisation

The mineralogical determination has allowed to identify 27 different mineral phases. These compounds have been assembled in two sequences. The former corresponds to the majority crystalline phases group, indicative of the main source of particles in the atmospheric charge of the area. The latter is formed by the minority crystalline phases group that traces the anthropogenic activities and more specific industrial processes. After the compounds' identification, a semi-quantitative and orientative method of the mineral phases was applied (Gómez et al. 2002; Jordan et al. 2002).

On the one hand, the analysis and interpretation of the X-ray diagrams obtained from the atmospheric inputs of particulate pollutants on filters studied through X-ray diffraction have made it possible for the following crystalline phases to be identified: quartz, calcite, dolomite, illite, kaolinite, chlorite/montmorillonite, montmorillonite, microcline, barium orthoclase, albite, anorthite, hematite, talc and halite. The majority phases are composed of illite, quartz, kaolinite, calcite and/or dolomite, the other phases being present in lower proportion (Fig. 3). The importance of the clay minerals and of high rates of calcite in the local atmospheric particles is shown.

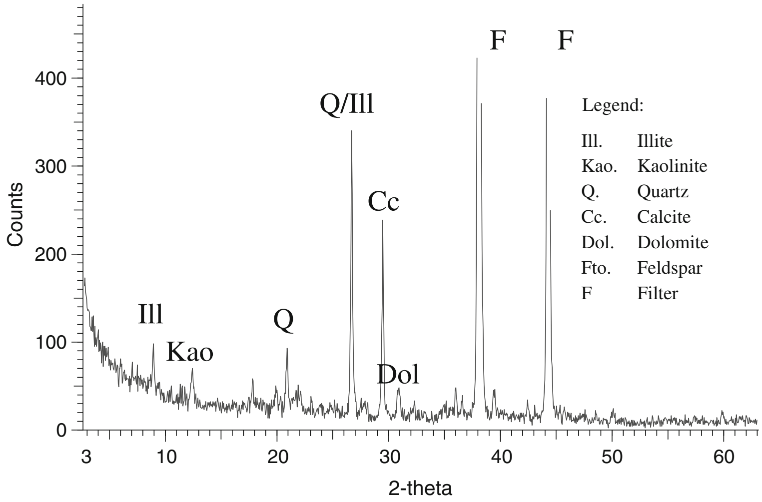
On the other hand, the XRD analysis of the bulk dust (Fig. 4) shows the preference of certain mineral phases to shelter under certain size distribution fractions. The analysis also shows the tendency of the amorphous material to concentrate mainly in the fines enrichment fraction.

An increase of clayed materials has been detected in the medium- and mainly in the fine-size fraction, whereas feldspar, carbonate and quartz are concentrated in the high-size fraction. The results obtained show the homogeneity in the mineralogical composition of the particles. This composition is similar among the different sampling sites and maintains a perfect correlation to the soil composition (Moral et al. 2005), except in the minor phases. Evidences of crystalline phases or traces have a higher environmental interest as they can act as local tracers or differentiating agents.

3.2 Chemical Characterisation

The chemical characterisation has allowed to identify the most characteristic elements in the research site by means of the ICP-AES and ICP-MS analysis. The results of some elements in relation to three localities are shown in Fig. 5. The concentration values (nanograms per cubic meter) have a 1-m^3 air referential basis; the

Fig. 3 X-ray diffractogram obtained from the atmospheric particulate

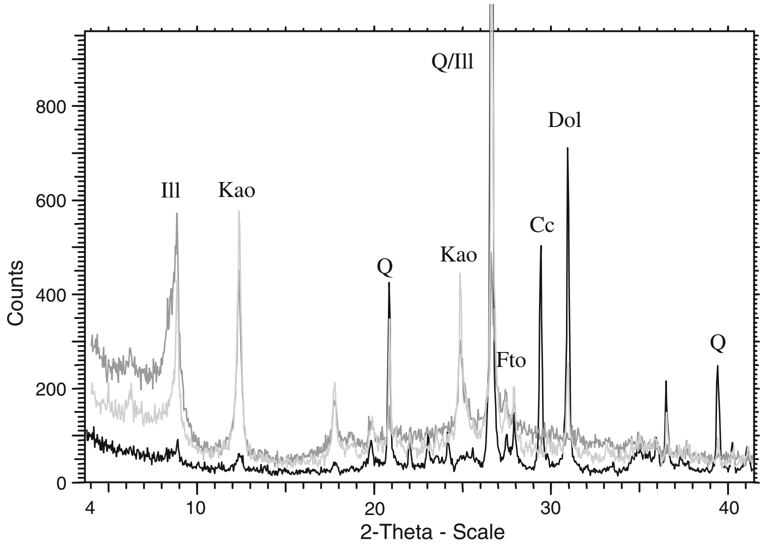


air has been measured at the particle collection temperature and humidity conditions. Among the chemical elements analysed, Al, Fe, Ca, Mg, Cu, Zr and Zn show the highest concentrations compared with another sites of research. The concentrations of Al, Fe and Mg are a consequence of the concentration of tile industries in this area, which is well known as a ceramic cluster, mainly associated to the handling of raw materials (Jordan et al. 2006). Ca and Mg are associated to the area lithology and also to the presence of exploitations of rich carbonate clays and calcite–dolomite rocks (Boix et al. 2001). Cu and Zn are associated to high temperature processes, and Zr comes from the use of raw materials in the enamel and frits compositions (Sanfeliu et al. 2002). Thus, the chemical analysis results show the influence of the local industry in the atmospheric particles composition (Jordan et al. 2006).

3.3 Study of the Acid Deposition of the Atmospheric Aerosol

Spectroscopy of plasma emission by inductive coupling (ICP-AES) is a very useful analytic technique

Fig. 4 X-ray diffraction of bulk dust samples. Each of these fractions are enriched in high- (*black*), medium- (*grey*) and fine-size particles (*light grey*)



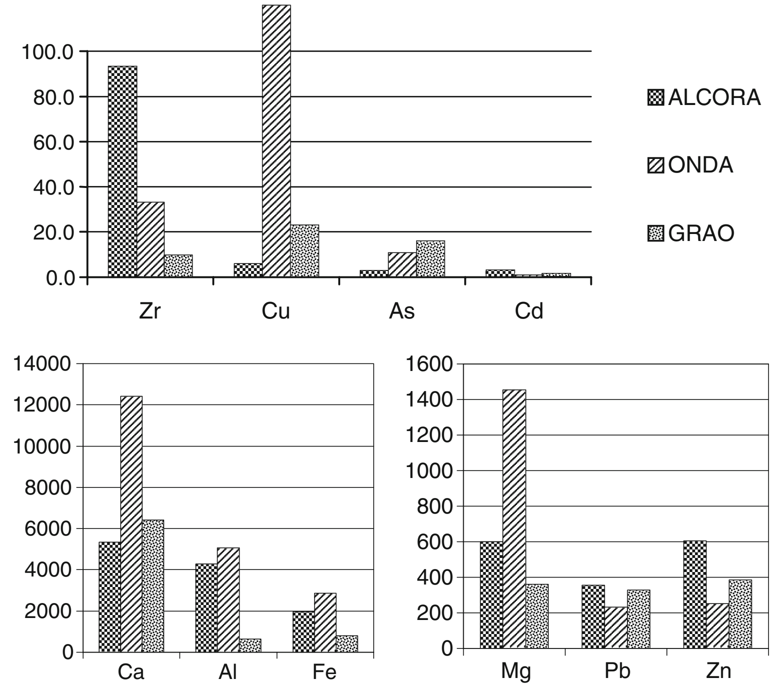


Fig. 5 Chemical analysis of particulate matter. All elements in nanograms per cubic meter

since it features a high degree of sensitivity for determining the concentration of two key elements (Ca and S) in the study of the acid deposition of the atmospheric aerosol. In order to evaluate the acid deposition, the relation Ca/S in the samples has been calculated. The theoretical value Ca/S should be equal to 1.25 given the assumption that all the Ca found in the samples arises from $CaSO_4$. As it can be observed in the graphics enclosed (Figs. 5 and 6), the relation mentioned is always superior to the referential value in all three sampling sites. This fact can be explained to be attending to an abundance in carbonates (calcite and dolomite) in the research site geology and attending to the presence of mine working on this materials (Boix et al. 2001). As could be verified in the X-ray diffraction tests, the Ca stems from high percentages of calcite and dolomite in the atmospheric particles. Instead, S can arise from the oxide in gaseous form derived from its reaction with carbonates in certain circumstances, as well as being an original component of primary polluters in particle form.

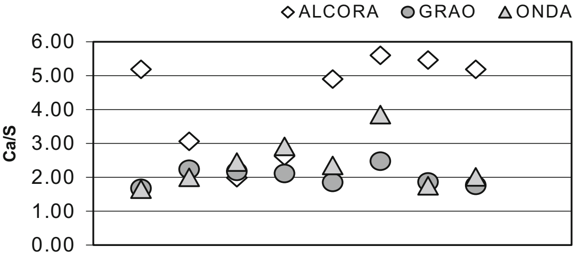


Fig. 6 Ratio Ca/S in the samples studied

4 Conclusions

We can conclude that the rain and the carbon particles, though important, are not the only agents causing alteration in the monuments sited in the study area. The water fluxing in relation with the inorganic particles is a critical parameter for such alteration. Thus, in the areas with a strong water deficit, the inorganic particles (carbonate, sulphate, silicate, oxide, etc.) have an important role on this alteration; for this reason, a research and model of the causes and agents influencing directly in their actual state of alteration are needed. The high proportions of clayed particles detected may be helping the metallic corrosion processes due to the huge specific surface and consequently, the high reactivity of these compounds. These compounds also act as a vehicle, absorbing other kinds of pollutants. The chemical analysis shows high concentrations in those elements peculiar of the industrial processes carried up in the area in which the research has been hold.

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