Air Pollution and Cultural Heritage

C. Saiz-Jimenez, editor

AIR POLLUTION AND CULTURAL HERITAGE

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Air Pollution and Cultural Heritage

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Foreword

The research findings we report emerge from a background in which international summits on environment and sustainable development, e.g. Johannesburg 2002, underlined the alarming rate at which we are depleting our resource base, driven by unsustainable population growth, and unsustainable production and consumption patterns.

One of the key lessons decision-makers have learned over the last thirty years is that pollution knows no border, the main issue highlighting transboundary pollution being at the time that of acid rain, and shifting now to concern for ozone and particle atmospheric levels.

Over the years, research has shown growing evidence of the impact of air pollution not only on human health and the natural environment, but also the built environment. Rapid urbanization also presents us with the enormous challenge to design and develop sustainable cities that offer integrated transport systems, systems in which intelligent use of information and communications technology (ICT) enables the city dweller/inhabitant to do teleworking from home, cycle to the station and travel to the countryside using combination of metro and bus. But these futuristic cities cannot be modern concrete jungles without colour and flavour. We owe it to future generations to leave behind not only sufficient natural and economic capital, but also our Cultural Heritage. A generation without a cultural memory is a generation that shows no tolerance and starts new wars. If we wish to preserve the durability of our life on this planet, we need to conserve, protect and repair our biological and cultural diversity.

Our cities will therefore have to take drastic action in improving the ability of their inhabitants to make informed choices. Local authorities need to raise the awareness of the public of what damage air pollution, driven by wasteful use of non-renewable energy, is causing to our precious environment. Authorities also need to create the right enabling environment, ensuring that the market gives business and industry the right price signals, encouraging them to adopt pollution avoiding behaviours. Added to this, and this is a call you will expect from a scientist, we need to support ongoing research, development and innovation in order to apply precaution in an effective and sensible manner.

Although public perception of pollution does not address the same criteria for human health or monument soiling, it is clear that preservation of both people and monuments come within the scope of the same action. Thus our future in the City of Tomorrow depends heavily on the capability of the different communities of scientists and deciders to join their efforts and reduce air pollution in the frame of a sustainable development.

During the European project CARAMEL (running in the frame of the 5th Framework Programme) and after three years of intensive work, evidence was given that the future of our Cultural Heritage is related to atmospheric pollution, itself heavily dependent upon pollution created by traffic. At the end of the CARAMEL project it was a great pleasure to organize the workshop «Air Pollution and Cultural Heritage» and share our enthusiasm and advertise our results. The number and the quality of participants and the numerous communications received confirm the interest of a broad community for this society problem.

The workshop was held in Seville (1st to 3rd December 2003) in the marvellous site of the Cathedral Chapter Hall. I would like to thank the European Community for their constant support of CARAMEL. I acknowledge too Cabildo Catedral for welcoming us in the Cathedral and CSIC Thematic Network on Cultural Heritage for their warm support and financial help. Finally, I personally present special thanks to Professor C. Saiz-Jimenez for his enthusiastic and unfailing help in the organization of the workshop.

Dr Hélène Cachier
CARAMEL coordinator

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Organization

The International Workshop on Air Pollution and Cultural Heritage was organized by the Instituto de Recursos Naturales y Agrobiología, CSIC, Sevilla, Spain, on behalf of CARAMEL project (Carbon content and origin of damage layers in European monuments, contract EVK4-CT-2000-00029). Support for this workshop, in addition to that given by the European Commission for research activities between January 1, 2001 and December 31, 2003, came from Ministerio de Educación y Ciencia (MEC), Dirección General de Investigación (MAT2002-10132-E), Consejo Superior de Investigaciones Científicas, Red Temática de Patrimonio Histórico y Cultural, and Cabildo Catedral de Sevilla. This volume collects the communications presented at the workshop to which were subsequently added six invited papers for completing the content. The printing has been supported by the Red Temática de Patrimonio Histórico y Cultural, Consejo Superior de Investigaciones Científicas, through MEC funds.

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Part 1. Aerosols, particulate matter and black crust characterization

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Aerosol characterization and sources in different European urban atmospheres: Paris, Seville, Florence and Milan

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ABSTRACT: This paper presents the main results obtained during the CARAMEL EC project for the characterization of atmospheric particles in four different European cities: Paris, Seville, Florence and Milan. The aim of our investigation was to find the main atmospheric sources responsible for the damage of exposed surfaces of monuments and to define relationships between atmospheric concentrations in multi-pollutant environments and the aesthetic effect of soiling. For this purpose, experiments were conducted at each site during a one-week intensive campaign followed by a whole-year monitoring of the basic parameters of the aerosol (mass, and chemical composition comprising carbon and major ions in two size fractions) in order to capture weekly and seasonal trends. Although the four sites were selected for their different atmospheric conditions, the study results underline common features which could provide an average picture of urban pollution in Western Europe. Traffic appears to be by far the major responsible source of atmospheric particulate pollution and differences among the sites are mostly connected to differences in traffic fleet, traffic density and prevailing meteorological conditions. Due to a shift of fuel usage from solid fuel (coal) to liquid and gas fuels and parallely to an important and voluntarist reduction of the sulphur content of fuels the role of sulphur species (SO_2 and sulphates) in atmospheric pollution is declining. Conversely, nitrogen species (NO_x and nitrate) and carbonaceous species (organic gases, elemental and organic particles) are gaining more importance especially due to the increasing use of diesel motors in the fleet of light and heavy-duty vehicles. The carbonaceous particles emitted in the atmosphere by traffic either as primary aerosols or as secondary particles are found in the submicrometre-sized range. This predominance of fine particles is found for both particle number and particle mass. This important result suggests that PM-1 (or PM-2.5) are now more appropriate than PM-10 to follow progress in urban air quality. Modern soiling of monument surfaces is thus produced by a totally different atmospheric mix than that from which historical black crusts originated. From our results it may be assessed that traffic regulation is nowadays a key and almost the only factor to target on, for both the improvement of air quality and the decrease of monument soiling rate.

1 INTRODUCTION

In the historical centre of cities in Western Europe, cultural heritage and modern buildings present dark and soiled facades in spite of repetitive cleaning (Hamilton & Mansfield 1993, Watt & Hamilton 2003).

In the past, industrial activities and domestic heating were known to be the dominant agents of both atmospheric pollution and building blackening (Hamilton & Mansfield 1991). But it is well known that a severe abatement policy has been applied since four decades to polluting combustions and industrial activities, especially in the vicinity of urban areas, accompanied by a drastic control of sulphur emissions. Consequently, at present, atmospheric concentrations of sulphur dioxide and acidic sulphate species have been significantly reduced. However in spite of these efforts, urban environments are still heavily polluted and in some cities the soiling of monuments or at least the turnover of their cleaning is accelerating.

Concern about atmospheric pollution and related damage on monuments raises similar questions than in

the past: what are the multiple atmospheric agents responsible of the damage and soiling of monuments and at what rate does the soiling appear?

However in this new situation, further investigations are needed to target the atmospheric sources, the pollutant transformations and their deposition onto monument surfaces. As a large increase of traffic is observed in the cities and their surroundings, this source could be at present the predominant cause of urban atmospheric pollution and as a consequence, the main agent of the continuous blackening of buildings.

The CARAMEL EC-project (EVK4-CT2000-00029, www.caramel.cnrs-gif.fr) occurred during the 2000–2003 time period and was designed in the general context of a better understanding of the monument soiling in this new multi-pollutant atmospheric situation. A focus was put on the analysis of carbonaceous particles (and particularly Elemental Carbon) which are known to be a significant fraction of both urban aerosols and monument black crusts and patinas (Sabbioni 1995, Lefèvre & Ausset 2002, Bonazza et al. 2004, Ghedini et al. 2004). Combustion molecular tracers were also investigated in order to identify the modern combustion agents of pollution (Reyes et al. 2004). As soiling is both objective and subjective, the project comprised various measurements of pollution species in the atmosphere and in black patinas, the modelling of deposition and soiling processes (Brimblecombe & Grossi 2004) but also investigation of the perception by people of soiling aesthetic effects (Grossi & Brimblecombe 2004).

We present here the most important results of the first task of the project devoted to studies of urban atmospheric particles at the four sites that have been selected: Paris, Seville, Florence and Milan. Particles were separated in two size-fractions and chemically characterized in order to identify their sources. This characterization was completed by investigations of the diurnal, weekly and seasonal patterns obtained by adapted particle monitoring. For the purpose of our study, experiments were conducted at each site during one-week intensive campaign generally followed by a whole-year monitoring of the basic parameters of the aerosol (mass, and chemical composition comprising carbon and major ions in two size fractions) in order to capture daily, weekly and seasonal trends.

2 EXPERIMENTAL

2.1 *Sampling sites*

Sampling sites dedicated to atmospheric particle sampling were chosen among the numerous sites which had been selected for the analysis of black crusts and patinas. All of them were directly located on the monument of interest or very close to it.

2.1.1 *Saint Eustache Church, Paris*

The church is situated among a vast pedestrian area in the centre of Paris (4th district). The site was a terrace of the church at an elevation of about 40 m (Fig. 1).

Experiments began March 2001. An intensive experiment of one-month duration took place at that time. Since then, the aerosol has been monitored on a weekly and/or monthly basis.

2.1.2 *Seville Cathedral*

The Cathedral is located south of the pedestrian area of the Seville center.

Among the four sides of the Cathedral, one side is along a busy street "Avenida de la Constitucion" (Fig. 2)

Figure 1. Saint Eustache Church (Paris). Sampling site.

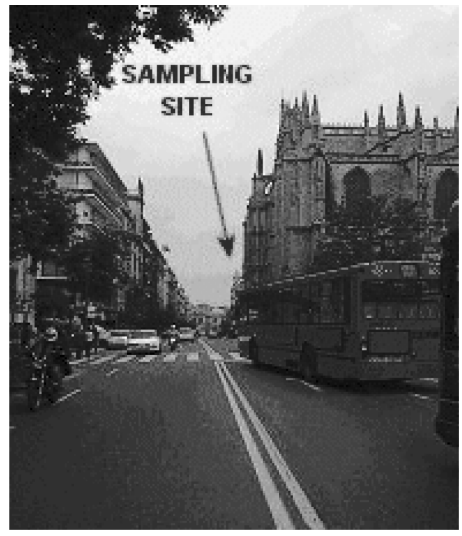

Figure 2. Seville Cathedral. Sampling site in the west side: Avenida de la Constitucion.

whereas two other sides are mainly off direct vicinal traffic. The fourth side has moderate traffic. Samplings were conducted on a platform of the cathedral at mid-height (about 20 m) along the busy street which is channeling traffic and especially the bus fleet joining Seville downtown. On this side, it may observed that the blackening of the cathedral is strikingly more important than on the other parts of the monument.

Experiments began February 2002 with an intensive experiment of 8 days followed by an aerosol weekly monitoring of 14 months.

2.1.3 *Milan Cathedral*

The Cathedral is situated in the center of the city pedestrian area. The whole monument is off direct influence of traffic. The aerosol sampling site was located on the roof of the "Palazzo dell'Arcivescovado", in front of the back part of the Cathedral, at about 20 m elevation (Fig. 3).

The intensive experiment was conducted in March 2002 and was followed by a 3 month-sampling campaign (ending June 2002) based on a weekly basis.

2.1.4 *Santa Maria del Fiore Cathedral, Florence*

The Cathedral is situated at the border of the pedestrian area. Part of the monument and the Batistero (facing the Cathedral entrance) is close to a busy street taken by several bus lines. A small street surrounding half of the Cathedral is opened to residential traffic, taxis, buses and motorbikes. Finally it must be underlined that although forbidden, some motorbikes can be seen around the cathedral even in the pedestrian area. The sampling site was situated on the roof of the "Museo dell'Opera del Duomo", a museum located just at the back of the Cathedral (Fig. 4).

Experiments began by a nine-day intensive campaign (in July 2002) followed by a whole year of weekly monitoring of the aerosol ending in July 2003.

2.2 *Sampling details*

2.2.1 *Aerosol basic monitoring*

Aerosol particles were sampled for an exhaustive speciation comprising EC and OC (Elemental and Organic Carbon), major soluble ions and total weight. This strategy necessitated two different sampling lines: one line for carbon analysis for which aerosols were collected on carbon-free precleaned quartz fiber filtres, and another one dedicated to weighing and ion analysis and working with Nuclepore membranes. Filters used here for both type of analysis were 47 mm circles.

The aerosol was also divided into two main fractions: the coarse fraction (>2 μm in diameter) and the fine fraction (<2 μm). This can be simply obtained using two-stage SFU's (Stack Filter Units) working at the flow rate of 1 m^3/hr and mounted with Nuclepore membranes (8 μm porosity for the front stage and 0.4 μm porosity for the back stage) (John et al. 1983).

Figure 3. Milan Cathedral sampling site.

Figure 4. Back part of Florence Cathedral, in front of our sampling site.

Sampling scheme was adapted in order to obtain a satisfactory deposit: from continuous sampling for day/night samples to a few minutes per hour for longer durations (15 min per hour for weekly samples, 5 minutes per hour for monthly samples). For the purpose of a reliable aerosol speciation sampling timing was strictly parallel for both lines.

2.2.2 *Aerosol size segregation*

Aerosol particles were also sampled in different class bins using a Dekati impactor sampler. With this instrument (Fig. 5) working at the flow rate of 30 m^3/hr, particles are separated in 13 mass class bins following their aerodynamic size.

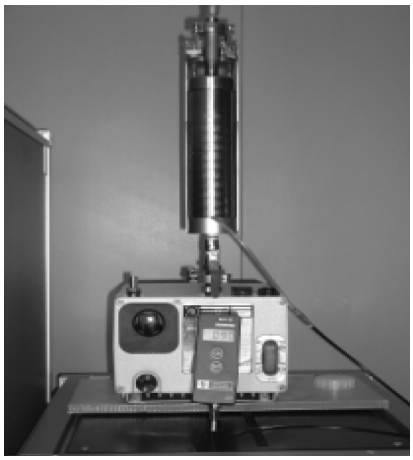

Figure 5. Dekati 13-stage impactor working at 30 m^3/hr and at 100 mbar pressure.

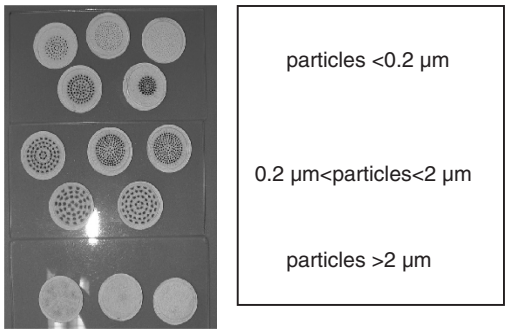

Figure 6. Aspect of the filters.

From Figure 6, it may be seen that this separation allows to trace the aerosol modes as the various stages present very different aerosol loadings.

As urban aerosols are very fine particles (Harrison et al. 1999, Hitzenberger & Tohno 2001, Langley et al. 2003), the resolution of this instrument providing eight stages for the submicron aerosol is particularly adequate.

2.3 *Analyses*

Aerosol weighing was obtained with a Mettler ME-30 model electronic balance. Aerosol filters were conditioned at least 2 days in a dry atmosphere (silica gel desiccators) and then weighted. To avoid interactions with static charges, a U electrode (Mettler) was placed near the balance cage. Although the precision of the balance is 1 µg, due to the conjunction of different unfavourable factors, it may be assumed that the mass accuracy is of the order of 10 µg (or better) by weighing stage, which means better than 20 µg per filter aerosol sample mass.

2.3.1 *Carbon analyses*

Carbon analysis comprises the evaluation of the carbonaceous content of aerosols (TC) but more importantly its distribution between the two components EC and OC which have very different atmospheric and chemical properties (TC = EC + OC). Indeed, EC which is the dark, black component of aerosols is an efficient light absorbant (Horvath 1993, Liousse et al. 1993), a vector of pollution gases due its absorption surface properties (Cachier 1998) and thus the main agent for the formation of black patinas. On the other hand, OC particles form a complex evolutive mixture and could be the main agent responsible for the laser yellowing (Gaviño et al. 2004). Analyses were firstly conducted following a protocol set up previously at LSCE (Cachier et al. 1989) internationally recognized and calibrated. In this *LSCE protocol*, carbonates are firstly removed by exposure to HCl fumes. Acidity is then neutralized by a prolonged exposure in a basic (NaOH pellets) atmosphere. Then two identical filter punches are placed into combustion boats, one punch is analysed directly for its total carbon content whereas the second half is submitted to a pre-combustion step (2 hours at 340°C under a pure oxygen atmosphere) for the purpose of elimination of OC which is less thermally resistant than the EC component. After this thermal pre-treatment, only EC is present in the sample and then can be analysed. OC is calculated as the difference between TC and EC contents. Carbon contents were obtained by *coulometry* using a Strölhein Coulomat 702C analyser, working at pH 10. The precision of the instrument is 0.02 µg but aliquoting the filters, the proper instrument blanks and filter blank variability limit the measurement repeatability in the range of 5–10%.

One of the major challenges for the reliable measurements of carbon particle concentrations is by far the EC/OC speciation (Cachier 1998). Actually, there is no universal methodology and the question is still under debate. See for example http://occ.fortlewis.edu/Aerosols/OCEC/articles.htm whereas numerous international intercomparisons show important discrepancies between different protocols and even within laboratory groups using the same method (Birch 1998, Hitzenberger et al. 1999, Schmid et al. 2001, Currie et al. 2002). Among the so-called reference methods, two of them are widely employed: the IMPROVE method developped at the Desert Research Laboratory DRI and the NIOSH method developped at the Sunset Laboratory. Both methods are based on a thermal analysis and comprise two steps of increasing temperature: the first step is under an inert atmosphere (pure helium) while the second

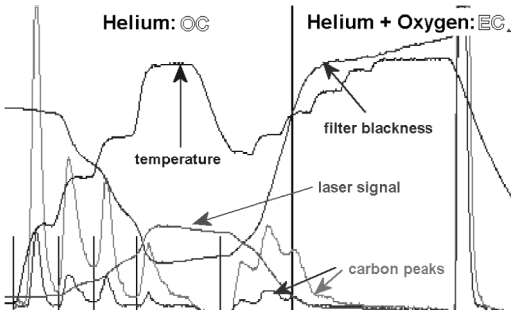

Figure 7. Thermo-optical analysis of a carbonaceous aerosol sample (Sunset Instrument).

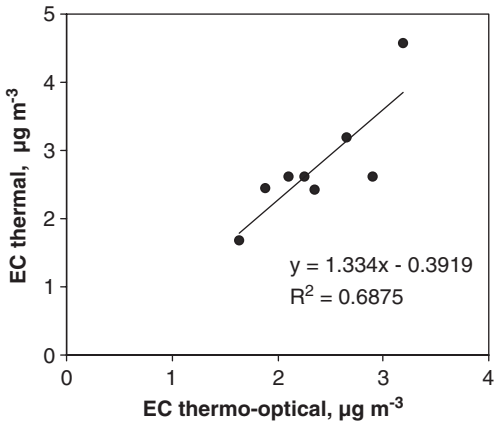

Figure 8. Intercomparison of EC results obtained with the LSCE thermal method and the DRI thermo-optical method (Milan aerosols).

step is under an oxidative one (helium and oxygen). The OC aerosol fraction (and the carbonates) are supposed to evolve during the first step whereas EC evolves during the last one only (Fig. 7). As OC may undergo some charring (and thus may appear as EC), optical measurement with a laser beam of the filter blackness during the whole temperature set up process allows in principle adequate corrections of this artefact.

The two instruments available in the market for carbon analysis are designed for these two methods. But intercomparison exercises show discrepancies for EC/OC ratio results obtained for the same samples (Chow et al. 2003). In short, discrepancies between the different protocols are related to the different temperature steps, the presence of carbonates and the charring of the OC fraction which cannot be satisfactorily corrected (Cachier 2003).

Discrepancies between the different analytical protocols are probably dependent on the nature (origin and age) of the aerosol. For the CARAMEL experiment samples, we applied systematically three different carbon analytical protocols in order to capture common features of the European urban aerosols and to investigate sources of discrepancies between the protocols for that particular type of combustion aerosols. However all over this work, the *LSCE method* was used as the reference method. As an example, Figure 8 shows the correlation between two data sets obtained for Milan aerosols.

2.3.2 *Ions analyses*

Major ion concentrations were obtained by Ion Chromatography using a Dionex DX-100 equipped with a AG11 separator column for cations (Na^+, Mg^{2+}, Ca^{2+}, NH_4^+), and a Dionex DX-500 equipped with a ASS11 separator column for anions (SO_4^-, NO_3^-, chloride, oxalate).

Aerosol dissolution was performed by soaking the filters placed in plastic vials with 20 ml of ultra pure water. The solutions were then submitted to ultra sounding during 20 minutes. In order to avoid species absorption onto the vial walls, analyses were conducted immediately after the soaking step. Aerosol dissolution was regularly checked by repeating a second dissolution: the process was considered satisfactory if the second dissolution showed concentrations less than 10% of the first one, which was the case most of the time. Concentrations were obtained with an average accuracy of 10%.

2.4 *Real-time analysers*

Real-time analysers were used during the intensive campaigns in order to gain information on the spatial or temporal (diurnal or day to day) variability of aerosols and related sources.

Magee Scientific aethalometers (Hansen et al. 1984) were used to obtain real time data for EC particle mass. The observational periods varied from site to site from 2 weeks to several months.

The aethalometer filters air continuously through a white quartz fiber tape and gives an optical measurement of the filter darkness, which may be directly related to the EC mass which has been accumulated on the filter, as EC is considered as the only absorbing component of the atmospheric aerosol phase (see Cachier 1998 and references herein). EC (optical) aethalometer data were compared against EC thermal data obtained by filter thermal or thermo-optical analysis sampled in parallel. For a given site, the comparison is generally satisfactory (Fig. 9).

But it may be underlined that the slope of the correlation line is almost never 1.0 and more importantly displays site to site variations (Table 1).

This may be explained primarily with the Mie theory showing dependency of the aerosol specific absorption coefficient with the particle aerosol size (Horvarth 1993, Liousse et al. 1993).

However at a given site, in spite of the potential calibration problems, it may be considered that non-calibrated aethalometer data give valuable insights of EC concentration short-term variability and thus allow a better knowledge of prevailing sources.

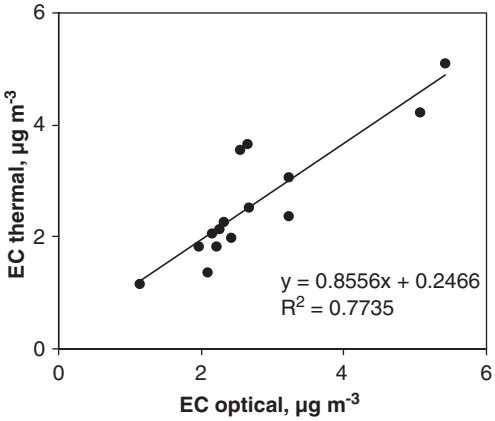

Figure 9. Intercomparison of EC results obtained with the LSCE thermal method and the aethalometer-optical method (Milan aerosols).

Table 1. Correlation for EC concentrations obtained on the same filter sample by a thermal method (LSCE), a thermo-optical method (DRI) and an optical method (aethalometer).

	Thermal/thermo-optical		Thermal/optical	
Site	λ	r^2	λ	r^2
Paris	0.91	0.87	0.93	0.78
Seville	0.95	0.92	0.85	0.95
Milan	1.33	0.69	0.86	0.77
Florence	0.58	0.74	0.49	0.64

A CNC analyser (TSI 3020) was also used. This instrument gives particle number concentrations (in p/cm^3) for fine (Condensation Nuclei) particles (diameter from 7 nm to 3 μm) and is thus very sensitive to small particles which is the case of primary and secondary particles originating from the various combustion processes such as burning or traffic (Harrison et al. 1999, Shi et al. 1999, Cachier et al. 2004).

Finally, an optical particle counter (GRIMM counter) provided particle distribution in size bins for particle over 300 nm in diameter.

3 RESULTS

3.1 *Common features*

Although site to site differences are observed, striking common features for all sites sort out from the analysis of our data (Table 2).

3.1.1 *The importance of the fine aerosol fraction*

The fine aerosol mass fraction (PM-2, as obtained with the SFU) is a little less important but still of the order of the coarse fraction (above 2 μm), representing more than 40% of the total mass on average. Although meteorological and/or local conditions (such as rain or building repair and cleaning) may modify the fine/coarse ratio this feature is characteristic of modern urban atmosphere (Ruellan & Cachier 2001). From this data, it may be easily understood that particle number distribution data enhance the predominance of fine particles with more than one order of magnitude between ultrafine (<0.100 μm) and fine particles, and between fine and coarse particles.

3.1.2 *The carbonaceous aerosol is dominated by organic aerosols and both EC and OC are found predominantly attached to the fine fraction*

The particulate organic matter (POM) is calculated by scaling OC concentrations: POM = OC × 1.4 (Hugues et al. 2000). Interestingly, carbonaceous particle concentrations are quite similar for the four sites. Although filters display a grey colour, the EC content is always less than the POM content but there is a

Table 2. Mean mass (in μg/m^3) concentration data **(bold is fine particle data)**

	Mass	POM	EC	SO_4^{2}	NO_3^{-}	NH_4^{+}	Ca^{2+}
Florence	24.7	3.52	0.48	0.89	2.04	0.21	1.57
	22.84	**8.21**	**1.92**	**3.46**	**0.83**	**1.24**	**0.21**
Milan	2558	2.78	0.53	1.00	2.33	0.40	0.74
	17.87	**6.49**	**2.13**	**3.35**	**1.44**	**1.67**	**0.13**
Paris	25.93	2.55	0.47	1.96	2.35	0.17	2.25
	17.85	**5.95**	**1.88**	**2.85**	**1.76**	**1.26**	**0.17**

significant EC/TC ratio variability among the sites (Table 3).

EC/TC ratio is of the first order, a reflect of the nature of the combustion source. From our data it may be assessed that the two extremes: Seville and Florence are influenced by a different source mix. A hypothesis to be confirmed is that on the one hand the Seville site is heavily influenced by heavy-duty diesel mobile sources (buses) which are known to produce predominantly fine EC particles.

On the other hand in Florence, there might be an overproduction of fine OC particles by 2-stroke engines (scooters), which are still numerous in the Cathedral surroundings.

3.1.3 *The predominance of the carbonaceous fraction over the ion fraction*

The carbonaceous fraction is overwhelming at all sites in the fine fraction and sulphate, although the most abundant ion species is less important. This result reinforces many data and assessments on sulphate abatement due to a strong and efficient policy of fuel desulphurization in Western Europe accompanied by a disapearance of polluting combustion activities (heavy industries and domestic heating with liquid and solid fuels) in the vicinity of urban areas.

However, the importance of carbonaceous particle concentrations in urban atmospheres is now the major and increasing concern for air quality. This problem is probably due to mobile sources (including, cars, light duty and heavy duty and 2-stroke engines). The traffic sources are poorly controlled by comparison of industry plants (excepted for CO) and both their particulate (EC and OC) and gaseous emissions (NOx and Volatile Organic Carbon: VOC) have the potential to enrich the submicrometer sized range of the aerosol phase with primary and secondary particles (Odum et al. 1997, Cachier et al. 2004).

3.1.4 *The predominant influence of the traffic source*

Figure 10 presents a typical EC aerosol mass monitoring performed with the aethalometer. EC concentrations exhibit a daily pattern which can be almost completely understood and interpreted by traffic intensity, with morning peaks and in a lesser extend late afternoon peaks. The circles underline the two sundays of the data set which apparently have a different design. These peaks are superimposed to a variable background which depends probably on the meteorological conditions and/or the regional activity.

In order to remove this day to day variability with the purpose of verifying the influence of the traffic source, it is possible to convert the data in normalized hourly concentrations (giving day by day deviation from the day mean concentration). In Figure 11, it may be seen that the four cities of our study present the same daily pattern with a morning traffic peak, late afternoon traffic peak, low concentrations in the afternoon and at night. In Seville the important difference between mid-afternoon and evening activity reflects perfectly the people way of living. Although no striking seasonal trends were observed at all sites, some specificities may be enlightened.

Interestingly in Florence, EC aethalometer data obtained during 4 months, as displayed in Figure 12, show an increase trend from the summer days to fall indicating that more than tourism activity, regional traffic activity of people (back to work) is an important contribution to local pollution near the cathedral. The peak of traffic activity observed in October might have to be related to demonstrations and international meetings hold in the City at that time.

Table 3. Carbon fraction of the mean aerosol at the four CARAMEL sites.

	EC ($\mu gC/m^3$)	TC ($\mu gC/m^3$)	EC/TC (%)
Paris	2.5	8.8	30
Seville	5.9	16.7	36
Milan	2.7	9.3	29
Florence	1.8	9.3	22

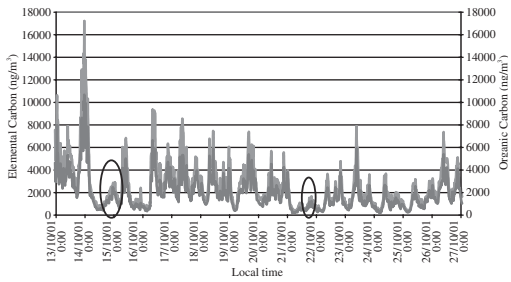

Figure 10. EC monitoring with the aethalometer at Saint Eustache (October 2001).

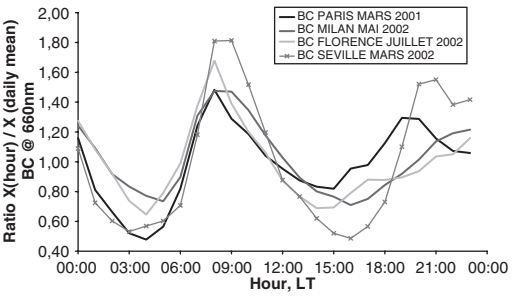

Figure 11. Daily pattern of EC normalized concentrations at the four urban sites of the study.

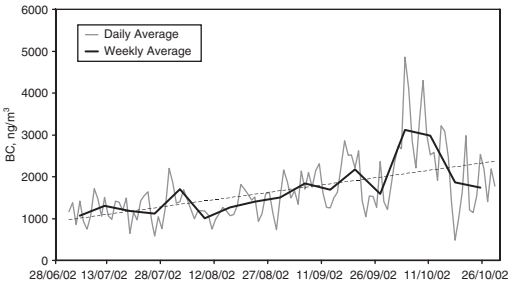

Figure 12. EC aethalometer data in Florence for the period July/October 2002 (hourly concentrations).

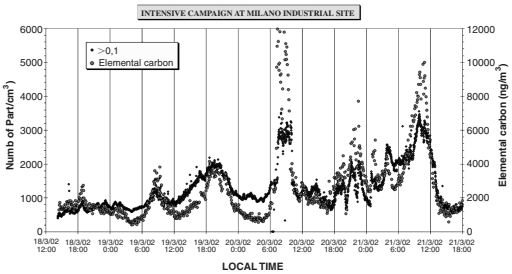

Figure 13. Parallel evolution of EC mass and particle number concentration for Milan aerosols (March 2002).

The predominance of the traffic source may be also shown by particle counter data. At each site, parallel measurements of particles and EC particle mass show a correlation particularly during pollution episodes (traffic peaks). This assessment is illustrated here for Milan site (Fig. 13) showing the parallel evolution of the two indicators either during traffic peaks or during background conditions. From this result it may be concluded that either a single source or most likely a constant source mix is prevailing for the pollution. This source mix is most likely composed predominantly by a given traffic fleet with qualitatively stable emissions.

In Seville, we operated a tour around the Cathedral while recording particle number with a portable CNC (condensation nuclei counter). The good correlation found at the sampling site between EC mass and particle number could allow to parallel any CN evolution with EC mass.

Results presented in Figure 14 show that the background of particles is low (about 20,000 particles/cm^3) and quite constant around the cathedral whereas a single façade, along the busy street, shows particle number multiplied by more than one order of magnitude. This experiment illustrates the deleterious effect of traffic channelling in the Avenida de la Constitucion, enhancing particulate pollution by a factor of 10.

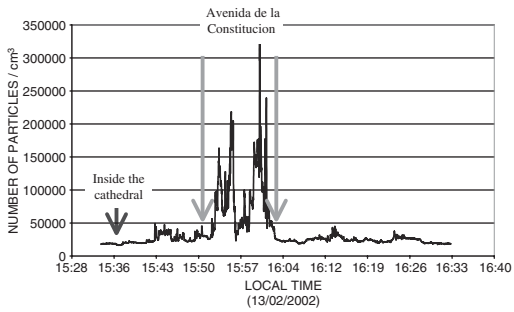

Figure 14. Particle number (CN) along the Seville Cathedral.

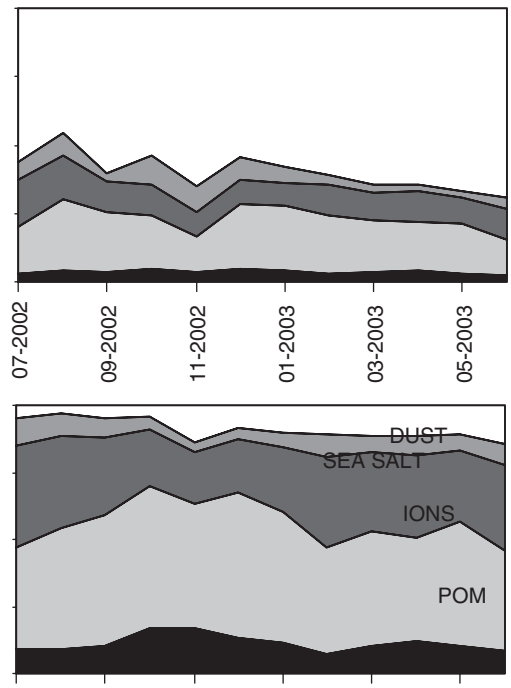

Figure 15. One year (2002–2003) monitoring of the chemical composition of Florence aerosols (divided into coarse and fine fractions).

3.2 *Chemical composition of the aerosols and its seasonal variations*

Our data allows to propose a mass closure of the aerosol. At all sites the fine and coarse particles are strikingly different (Fig. 15), indicating that the sources producing fine and coarse particles are of different nature.

The coarse aerosol is dominated by insoluble particles (dust). Notable portions of nitrate are found in

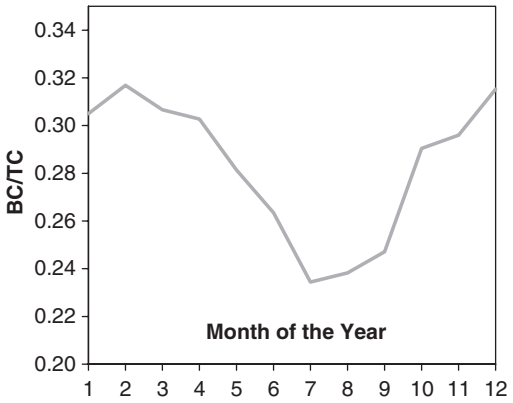

Figure 16. Seasonal evolution of the EC/TC ratio for Paris aerosols, showing the formation of secondary OC in summer.

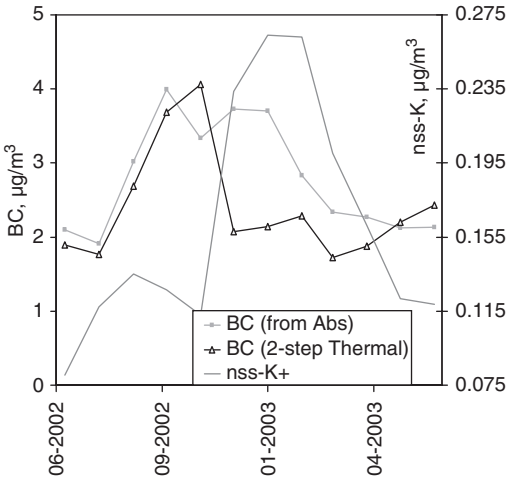

Figure 17. EC (also referred to as BC) monthly means obtained by the LSCE thermal method and the aethalometer, for Florence aerosols. The potassium data shows that the discrepancy in winter is due to additional aerosols emitted by biomass burning (probably fuel wood) for heating.

this mode. This is probably due to the formation of secondary aerosols by neutralization of gaseous nitric acid by coarse alkaline particles (sea salt or dust). The attachment of gases onto particles might also be the cause of the attachment of notable amounts of particulate OC.

The fine aerosols are dominated by POM and sulphate with however always a dominance of carbonaceous species.

As it may be seen in Table 2, nitrate is quite abundant in the fine mode although less than in the coarse mode. This data denote the existence of ammonium nitrate (in the fine mode). For our four sites of study, nitrate is thus shared between the fine and coarse particles probably because ammonia is not abundant enough to neutralize both sulphate and nitrate.

A careful look at the seasonal chemical composition of the aerosols show interesting trends although these trends are not captured in the raw atmospheric concentration data. A first important result is the formation of secondary particles which occurs in the fine mode of the aerosol. This formation is particularly intense in summer when photochemistry allows the oxidation of SO_2, NO_x or VOC and their conversion from the gaseous to secondary particles in the aerosol phase. The abundance of sulphate in summer is likely to shift the aerosol pH to an acidic state. For VOC, the gas-to particle conversion is captured principally by the EC/TC ratio; when OC is more abundant, EC is relatively less abundant and the ration EC/TC decreases. Figure 16 shows such a trend for the aerosol in Paris.

Seasonality of the aerosol may be also a consequence of differences in the prevailing sources. For Florence aerosols, it has been observed that the agreement between the thermal method and the aethalometer optical method was season-dependent.

Indeed, as shown in Figure 17, EC results are consistent excepted for winter months. From these results it may be assessed that during winter, the mixture of combustion aerosols differs from that of the rest of the year. This hypothesis is strongly reinforced by the potassium data obtained on allocated filters. As potassium is now recognized to be a biomass burning tracer (Andreae 1983, Cachier et al. 1991), it may be assessed that during the winter months, there is a regional use of fuel wood in fire places or domestic heating settings important enough to compete with the influence of traffic in the aerosol atmospheric mix.

Finally, an interesting point to discuss is the seasonality of the presence of ammonium nitrate concentrations in the aerosol. Ammonium nitrate aerosol is very sensitive to ambient temperature and almost does not exist above 15°C (Mozurkewich 1994). At the four sites of our study, nitrate is thus likely to show a seasonal pattern with a relative abundance peak during the cold winter months. This is indeed what was observed.

Interestingly, this sensitivity of indicators to ambient temperature is also recorded by other indicators such as the total aerosol mass.

In Figure 18, we reported total aerosol mass obtained by weighing and an average of PM-10 of four surrounding stations. Off winter months, there is a good agreement between the two types of measurements. It must be recalled here that PM-10 is the fraction of the aerosols phase with particles smaller than 10 µm in diameter. This fraction is most of the time comparable to the total aerosol mass as particles bigger than

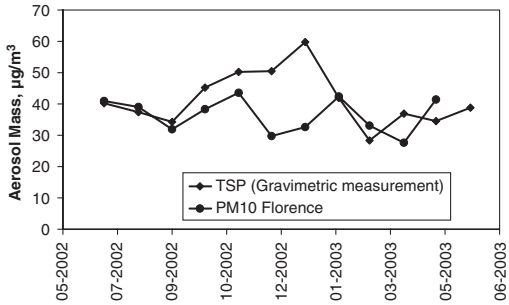

Figure 18. Aerosol monthly mean mass concentrations obtained by weighing at our sampling site and by TEOM PM-10 measurements at four stations of the Florence Air monitoring network.

10 µm are scarce and settle very rapidly. The important discrepancy observed during cold winter months may be attributed to TEOM artefacts and related to the heating of the sampling line at 50°C as recommended by the manufacturer in order to avoid water sampling with the aerosol. It may be thus concluded that during the cold months, when ammonium nitrate is abundant in urban particles, this aerosol is indeed collected onto the filters submitted to weighing and further chemical analyses whereas it escapes TEOM sampling. However, it may be checked that the wide mass difference between weighing data and TEOM data is by far more important than the ammonium nitrate only.

This results points to other semi-volatile species among which good candidates might be organic gases able to condensate into the particulate phase at low temperatures, but escape the TEOM sampling.

4 CONCLUDING REMARKS

The study of the four urban area aerosols underline common features which could provide an average picture of urban pollution in Western Europe. Traffic appears to be by far the major responsible source of atmospheric particulate pollution and differences among the sites are mostly connected to differences in traffic fleet, traffic density and prevailing meteorological conditions. Our results confirm the worldwide concern about traffic pollution in urban dense areas and the consequences on visibility, people health and degradation of built heritage. A striking illustration is the repetitive "nephos" in Athens (Valaoras et al. 1988), but less spectacular but still persistent is the deleterious presence of gaseous and particulate traffic-derived pollutants in all European cities, a pollution mix with its own characteristics.

Due to a shift of fuel usage from solid fuel (coal) to liquid and gas fuels and parallely to an important and voluntarist reduction of the sulphur content of fuels the role of sulphur species (SO_2 and sulphates) in atmospheric pollution is declining. Conversely and unfortunately, nitrogen species (NO_x and nitrates) and carbonaceous species (organic gases, elemental and organic particles) are gaining more importance especially due to the increasing use of diesel motors in the fleet of light and heavy-duty vehicles (Schaap et al. 2003, Cachier et al. 2004). The carbonaceous particles emitted in the atmosphere by traffic either as primary aerosols or as secondary particles are found in the submicrometre-sized range. This predominance of fine carbonaceous particles is found for both particle number and particle mass. This important results suggests that PM-1 or PM-2.5 are now more appropriate than PM-10 to follow progress in urban air quality.

Site to site differences are mostly due to differences in the vehicle fleet: in Florence it was possible to point to the significant influence of scooters, whereas in Seville the severe pollution by diesel buses is clearly shown. Interestingly, an additional significant source of pollution was found during winter in Florence due to the use of fuel wood. The fine fraction of the aerosol is likely to be neutral in winter and to shift to a more acidic state in summer due to the formation of secondary sulphates, nitrates and organic particles.

Modern soiling of monument surfaces appears to be produced by a totally different atmospheric mix than that from which historical black crusts originated. This difference resides in the chemical composition of the aerosols, which are less acidic than in the past, but also in their size as an overwhelming portion of the particles (>90%) is smaller than one micron, most of them smaller than 100 nm. From our results it may be assessed that traffic regulation is nowadays a key and almost the only factor to target on, for both the improvement of air quality and the decrease of monument soiling rate.

ACKNOWLEDGEMENTS

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Organic analysis of aerosols in Seville atmosphere

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ABSTRACT: For more than five decades, exhaust emissions from gasoline- and diesel-powered vehicles contributed to the deterioration of the cathedral of Seville, particularly of stone and terracotta statues from the three western façade portals. This is due to the location of the main façade in a narrow street with intense traffic. A study on the organic composition of aerosols sampled at different periods of the year, under distinct traffic regimes, is presented. A strong correspondence between the lipids present in the cathedral black crusts and those of collected from urban aerosols was found.

1 INTRODUCTION

Residents and public officials in urban areas around the world are concerned about traffic congestion and air pollution. Traffic congestion and air pollution are exemplified in the city of Seville with a historic centre formed by very narrow streets. One of the streets conducting to the very centre of the city is Constitution Avenue, which is delimited in one of the sides by the cathedral. For more than five decades, exhaust emissions from gasoline- and diesel-powered vehicles contributed to the deterioration of the cathedral of Seville. The years 60–80 were particularly harmful for the cathedral, since the trams were substituted by diesel buses. Until the mid-90s the belt of narrow streets surrounding the cathedral was fully active, routing all the traffic of the city centre as well as serving the surrounding areas, with continuous traffic congestion. In addition, the squares facing the eastern and southeastern façades were used as parking lots. Today, the traffic has been partially restricted, but only under the northern, southern and eastern façades, while intense traffic continues on Constitution Avenue where the main façade and the Birth, Assumption and Baptism portals, with sculptures from the 15th and 19th centuries, are located. It is on this narrow street where the greatest concentrations of gases and aerosols are reached as it routed all downtown traffic. The particular situation of the western façade permits to investigate the impact of air pollution on the cathedral and with this aim an aerosol monitoring was carried out. The data obtained are reported by Cachier et al. (2004). This paper focuses on organic characterization of the sampled aerosols. A few weeks every year, in Holy Week, the Sevillian municipality introduces traffic regulations resulting in partial or total closure of the street for religious processions. A study on the chemical composition of aerosols sampled at different periods of the year under distinct traffic regimes is presented. The aerosol composition was compared with previously studied black crusts from the cathedral.

2 MATERIAL AND METHODS

2.1 *Sample collection*

Aerosols were collected in a high volume air sampler (Staplex Co., New York, USA, model TFIA-2) operating at a flow rate of 2 m^3/min. The sampler was installed in the roof of the Assumption portal, at about 22 m height, and facing the traffic-congested Constitution Avenue. Different traffic regimes were considered:

1. Sampling A in regular traffic conditions, carried out between 11 and 14 June 2002 from 9.00–20.00. Vehicular traffic included buses, cars and mopeds (Fig. 1).
2. Sampling B under partial restricted traffic conditions: from 24–30 March 2002, from 9.00–17.00. Vehicular traffic permitted only for cars and mopeds during the morning (Fig. 2).
3. Sampling C under no traffic: from 24–30 March 2002. Sampling was carried out from 17.00–2.00, except for 29 March in which sampling continued from 2.00–8.00. No vehicular traffic, but continuous religious processions carrying several hundred thousands candles occupied the street and were observed by many thousands of people (Fig. 3).

Figure 1. Regular traffic at Constitution Avenue. Buses contribute largely to air pollution.

Figure 2. Partial traffic restrictions. Morning traffic permitted for cars and mopeds during Holy Week.

Black crusts were collected from the Baptism portal during the cleaning and restorations works carried out in 2000. Sampling area was located at 20 m height.

2.2 *Analysis of compounds*

The analytical procedure for identification of compounds present in aerosols and black crusts was as follows: 5–10 g of a filter (or 20 g of black crusts) were extracted in a Soxhlet apparatus with dichloromethane-methanol (2:1) for 72 h. The extracts were evaporated under vacuum at low temperature (below 40°C) and redissolved in dichloromethane-methanol (2:1). The resulting extract was chromatographed using a silica column, eluted with hexane (fraction I), hexane-dichloromethane (1:1) (fraction II), dichloromethane (fraction III), and finally with methanol (fraction IV). Compounds present in fractions III and IV were methylated with trimethylsilyldiazomethane ($TMSCHN_2$). In this paper we will concentrate in the study of fraction I containing the most characteristic series of compounds and molecular markers. A detailed study of the four fractions obtained from black crusts of Saint Denis Basilica was reported by Gaviño et al. (2004).

Figure 3. No vehicular traffic during Holy Week afternoons and nights. Avenue occupied by religious processions.

For analysis, 2 μL of each fraction were injected in a Fisons gas chromatography-mass spectrometry (GC-MS) instrument, model GC 8000/MD 800, using a 30 m × 0.25 mm TRB-5HT column (film thickness 0.1 μm). The GC oven was programmed from 80 to 120°C at 30°C min^{-1} and then to 320°C. The final temperature was held for 20 min.

In the analytical procedure followed in this work, the carboxylic acids were recovered as the corresponding methyl esters, and the hydroxyls as methoxyls. Throughout this paper they are referred to as acids and hydroxyls – their original forms – rather than as derivatized methyl esters and methoxyls.

The compounds were identified by comparison of their mass spectra with a self-compiled data bank of compounds from a variety of samples (Saiz-Jimenez, 1993, 2003; Gaviño et al. 2004). In some cases, identification was achieved by computer analysis from a National Bureau of Standards library of about 54,000 spectra, with the computer matching being checked against standards whenever possible.

3 RESULTS AND DISCUSSION

Great concentrations of gases and aerosols are reached in Constitution Avenue, a very narrow street delimited by the cathedral western façade. This street routes all traffic to the city centre. A study estimated daily traffic in this street in 2,200 buses, 7,000 motorcycles and 13,600 cars as average for 1997 (Saiz-Jimenez et al. 2004). Nowadays the figures could likely be higher. Cachier et al. (2004) found that elemental carbon (EC) in Seville aerosols (sampling in the same place used in this study) was three times higher than in Florence cathedral and twice than in Paris (Saint Eustache church) or Milan cathedral. This was explained by the fact that Seville is heavily influenced by heavy-duty diesel buses which are known to produce predominantly fine EC particles.

A sampling tour around the cathedral of Seville while recording particle number with a portable condensation nuclei counter showed that background was about 20,000 particles/cm^3. However, Constitution Avenue revealed particles number as high as 329,000 particles/cm^3. The higher values (>300,000 particles/cm^3) corresponded to the pass of diesel buses routing the street. This experiment illustrates the deleterious effect of traffic channelling in Constitution Avenue enhancing particulate pollution (Cachier et al. 2004).

Sagebiel et al. (1997) studied the importance of diesel vehicles in the production of particulate emissions and reported that 31 diesel vehicles whose age averaged 22 years showed average emissions of 944 mg/km, with one vehicle emitting at a rate of 10,500 mg/km. For comparison, emission rates of total particles were below 6 mg/km for most production catalyst vehicles.

Figure 4 shows the street and the place where the aerosol sampler was located. After sampling, the filters were extracted with solvents and the total extracts analysed by GC-MS. The total ion current chromatogram traces (not shown) confirmed that the extracts contained a complex mixture of compounds dominated by *n*-fatty acids (C_{12}-C_{18}), aliphatic dicarboxylic acids (C_8, C_9), aromatic compounds (benzenecarboxylic acids) and nicotine. In addition, the series of *n*-alkanes (C_{13}-C_{29}) was evident. Many other compounds present in minor or trace amounts could be discerned. A further

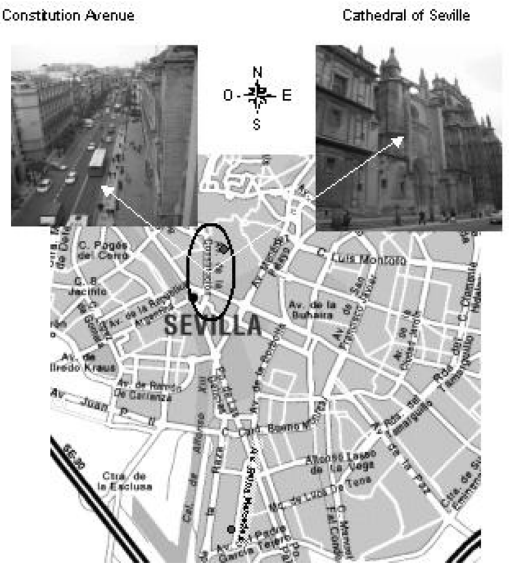

Figure 4. Aerosol sampler location.

fractionation was necessary in order to individualise specific series of compounds for source apportionments and to avoid overlapping and/or complex unresolved mixtures.

Although four different fractions were obtained from the total extracts by column chromatography, here we will refer only to fraction I having a diagnostic interest (e.g. biomarkers). Figure 5 shows a selected ion mass chromatogram (m/z 85) for fraction I, indicating the distribution of *n*-alkanes in sampling A (no traffic restrictions), B (partial traffic restrictions) and C (no traffic). The traces are dominated (in decreasing order) by a large unresolved complex mixture (UCM) or "hump", with the main resolved components being *n*-alkanes. Isoprenoid hydrocarbons (pristane and phytane) were identified as well. While similar *n*-alkane distribution was observed in all the three chromatograms, differences in maximum at C_{29} for A, and at C_{27} for B and C, and in the intensity of the UCM formed by the presence of many overlapping peaks were evident. Similar patterns of *n*-alkanes maximising at C_{29} were reported for urban areas in Western United States aerosols (Simoneit 1986).

Figure 5D shows the ion mass chromatogram trace (m/z 85) for fraction I obtained from black crusts collected from the Baptism portal.

A bimodal distribution of *n*-alkanes was observed. The first part maximised at *n*-C_{21}, and the second part of the series had a maximum at *n*-C_{29}. Patterns of *n*-alkanes maximising at C_{21} were reported for diesel and gasoline engine exhausts and patterns maximising at C_{29} were typical of urban aerosols