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Organic and elemental carbon concentrations in carbonaceous aerosols during summer and winter sampling campaigns in Barcelona, Spain

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Abstract

Daily PM10 and PM2.5 samples were collected at an urban background monitoring site in Barcelona (Spain) in summer and winter 2004. The instrumentation used consisted of two high-volume (PM10 and PM2.5) and two low-volume samplers (PM2.5), one of them coupled to an annular diffusion denuder aiming to evaluate the influence of sampling artefacts related to the adsorption of volatile carbonaceous species. Quartz fibre filters of 15 cm and 47 mm diameter were used as collection substrates (Schleicher & Schuell QF20 and Whatman QM-A, respectively). The resulting samples were analysed for organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC). Total carbon (TC) was calculated as OC + EC. The present study aimed to (a) determine maximum (winter) and minimum (summer) OC/EC/TC/WSOC levels in the study area, and (b) assess the magnitude and influence of positive sampling artefacts. Mean levels of TC in PM2.5 ranged from 4 to 5 $\mu g\,m^{-3}$ in summer to 7–10 $\mu g\,m^{-3}$ in winter with the different samplers (5 and 8 $\mu g\,m^{-3}$, respectively, in PM10, one sampler); OC levels in PM2.5 were 3–4 $\mu g\,m^{-3}$ in summer and 6–7 $\mu g\,m^{-3}$ in winter (4 and 6 $\mu g\,m^{-3}$ in PM10); EC levels in PM2.5 ranged from 1 to 2 $\mu g\,m^{-3}$ in summer to 1–3 $\mu g\,m^{-3}$ in winter (1 and 2 $\mu g\,m^{-3}$ in PM10). Thus, OC/EC/TC winter levels were higher than summer levels by a factor of 1.7–2. WSOC levels were 1.6 $\mu g\,m^{-3}$ in PM2.5 and PM10 in summer, and 2.1 $\mu g\,m^{-3}$ (PM2.5) and 1.9 $\mu g\,m^{-3}$ (PM10) in winter. The results indicate that positive artefacts for OC accounted for 0.5–0.7 $\mu g\,m^{-3}$, representing 11–16% of the raw OC mass and 3% of the PM2.5 mass. Sampling artefacts for OC were slightly higher in summer. EC levels were similar for the low-volume samplers and unusually low for the high-volume samplers, suggesting that EC determination could be influenced by the filter type.

1. Introduction

Road transport is widely recognised to be a significant and increasing source of atmospheric particulate matter (PM) in urban environments

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(Colvile et al., 2001). A number of studies (Kuhlbusch et al., 2004; Querol et al., 2004; Salvador et al., 2004; Vallius et al., 2005) have estimated the traffic contribution to range between 30% and 50% of the PM10 mass at urban and kerbside sites throughout Europe. Road transport is distinguished from other sources of air pollution in that the emissions are released in very close proximity to human receptors, thus reducing the opportunity for atmospheric dilution of the emissions, which would render them less likely to damage human health. Furthermore, the major impact of road traffic emissions on human health can occur inside the buildings that line city streets, where concentrations of pollutants from road traffic are determined largely by the outdoor concentration adjacent to windows and doors (Kukadia and Palmer, 1998).

Traffic-derived aerosol particles are emitted directly into the atmosphere as a result of incomplete combustion of fossil fuels and abrasion processes of automobile components such as brake or tyre wear (Fraser et al., 1999; Colvile et al., 2001; Sternbeck et al., 2002; Adachi and Tainosho, 2004). Furthermore, traffic also constitutes a source of primary atmospheric particles by means of road dust re-suspension through mechanical and thermal turbulence (Weckwerth, 2001; Sternbeck et al., 2002; Adachi and Tainosho, 2004). On the other hand, secondary atmospheric particles are also derived indirectly from traffic through physico-chemical reactions taking place in the atmosphere, mostly related to hydrocarbons emitted as vapour in the exhaust (Fraser et al., 1999; Colvile et al., 2001).

Two of the major components of atmospheric particles emitted by traffic (both diesel and gasoline) are organic carbon (OC) and elemental carbon (EC) (Fraser et al., 1999). However, the amount of information found in the literature regarding the levels or the behaviour of these PM components is limited due to a number of factors among which are the large number of existing organic compounds, the influence of artefacts during sampling and storage of the samples; the absence of a reference method for comparable sampling of carbonaceous aerosol, and the difficulty to distinguish between OC and EC (Salma et al., 2004). With regard to artefacts arising during carbonaceous aerosol sampling, a number of authors (Turpin et al., 2000; Mader et al., 2001) demonstrated the prevalence of positive over negative artefacts. Positive sampling artefacts consist of the adsorption of organic gaseous compounds onto the filter or the particles collected on it. As a consequence, the occurrence of positive artefacts results in overestimated OC and PM mass levels.

Another interesting form of carbon is water-soluble organic carbon (WSOC), as it has a potentially important role in aerosol–cloud interaction (Cruz and Pandis, 1997; Matsumoto et al., 1997), due to the fact that WSOC contributes to cloud condensation nuclei (CCN). Emitted VOCs or primary organic aerosols react with oxidants forming polar functional groups, which result in more water-soluble compounds (Ruellan and Cachier, 2001, and references cited therein). The levels of WSOC in aerosols are closely related to nucleation processes during rain and cloud growth, even though water-soluble inorganic salts such as sulphate have been taken by classical theory as major factor of cloud nucleation. Due to their high water-solubility, WSOCs have the potential to modify the hygroscopic properties of atmospheric particles (Saxena et al., 1995).

Taking into account the above considerations, the city of Barcelona was selected in order to evaluate total carbon (TC)/OC/EC/WSOC levels and sampling artefacts related to carbonaceous aerosols in North-eastern Spain. One summer and one winter sampling campaign were designed with the aim to determine maximum and minimum annual levels of these parameters, since the Western Mediterranean basin is characterised by distinctly different winter and summer meteorological scenarios. As a consequence of the influence of the Azores anticyclone, the meteorological scenario typical of the study area during winter is frequently dominated by atmospheric stagnation favouring the accumulation of atmospheric pollutants, which alternates with northerly winds and the frequent passage of cold fronts and low temperatures (11–13 °C and 63–76% relative humidity in winter vs. 27–29 °C and 63–66% in summer). High-pressure systems dominate during the summer months, resulting in the development of meso-scale circulations and the prevalence of sea/land breeze (Millán et al., 1997). Atmospheric circulations during the summer months are characterised by regional re-circulations owing to a significantly low barometric gradient, which favours the stagnation and subsequent ageing of the air masses. In this context, secondary aerosol formation and mineral dust re-suspension are enhanced (Rodríguez et al., 2003).

As regards anthropogenic PM emissions in Barcelona, the main sources are road traffic and

industry (including also power generation, waste incineration), although traffic is the main source of carbonaceous aerosols at the monitoring site. It must be stated that August is the usual holiday month in Spain, and thus ambient PM mass levels reach annual minima in this month ($17 \mu g m^{-3}$ in August vs. $25 \mu g m^{-3}$ PM2.5 annual mean, Querol et al., unpublished data). Despite the reduction in PM emissions, traffic (especially diesel-derived vehicles) remains as the main source for carbonaceous aerosols during this month.

Finally, the main aims of the sampling campaigns performed in summer and winter 2004 in Barcelona were:

(a) to determine maximum and minimum OC/EC/ TC/WSOC levels in atmospheric particulates in the study area. The only previously available data on OC/EC ratios found for Spain (Rodríguez, 2002) showed that OC levels accounted for 75% of TC (defined as OC+EC) at one traffic site and one rural site with industrial influence in Eastern Spain.
(b) to assess the magnitude and influence of positive sampling artefacts related to carbonaceous species, by coupling an annular diffusion denuder (Mikuška et al., 2003) to one of the low-volume samplers.

2. Methodology

PM10 and PM2.5 aerosols were sampled in Barcelona between 27/07/04 and 31/08/04 (summer campaign) and between 16/11/04 and 15/12/04 (winter campaign), at an urban background site under the influence of traffic located on the roof of the Institute of Earth Sciences "Jaume Almera". The building has two storeys and is found within the University campus at approximately 150 m distance from one of the city's main traffic avenues, the Diagonal Ave. Thus the main source of carbonaceous aerosols in this area is road traffic. The setup used for aerosol sampling was the same as the one used in a similar campaign carried out in June 2004 in Ghent (Belgium) and described in depth in Viana et al. (2006). The following instrumentation was used:

- One high-volume PM10 MCV (Barcelona, Spain) sampler ($500 L min^{-1}$) with a filter holder for a single 15 cm diameter quartz fibre filter (B10H).

- One high-volume PM2.5 MCV sampler ($500 L min^{-1}$) with a filter holder for a single 15 cm diameter quartz fibre filter (B25H). The face velocity for the high-volume samplers was $74 cm s^{-1}$ (the diameter of the aerosol deposit was 12 cm).
- One low-volume PM2.5 sampler ($17 L min^{-1}$) with a stacked filter holder with two 47 mm quartz fibre filters in series (B25WW, filters Q1 and Q2). The front filter (Q1) collects 100% of the particulate matter. The backup filter in this undenuded low-volume sampler (Q2) allows to assess the amount of gaseous species adsorbed on the sampling filter Q1 (Turpin et al., 2000; Mader et al., 2001). The face velocity for the low-volume samplers was $22 cm s^{-1}$ (the diameter of the aerosol deposit was 4 cm).
- One low-volume PM2.5 sampler ($17 L min^{-1}$) with a stacked filter holder with two 47 mm quartz fibre filters in series (B25DW, filters DQ1 and DQ2), preceded by an annular diffusion denuder developed at the Institute of Analytical Chemistry, Czech Republic (Mikuška et al., 2003). The annular diffusion denuder (Mikuška et al., 2003) consists of a stainless steel tube in which two tubes from copper wire net are coaxially placed to form an annulus. The space within of the inner cupreous net and the space between the outer cupreous net and the stainless steel tube are filled up with relevant sorbent. The denuder consisted of two sections, the first one collects atmospheric oxidants such as NO_2 and O_3 ($>99\%$ collection efficiency), and the second one removes gas-phase organic compounds ($>99\%$ collection efficiency; Mikuška et al., 2003). Material found on the backup filter in the denuded low-volume sampler (DQ2) would result from: (a) the presence of negative artefacts (volatilisation of organic compounds from the front filter); (b) adsorption of volatile inorganic compounds, or (c) the fact that the collection efficiency of the denuder for some gas-phase organic compounds is $<100\%$.

The setup with the denuders is intended to minimise positive artefacts derived from the interaction of gaseous organic compounds and atmospheric oxidants (NO_2, O_3) with the filter substrate and/or the particles collected on it. The evaluation of negative artefacts such as the loss of ammonium nitrate by volatilisation is not the aim of this paper, and it is thus not resolved by this setup.

The quartz fibre filters used were Whatman QM-A for the low-volume samplers and Schleicher & Schuell QF20 for the high-volume samplers. All the filters were pre-fired at 550 °C overnight before use, and stored in baked aluminium foil. After collection, the samples were stored at −5 °C in Barcelona and at −25 °C in Ghent (the samples were kept frozen during transport from Barcelona to Ghent).

The names of the samplers and filters are constructed according to: Barcelona (B); Quartz fibre filter (Q); Denuded Quartz fibre filter (DQ); PM2.5 (25); PM10 (10); High-volume sampler (H); Whatman-Whatman filters (WW).

Samples were collected on a daily basis over 24 h (including week-ends) with nominal start time at 9–10 am (local time). The sampling campaigns resulted in the collection of:

- Summer: 29 and 32 samples for the denuded and undenuded low-volume samplers (B25DWW and B25WW, respectively), 30 samples for the PM2.5 high-volume (B25H) and 31 samples for the PM10 high-volume sampler (B10H). Eight field blanks were collected for each sampler.
- Winter: 27 samples for the denuded and undenuded low-volume samplers (B25DWW and B25WW, respectively), 30 samples for the PM2.5 high-volume (B25H) and 29 samples for the PM10 high-volume sampler (B10H). Seven field blanks were collected for each PM2.5 sampler, and 8 for B10H.

PM mass was determined by weighing at 20 °C and 50% relative humidity with a Mettler MT5 microbalance (1 μg sensitivity), after the filters (samples and blanks) had acclimatised to these conditions for at least 24 h. All filters were then analysed for OC and EC by a thermal-optical transmission (TOT) technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC Analyser with the temperature programme described by Schmid et al. (2001). TC was determined as the sum of OC + EC. For the measurement of WSOC, filter punches of 1.5 cm^2 were placed in a 15 mL tube, 5 mL Millipore Simplicity water was added and the tube was hand-shaken during 5 min, after which it was allowed to stand for 30 min. The sample extract was then filtered through a PVDF syringe filter (pore size 0.2 μm) and the filtered extract was analysed for total organic carbon (TOC) using a Shimadzu TOC-V CPH high-sensitivity

Total Carbon Analyzer. Total water-soluble OC was calculated by difference between total water-soluble carbon and inorganic water-soluble carbon (TOC$_{WS}$ = TC$_{WS}$–IC$_{WS}$), and was used as WSOC. IC$_{WS}$ was, on average, 7% of TC$_{WS}$ for the B25H samples, and 13% in the case of the B10H samples. The PM mass, OC/EC/TC and WSOC data for the samples were all corrected for the blank levels obtained for the field blanks. In the case of WSOC, the percentage standard deviation for WSOC in the blanks, as calculated from the spread in the data for the 7 or 8 field blanks, was around 35%. However, the blank correction in WSOC for the actual samples remained, on average, limited to 8%.

A detailed description of the uncertainties associated with the PM mass and OC/EC/TC measurements is given in Viana et al. (2006). The average uncertainty of the mass determination for the filter samples is estimated as 1.4 and 1.5 μg m^{-3} for the low- and high-volume samplers, respectively. The uncertainty for the OC/EC/TC analyses for both high- and low-volume samplers was around 0.2 μg m^{-3} for OC, 0.1 μg m^{-3} for EC and 0.3 μg m^{-3} for TC.

OC levels presented in this paper are expressed as raw OC data and as corrected OC (OC$_{corr}$). According to Mader et al. (2003):

- if the positive artefacts prevail for the front filters in the undenuded samples and
- if the negative artefacts prevail for the front filters in the denuded samples

then artefact-free OC data may be obtained as

- for undenuded samples: OC$_{corr}$ = OC front filter−OC backup filter
- for denuded samples: OC$_{corr}$ = OC front filter + OC backup filter

Once this correction is applied the OC data from the two low-volume samplers should be the same. This correction is not applied to EC levels, as no volatilisation or adsorption artefacts should exist for this component. As expected, the EC data for the backup filters were insignificant.

3. Results and discussion

3.1. PM mass levels

Mean PM2.5 mass levels varied between 16.4 and 17.7 μg m^{-3} in summer and between 22.7 and

$29.1 \, \mu g \, m^{-3}$ in winter depending on the type of sampler (high- vs. low-volume) and the use of the diffusion denuders (Table 1). Levels of PM10 mass reached on average $29.5 \, \mu g \, m^{-3}$ in summer and $34.0 \, \mu g \, m^{-3}$ in winter, indicating that the particulate matter is predominantly in the fine fraction and that the proportion of the fine fraction increases during winter time (the mean B25H/B10H ratio and associated standard deviation for the PM mass was 0.56 ± 0.09 in summer vs. 0.76 ± 0.14 in winter). This increase is caused by the decrease of coarse dust re-suspension by summer convective circulations characteristic for Eastern Spain (Millán et al., 1997; Rodríguez et al., 2003). The large difference between the winter and summer levels (5–$13 \, \mu g \, m^{-3}$ for PM2.5 mass, $4 \, \mu g \, m^{-3}$ for PM10 mass) is attributed to the strong increase in anthropogenic emissions, with a higher impact on the finer grain size fractions (Querol et al., 2001), and to the lower dispersive capacity of the lower atmospheric layers in winter (lower mixing layer height). PM10 and PM2.5 mass levels in the current study are relatively low when compared to the annual means obtained for 2004 at the same monitoring site by Querol et al.

(unpublished data, PM2.5 mass $= 25 \, \mu g \, m^{-3}$, PM10 mass $= 38 \, \mu g \, m^{-3}$).

The ratios between the PM mass levels obtained by means of the different samplers show different behaviour in summer and in winter. In summer, as shown by the ratios between the front filters of the low- and high-volume samplers (1.02–1.04, Table 1), PM2.5 mass levels obtained were similar (Fig. 1). The highest levels were obtained with the low-volume undenuded sampler (B25WW, $17.7 \, \mu g \, m^{-3}$), which were only slightly higher than those obtained with the denuded low-volume sampler (B25DWW, $17.2 \, \mu g \, m^{-3}$). This difference is within the uncertainty of the PM2.5 mass measurements ($1.4 \, \mu g \, m^{-3} \, m^{-3}$) and thus may not be strictly attributed to the presence of the diffusion denuders. PM2.5 mass levels obtained with the high-volume sampler (B25H, $16.4 \, \mu g \, m^{-3}$) were the lowest, although the difference with respect to the low-volume samplers falls also within the uncertainty of the measurements ($1.5 \, \mu g \, m^{-3}$). PM mass levels obtained for the denuded and undenuded low-volume backup filters were within the uncertainty ($-0.7 \, \mu g \, m^{-3}$ for B25DWW, $-0.1 \, \mu g \, m^{-3}$ for B25WW, Table 1).

Table 1
Mean PM10 and PM2.5 mass levels ($\mu g \, m^{-3}$) obtained with the different instruments used in the summer and winter sampling campaigns

Summer 2004	B25DW PM2.5 ($n = 32$)		B25WW PM2.5 ($n = 32$)		B25H PM2.5 ($n = 31$)	B10H PM10 ($n = 32$)
	Front (DQ1)	Backup (DQ2)	Front (Q1)	Backup (Q2)		
Mean	17.2	−0.7	17.7	−0.1	16.4	29.5
Std. dev.	5.6	2.3	6.0	2.4	5.2	8.5
Ratios	Q1/B25H	DQ1/B25H	B25H/B10H	DQ1/Q1	Q2/Q1	DQ2/DQ1
Mean	1.03	1.04	0.56	1.02	−0.01	−0.05
Std. dev.	0.17	0.15	0.09	0.17	0.12	0.16
Winter 2004	B25DW PM2.5 ($n = 27$)		B25WW PM2.5 ($n = 27$)		B25H PM2.5 ($n = 30$)	B10H PM10 ($n = 29$)
	Front (DQ1)	Backup (DQ2)	Front (Q1)	Backup (Q2)		
Mean	22.7	1.3	29.1	1.7	25.8	34.0
Std. dev.	15.7	1.5	15.3	1.7	12.7	14.3
Ratios	Q1/B25H	DQ1/B25H	B25H/B10H	DQ1/Q1	Q2/Q1	DQ2/DQ1
Mean	1.07	0.82	0.76	0.77	0.07	0.10
Std. dev.	0.21	0.27	0.14	0.28	0.08	0.17

B25DWW: PM2.5 low-volume, denuded sampler with two quartz fibre filters; B25WW: PM2.5 low-volume, undenuded sampler with two quartz fibre filters; B25H: PM2.5 high-volume sampler with a single quartz fibre filter; B10H: PM10 high-volume sampler with a single quartz fibre filter. Ratios obtained for the different filters: Q1, undenuded front filter; Q2 undenuded backup filter; DQ1 denuded front filter; DQ2, denuded backup filter. Ratios calculated on a sample by sample basis.
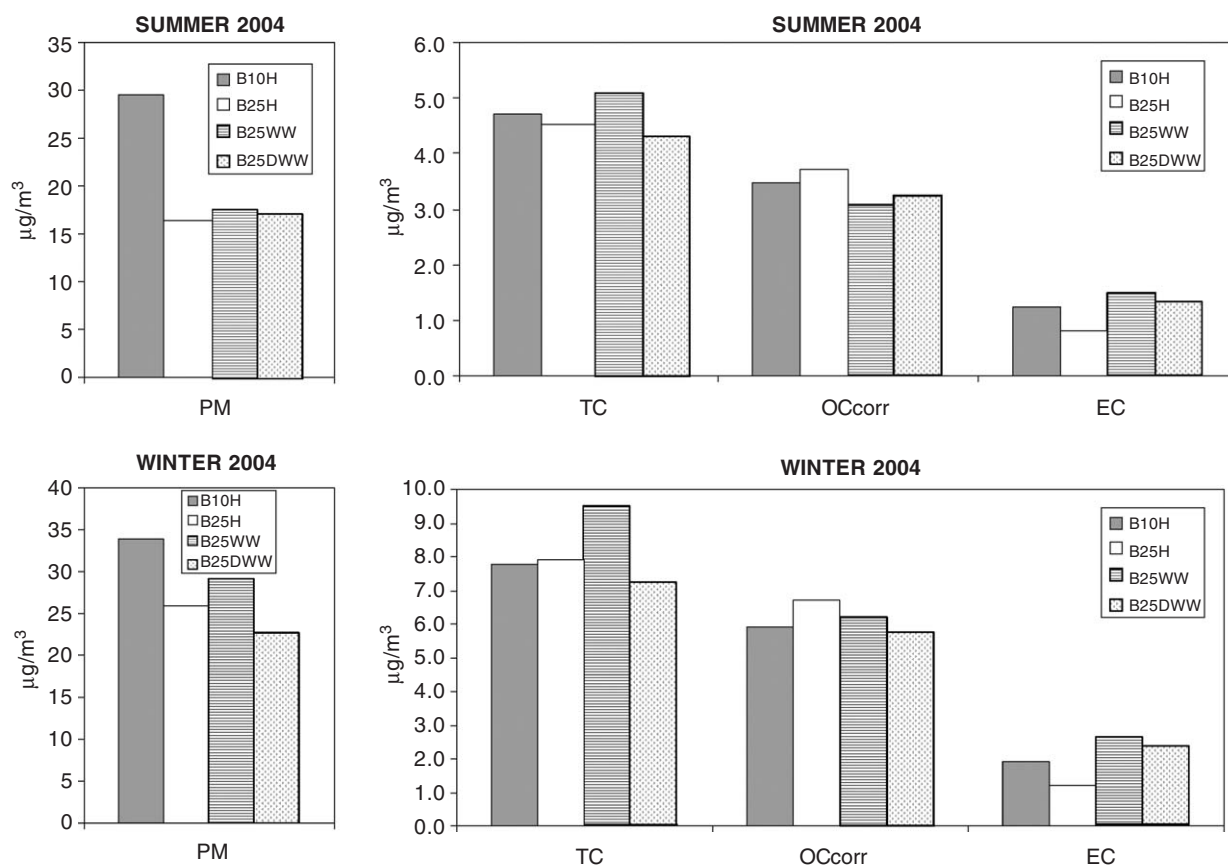
Fig. 1. Mean PM mass, TC, OC_{corr} (uncorrected for B25H and B10H) and EC levels obtained with the different samplers during the summer and winter 2004 sampling campaigns.

In winter, on the contrary, PM2.5 mass levels showed larger differences between different types of samplers. PM2.5 mass levels were the highest for the undenuded low-volume sampler ($29.1\,\mu g\,m^{-3}$), followed by the high-volume sampler ($25.8\,\mu g\,m^{-3}$) and the denuded low-volume sampler ($22.7\,\mu g\,m^{-3}$, Table 1). PM10 mass levels reached $34\,\mu g\,m^{-3}$. As opposed to the summer results, the differences between samplers in winter are larger than the uncertainty of the measurements, and thus may be attributed to differences in sampling artefacts within the different setups. It is important to consider that at this stage sampling artefacts may be related to organic but also to inorganic species. Thus, as expected, PM2.5 mass levels were the lowest when sampled in combination with the diffusion denuders partially owing to the collection of organic volatile species and atmospheric oxidants. The lower PM2.5 mass levels obtained with the high-volume sampler with respect to the undenuded low-volume sampler could be related to the lower adsorption rate of

organic gaseous species, as it decreases with increasing face velocity (Hitzenberger et al., 2004). These results are consistent with those obtained for Ghent by Viana et al. (2006). PM mass obtained for the denuded and undenuded backup filters was 1.3 and $1.7\,\mu g\,m^{-3}$, respectively.

3.2. OC/EC/TC/WSOC levels

Levels of $OC/OC_{corr}/EC/TC$ are presented in Fig. 1 and Table 2, along with the standard deviations for each of the measured parameters. According to these data, within the uncertainty ($0.2\,\mu g\,m^{-3}$), the levels of OC_{corr} in summer are similar for the denuded and undenuded low-volume samples (3.1 and $3.2\,\mu g\,m^{-3}$, Q1/DQ1 = 0.93 for OC_{corr}; note that the ratio Q1/DQ1 for OC_{corr} is calculated with corrected OC data, thus with the difference between front and backup filter OC for Q1 and with the sum of front and backup filter OC for DQ1). This would indicate that the assumptions

Table 2
Mean OC, OC_{corr}, EC and TC levels obtained with the different sampling devices used in the summer and winter sampling campaigns

Summer 2004	OC ($\mu g\,m^{-3}$)	Std. dev. ($\mu g\,m^{-3}$)	OC_{corr} ($\mu g\,m^{-3}$)	EC ($\mu g\,m^{-3}$)	Std. dev. ($\mu g\,m^{-3}$)	TC ($\mu g\,m^{-3}$)	Std. dev. ($\mu g\,m^{-3}$)	OC/TC	TC/PM
B25DWW	3.0	1.3	3.2	1.3	0.6	4.3	1.8	0.69	0.25
B25WW	3.6	1.4	3.1	1.5	0.7	5.1	2.0	0.71	0.29
B25H	3.7	1.5	—	0.8	0.5	4.5	1.9	0.82	0.27
B10H	3.5	1.4	—	1.2	0.5	4.7	1.9	0.73	0.16
Ratios	DQ1/Q1			Q1/DQ1	Q2/Q1	DQ2/ DQ1			
	OC	OC_{corr}	EC	OC_{corr}	OC_{corr}	OC_{corr}			
Mean	0.83	1.10	0.90	0.93	0.16	0.09			
Std. dev.	0.10	0.19	0.33	0.13	0.06	0.05			
Winter 2004	OC ($\mu g\,m^{-3}$)	Std. dev. ($\mu g\,m^{-3}$)	OC_{corr} ($\mu g\,m^{-3}$)	EC ($\mu g\,m^{-3}$)	Std. dev. ($\mu g\,m^{-3}$)	TC ($\mu g\,m^{-3}$)	Std. dev. ($\mu g\,m^{-3}$)	OC/TC	TC/PM
B25DWW	4.9	2.4	5.8	2.3	1.2	7.2	3.2	0.68	0.46
B25WW	6.9	2.2	6.2	2.6	1.4	9.5	3.7	0.74	0.38
B25H	6.7	2.9	—	1.2	0.6	7.9	3.2	0.84	0.33
B10H	5.9	2.2	—	1.9	1.2	7.8	3.1	0.77	0.24
Ratios	DQ1/Q1			Q1/DQ1	Q2/Q1	DQ2/ DQ1			
	OC	OC_{corr}	EC	OC_{corr}	OC_{corr}	OC_{corr}			
Mean	0.70	1.04	0.95	1.15	0.11	0.10			
Std. dev.	0.11	0.64	0.28	0.37	0.02	0.29			

Ratios calculated on a sample-by-sample basis.

made by Mader et al. (2003, see Methodology) are correct for the Barcelona site during the summer campaign. The difference between the OC results from the same samplers obtained during the winter campaign is reduced when the OC correction is applied, although not as much as in the case of the summer values (Q1/DQ1 = 1.15 for winter OC_{corr}).

3.2.1. Total carbon

Average levels of uncorrected TC in PM2.5 ranged between 4.3 and $5.1\,\mu g\,m^{-3}$ in summer and between 7.2 and $9.5\,\mu g\,m^{-3}$ in winter (4.3–4.5 and 7.2–$8.7\,\mu g\,m^{-3}$, respectively, with corrected OC + EC values). TC levels in PM10 were $4.7\,\mu g\,m^{-3}$ in summer and $7.8\,\mu g\,m^{-3}$ in winter. These levels are slightly lower than the annual means presented by Rodríguez (2002) and Querol et al. (2004) for two kerbside sites in Barcelona (9–11 $\mu g\,m^{-3}$ in PM2.5). If the results from the summer and winter campaigns are averaged to obtain an estimation of the annual average (6.5 μg $TC\,m^{-3}$ for the low-volume samplers), TC levels fall within the normal range for urban background to kerbside sites according to data found in the literature (Table 3). TC levels at the study site show a marked seasonal trend with winter maxima (ratio TC winter/summer = 1.8) as a consequence of the higher anthropogenic PM emission rate and the lower atmospheric dispersive conditions, compared with summer (August in this study).

OC is the major component of TC in PM2.5, ranging from 69–82% in summer to 68–84% in winter (uncorrected OC values are used in order to ensure comparability between high- and low-volume samplers). OC accounted for 73–77% of TC in PM10. These results indicate the relative stability of this ratio throughout the year, which shows no seasonal trend. The OC/TC ratios found in the literature (Table 3) indicate that there is no clear dependence of OC/TC on the location type, as similar ratios are obtained for different sites (0.65 rural, Hueglin et al., 2005; 0.67 sub-urban, Hueglin et al. 2005; 0.63 kerbside, Salma et al., 2004). However, the highest ratios are obtained at rural sites (Salma et al., 2004; Rodríguez, 2002) and the lowest at the kerbside site in Milan (Lonati et al., 2005). The range obtained for the Barcelona site is similar to the ratios found at suburban, urban and

Table 3
OC, EC and OC/TC values in PM2.5 found in the literature

	Site	Period	OC ($\mu g\,m^{-3}$)	EC ($\mu g\,m^{-3}$)	OC/EC	OC/TC
Lonati et al., 2005	K (tunnel)	Summer	48	71	0.7	0.40
Rodríguez, 2002	K	1 year	8.0	3.0	2.7	0.73
Hueglin et al., 2005	K	1 year	5.4	4.2	1.3	0.56
Hueglin et al., 2005	K	1 year	3.4	1.8	1.9	0.65
Salma et al., 2004	K	Spring	8.1	4.7	1.7	0.63
Lonati et al., 2005	UB	Summer	5.1	1.2	4.5	0.81
Lonati et al., 2005	UB	Winter	13.4	1.6	8.8	0.89
Salma et al., 2004	UB[a]	Spring	4.0	0.3	12	0.92
Kubátová et al., 2002	UB[a]	Winter	8.6	2.9	3.0	0.75
Kubátová et al., 2002	UB[a]	Summer	3.7	1.5	2.5	0.71
Hueglin et al., 2005	SU	1 year	3.2	1.6	2.0	0.67
Hueglin et al., 2005	R <1000 m asl	1 year	2.4	1.3	1.8	0.65
Rodríguez, 2002	R	1 year	2.2	0.2	11	0.92
Hueglin et al., 2005	R >1000 m asl	1 year	1.1	0.4	2.8	0.73
Decesari et al., 2001	R	Winter	7.2	0.9	8	0.89
Decesari et al., 2001	R	Summer	2.9	0.3	10	0.90

K: kerbside; UB: urban background; SU: suburban; R: rural.
[a]PM2.0 fraction.

certain kerbside sites in Europe. TC/PM ratios were also analysed, with the result that at the study site TC represents 25–29% of the PM2.5 mass in summer (33–46% in winter), and 16% of the summer PM10 mass (24% in winter). These values are relatively lower than those found in more Northern European cities, where TC/PM2.5 ratios ranged between 28% and 68% (Hueglin et al., 2005; Lonati et al., 2005) for a 1-year period. No significant differences were observed between the different samplers at our study site, but once again winter maxima were observed. The larger proportion of carbonaceous species in PM2.5 and PM10 in winter is related to the higher degree of anthropogenic emissions (traffic, heating systems).

3.2.2. Organic carbon

Mean daily levels of corrected OC in PM2.5 at the study site range from 3.1–3.2 $\mu g\,m^{-3}$ for the low-volume samplers and 3.7 $\mu g\,m^{-3}$ (uncorrected) for the high-volume sampler in summer, to 5.8–6.2 $\mu g\,m^{-3}$ for the low-volume and 6.7 $\mu g\,m^{-3}$ (uncorrected) for the high-volume samplers in winter (Table 2 and Fig. 1). Thus, OC levels increase by a factor of 2 during winter with respect to summer.

The uncorrected values agree for the high- and undenuded low-volume samplers (especially in summer, 3.7 and 3.6 $\mu g\,m^{-3}$, 6.7 and 6.2 $\mu g\,m^{-3}$ in winter, respectively). OC levels found on the backup filters of the undenuded samples (Q2) were 0.54 $\mu g\,m^{-3}$ in summer and 0.74 $\mu g\,m^{-3}$ in winter. Back- to front-filter ratios (Q2/Q1) for OC for the undenuded samples were 0.16 in summer and 0.11 in winter (Table 2). Consequently, it may be concluded that positive artefacts related to the adsorption of carbonaceous species on the undenuded filter substrate in the study area accounted for 11–16% (0.5–0.7 $\mu g\,OC\,m^{-3}$) of the total OC mass collected on the front filter. The magnitude of these sampling artefacts is somewhat higher in summer.

OC levels found on the denuded backup filters were, on average, 0.26 and 0.35 $\mu g\,m^{-3}$. These values are only slightly higher than the uncertainty in the OC determination (0.2 $\mu g\,m^{-3}$) and thus marginally significant, if even at all. The OC on the denuded backup filters originates from the volatilisation of some organic species from the front filter or from the fact that the collection efficiency of the denuders could be <100%.

When compared with uncorrected OC levels in Spain found in the literature, the winter levels obtained for the Barcelona site are only slightly lower than those obtained by Rodríguez (2002) at a kerbside site in Barcelona (8 $\mu g\,OC\,m^{-3}$) over a yearly period. The summer values are similar too although higher than those registered in the same study at a rural site under industrial influence

($2.2 \, \mu g \, OC \, m^{-3}$). Therefore, levels of OC_{corr} at the study site range from values characteristic of rural sites in August (minimum annual levels) to those of kerbside sites in the winter, evidencing a wide range of OC_{corr} levels due to the specific climatic conditions and emission trends described in the previous sections. It must be noted that the OC values found in Rodríguez (2002) are uncorrected.

As shown in Table 3, summer OC levels in PM2.5 at urban background sites throughout Europe range between 4 and $5 \, \mu g \, m^{-3}$. The levels obtained for the Barcelona site are lower (3.1–$3.7 \, \mu g \, m^{-3}$) due to the marked August decrease in anthropogenic emissions described above. Averaging the summer and winter OC_{corr} levels from the sampling campaigns would result in an approximate annual mean of $4.6 \, \mu g$ $OC_{corr} \, m^{-3}$ (low-volume samplers) in the range of urban background to kerbside sites in the literature (annual means, Table 3). Owing to the direct influence of traffic emissions OC levels may reach extreme values such as presented by Lonati et al. (2005), where on average $47 \, \mu g \, OC \, m^{-3}$ were registered in a 250 m long tunnel in the centre of Milan (Italy). On the other hand, uncorrected OC levels vary between 1 and $2 \, \mu g \, m^{-3}$ at rural sites.

3.2.3. Elemental carbon

Mean EC levels ranged from 0.8 to $1.5 \, \mu g \, m^{-3}$ in PM2.5 and $1.2 \, \mu g \, m^{-3}$ in PM10 during the summer period to 1.2–$2.6 \, \mu g \, m^{-3}$ in PM2.5 and $1.9 \, \mu g \, m^{-3}$ in PM10 during winter (Table 2).

As in the case of OC, EC summer levels are similar to those found in the literature for urban background-monitoring sites (Lonati et al., 2005, $1.6 \, \mu g \, m^{-3}$, Table 3), whereas the winter values are higher than those presented in the same study. Averaging the summer and winter EC levels from the sampling campaigns would result in an approximate annual mean of $1.9 \, \mu g \, EC \, m^{-3}$ (low-volume samplers), which would again fall within the range of urban background to kerbside sites. This value is lower than the result obtained by Rodríguez (2002) for a kerbside site in Barcelona over a yearly period ($3.0 \, \mu g \, EC \, m^{-3}$).

Taking into account that sampling artefacts related to carbonaceous species do not in principle exert any influence on EC levels (Turpin et al., 2000), similar results were expected to be obtained for both high- and low-volume, denuded and undenuded samplers. It was thus surprising to observe consistently lower EC levels for the high-volume PM2.5 sampler during both sampling campaigns (B25H 0.8 vs. 1.3–$1.5 \, \mu g \, m^{-3}$ for B25DWW and B25WW in summer; B25H 1.2 vs. 2.3–$2.6 \, \mu g \, m^{-3}$ for B25DW and B25WW in winter, Fig. 1). EC levels obtained for B10H were also somewhat low ($1.2 \, \mu g \, m^{-3}$ in summer and 1.9 in winter $\mu g \, m^{-3}$, always lower than B25WW and B25DWW), and conversely EC levels obtained for both low-volume samplers were very similar (Q1/DQ1 = 1.05 for EC in summer, 1.12 in winter). These differences between the high- and low-volume samplers (larger than the uncertainty for EC, $0.1 \, \mu g \, m^{-3}$) suggest that the EC determination could be influenced to a certain extent by the filter type. The quartz fibre material was Schleicher & Schuell QF20 for the high-volume samplers and Whatman QM-A for the low-volume samplers. Similar results were obtained by Viana et al. (2006) in Ghent (Belgium). The ultimate cause for these differences in EC levels cannot be determined with the results provided by this study, and thus further research is required in this direction.

3.2.4. OC_{corr}/EC

Data obtained at the Barcelona site show a clear prevalence of organic over EC. The ratio OC_{corr}/EC for PM2.5 at the study site ranged from 2.1 to 4.0 (2.1–2.6 if the EC value for B25H is excluded) in summer to 2.2–5.2 (2.2–2.7 excluding B25H) in winter, values which are usual for urban environments. In both cases (including and excluding results from the high-volume samplers) the OC_{corr}/EC ratios seem to remain relatively constant throughout the year and show no defined seasonal pattern. Higher OC/EC ratios may have been expected during summer than winter considering the high summer temperatures, the expected enhanced volatilisation of organic species from the vegetation, and the expected increased secondary organic aerosol (SOA) formation from both biogenic and anthropogenic VOCs. We have no reasonable explanation for the absence of seasonality in the OC/EC ratio. For the denuded sampler, there is the possibility that a larger fraction of the OC is semi-volatile OC (SVOC) in summer, because of possibly higher levels of SOA formed in summer, and that this SVOC is partly volatilised from the front filter and not fully captured by the backup filter, and remains thus unaccounted for in the OC_{corr}. However, the fact that OC_{corr} of the undenuded sampler agrees with that for the denuded sampler (also in summer) is an argument against this.

As shown in Table 3, OC/EC ratios are <2 at kerbside sites (with the only exception of Rodríguez, 2002), and the ratios increase with decreasing anthropogenic emissions and reach values >10 at rural sites. This increase in the OC/EC ratio is due to the decrease in EC levels, typically linked to anthropogenic emissions (mostly traffic). This pattern suggests that the OC/EC ratio in Europe depends more on the emission sources affecting a certain site and thus on the type of site (urban, urban, industrial, …) than on the geographic location within Europe (values presented in Table 3 are from Spain, Italy, Hungary, Belgium and Switzerland). Rather similar OC/EC ratios are obtained at urban sites across Europe, and the same occurs for rural sites and for kerbside sites. This does not mean that the geographic location and the season do not affect the OC/EC ratio.

In order to further investigate the relationship between the OC_{corr}/EC ratio and the aerosol emissions around the study site, Fig. 2 shows the daily evolution of OC_{corr} and EC levels obtained with the denuded low-volume sampler (B25DWW) during the summer campaign, as well as the evolution of the OC_{corr}/EC ratio for the same period. The denuded low-volume sampler was

chosen for this analysis to obtain artefact free data. The summer campaign was selected because of the specific meteorological scenario dominant over the Western Mediterranean basin described above. Levels of the OC_{corr}/EC ratio for this sampler ranged from 1.6 to 5.1, with a mean and standard deviation of 2.6 ± 0.8. A detailed analysis of the daily oscillations of this ratio evidenced the existence of seven days in which the ratio was especially high (>3.5, marked with an arrow in Fig. 2) due to unusually low EC levels ($EC < 1\,\mu g\,m^{-3}$ in 5 out of 7 samples). Considering EC as a tracer for primary OC emissions (Turpin and Huntzicker, 1995; Salma et al., 2004), one may be tempted to conclude that these samples represent days in which there is a clear dominance of SOA over primary OC. However, OC/EC ratios should not only be used as tracers for SOA formation, as they can also serve as tracers for changes in emission sources or source regions. Four of the 7 days were consecutive, and a closer analysis of these days by means of 5-day isentropic back-trajectory analysis (Hysplit v.4, Draxler and Rolph, 2003) revealed that the synoptic scale scenario was dominated by the advection of Atlantic air towards the Iberian Peninsula (Fig. 3), contrasting with the stagnant low barometric gradient conditions
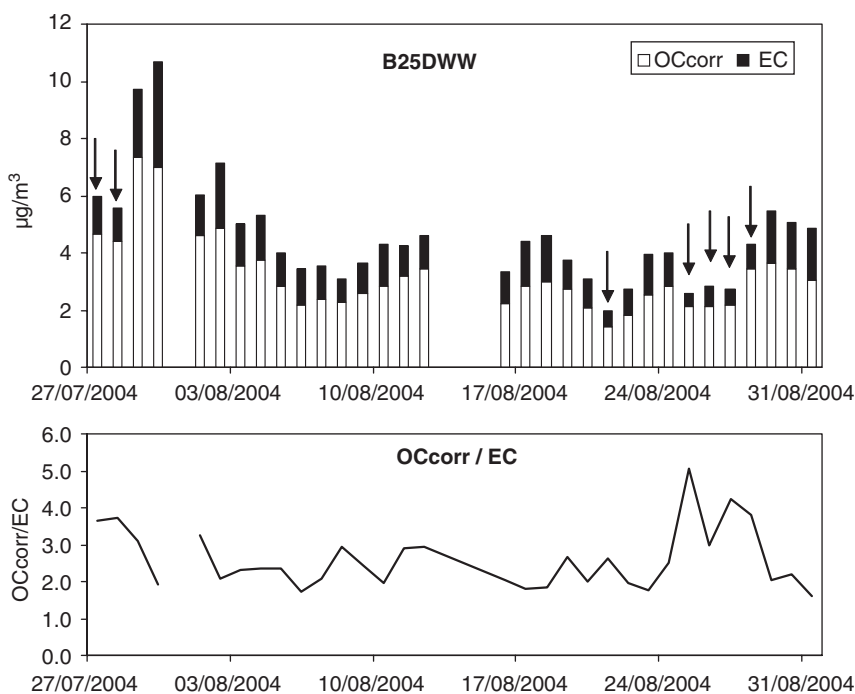

Fig. 2. Temporal evolution of daily levels of OC_{corr} and EC obtained with the denuded low-volume sampler (B25DWW) during the summer campaign. Temporal evolution of the OC_{corr}/EC ratio.
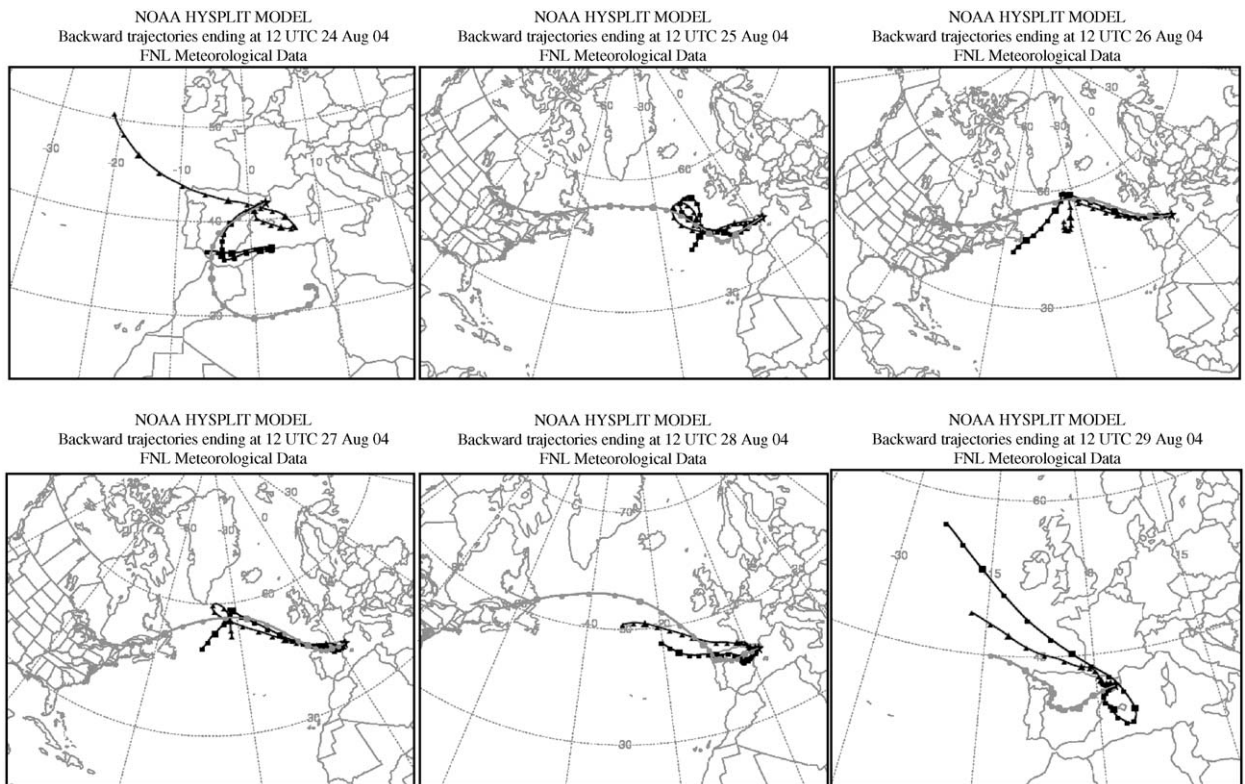
Fig. 3. Five-day back-trajectory analysis performed for the period 24/08/04–29/08/04 using the Hysplit model v.4 (Draxler and Rolph, 2003), with starting heights 750 (▲), 1500 (■) and 2500 (●) m a.s.l.

characteristic for the summer months in Spain (Millán et al., 1997; Rodríguez et al., 2003). As shown in Fig. 3, the origin of the 5-day trajectories at the beginning (24/08/04) and the end (29/08/04) of the episode was regional, with influence from the anthropogenic emissions generated in the Iberian Peninsula and the North African and Mediterranean source regions. OC_{corr}/EC ratios were <2 during these days. Conversely, between 25 and 28/08/05 the air mass transport took place across the Atlantic Ocean with very low sources of carbonaceous aerosol and in particular of EC, resulting in significantly high OC_{corr}/EC values (>3.5). The remaining 3 days with high OC_{corr}/EC ratios were also characterised by long-range Atlantic transport. Thus the high OC_{corr}/EC ratio at our study site seems to be not due to increased contribution from SOA, but rather to a change in carbonaceous aerosol sources. The same analysis was performed on the winter data but the results were not as conclusive due to the higher variability of the OC_{corr}/EC ratio (higher number and magnitude of anthropogenic emissions) and to the larger number of atmospheric scenarios encountered (from stable antic-

yclonic conditions to African dust outbreaks, precipitation and European and Atlantic air mass advection).

3.2.5. Water soluble organic carbon

WSOC analyses were only performed on the high-volume filters (B25H, B10H) due to the limited sample size for the low-volume filters. Daily WSOC levels in PM10 and PM2.5 were relatively similar throughout the year, ranging from 0.7 to $3.5\,\mu g\,m^{-3}$. Average values obtained for the different campaigns were $1.6\,\mu g\,m^{-3}$ in PM10 and PM2.5 in summer, and 2.1 and 1.9 in PM2.5 and PM10, respectively, in winter.

These levels represent 43% and 47% of the OC mass on the B25H and B10H filters in summer, respectively, and 33% of the OC mass for both size fractions in winter. As regards the TC mass, WSOC accounted for 36% and 34% of TC in PM2.5 and PM10 in summer, and 28% and 26%, respectively, in winter. These results show that the fraction of WSOC in the TC and/or OC fraction is maximal in summer. This is likely due to stronger

photochemical oxidation processes forming oxygen containing functional groups (increasing water solubility) in summer and to enhanced wet depositional losses of WSOC relative to the insoluble carbon in winter (Kleefeld et al., 2002).

The levels obtained for the Barcelona site were compared with those available in the literature for rural (Decesari et al., 2001; Kleefeld et al., 2002) and traffic sites in Europe (Ruellan and Cachier, 2001) and at urban sites in China (Yang et al., 2005). The water soluble organic fraction of TC is highest at rural sites (WSOC/TC = 46% in the Po Valley, 40–58% at Mace Head) as a consequence of the input of biogenic and anthropogenic SOA. At urban sites, on the other hand, Yang et al. (2005) obtained similar WSOC/TC ratios for winter to the ones observed in this study (20–32%) and Ruellan and Cachier (2001) obtained the lowest WSOC/TC ratios for the summer period in Paris (9%). This ratio thus shows an inverse relation with the degree of anthropogenic emissions, reaching minimum values at traffic sites. High WSOC/TC ratios imply low EC/TC ratios and thus represent relatively unpolluted environments.

4. Conclusions

Two 5-week sampling campaigns were performed in summer and winter 2004 at an urban background site in Barcelona, in which PM10 and PM2.5 samples were collected using high- and low-volume instrumentation. One of the low-volume samplers was coupled to an annular diffusion denuder with the aim to evaluate the influence of positive sampling artefacts related to carbonaceous species. The resulting samples were weighed for the PM mass and analysed for OC, EC and WSOC. TC levels were obtained as OC + EC.

The PM mass levels obtained with the high- and low-volume denuded and undenuded PM2.5 samplers during the summer campaign were identical to each other within the uncertainty of the PM mass measurements. In winter, owing to the higher concentrations of atmospheric aerosols, larger differences were observed between the samplers. Denuded low-volume samples gave the lowest PM2.5 mass levels. The high-volume sampler produced the lowest undenuded results owing to the higher face velocity (lower retention of gaseous species).

TC, OC and EC levels were maximum in winter, increasing by a factor of 1.7–2 with respect to summer. The mass fraction of WSOC in TC was smaller in winter than in summer. TC/OC/EC/WSOC levels obtained fall within the normal range for urban background to kerbside sites in Europe. TC accounted for 25–29% of PM2.5 in summer and for 33–46% in winter. In PM10, TC accounted for 16% of the PM mass in summer and for 24% in winter.

As regards OC levels, the assumptions made by Mader et al. (2003) seem to be valid for the summer period. Applying backup filter correction both low-volume samplers produced the same results. Before backup filter correction both undenuded samplers (high- and low-volume) produced the same results.

The influence of positive artefacts for OC was estimated as $0.5–0.7\,\mu g\,m^{-3}$, which accounts for 11–16% of the total OC mass and a maximum of 3% of the PM2.5 mass. The influence of sampling artefacts for OC was slightly higher in summer.

EC levels were similar for both low-volume samplers, and unusually low for the high-volume samplers. This fact suggests that EC measurement could be influenced by the filter type. Further research is required in this direction.

The OC_{corr}/EC ratio may be used as a reliable tracer of the variation in carbonaceous aerosol sources at the study site during the summer months. Significant differences were observed in this ratio during days with strong Atlantic air mass advection and days characterised by regional recirculation of the air masses.

References

Adachi, K., Tainosho, Y., 2004. Characterization of heavy metal particles embedded in tire dust. Environment International 30, 1009–1017.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Science and Technology 25, 221–241.

Colvile, R.N., Hutchinson, E.J., Mindell, J.S., Warren, R.F., 2001. The transport sector as a source of air pollution. Atmospheric Environment 35, 1537–1565.

Cruz, C.N., Pandis, S.N., 1997. A study of the ability of secondary organic aerosol to act as cloud condensation nuclei. Atmospheric Environment 31, 2205–2214.

Decesari, S., Facchini, M.C., Matta, E., Lettini, F., Mircea, M., Fuzzi, S., Tagliavini, E., Putaud, J.-P., 2001. Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy. Atmospheric Environment 35, 3691–3699.

Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website, http://www.arl.noaa.gov/ready/hysplit4.html.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 1999. Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere. Atmospheric Environment 33, 2715–2724.

Hitzenberger, R., Berner, A., Galambos, Z., Maenhaut, W., Cafmeyer, J., Schwarz, J., Miiller, K., Spindler, G., Wieprecht, W., Acker, K., Hillamo, R., Mäkelä, T., 2004. Intercomparison of methods to measure the mass concentration of the atmospheric aerosol during INTERCOMP2000—influence of instrumentation and size cuts. Atmospheric Environment 38, 6467–6476.

Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C., Vonmont, H., 2005. Chemical characterisation of PM2.5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment 39, 637–651.

Kleefeld, S., Hoffer, A., Krivácsy, Z., Jennings, S.G., 2002. Importance of organic and black carbon in atmospheric aerosols at Mace Head, on the West Coast of Ireland (53°19′N, 9°54′W). Atmospheric Environment 36, 4479–4490.

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J., Maenhaut, W., 2002. Organic compounds in urban aerosols from Ghent, Belgium: characterization, sources, and seasonal differences. Journal of Geophysical Research 107 (D21), 8343.

Kuhlbusch, T.A.J., Quass, U., Koch, M., Fissan, H., Schmidt, K.G., Bruckmann, P., Pfeffer, U., 2004. PM10 source apportionment at three urban background sites in the Western Ruhr-area, Germany. Journal of Aerosol Science, Abstracts of the European Aerosol Conference 2004, S79–S80.

Kukadia, V., Palmer, J., 1998. The effect of external atmospheric pollution on indoor air quality: a pilot study. Energy and Buildings 27, 223–230.

Lonati, G., Giugliano, M., Butelli, P., Romele, L., Tardivo, R., 2005. Major chemical components of PM2.5 in Milan (Italy). Atmospheric Environment 39, 1925–1934.

Mader, B.T., Flagan, R.C., Seinfeld, J.H., 2001. Sampling atmospheric carbonaceous aerosols using a particle trap impactor/denuder sampler. Environmental Science and Technology 35, 4857–4867.

Mader, B.T., Schauer, J.J., Seinfeld, J.H., Flagan, R.C., Yu, J.Z., Yang, H., Lim, H.J., Turpin, B.J., Deminter, J.T., Heidemann, G., Bae, M.S., Quinn, P., Bates, T., Eatough, D.J., Huebert, B.J., Bertram, T., Howell, S., 2003. Sampling methods used for the collection of particle-phase organic and elemental carbon during ACE-Asia. Atmospheric Environment 37, 1435–1449.

Matsumoto, K., Tanaka, H., Nagao, I., Ishizaka, Y., 1997. Contribution of particulate sulphate and organic carbon to cloud condensation nuclei in the marine atmosphere. Geophysical Research Letters 24, 655–658.

Mikuška, P., Večeřa, Z., Broškovičová, A., Štěpán, M., Chi, X., Maenhaut, W., 2003. Development of a diffusion denuder for the elimination of sampling artifacts for carbonaceous aerosols. Journal of Aerosol Science, Abstracts of the European Aerosol Conference 2003, S761–S762.

Millán, M., Salvador, R., Mantilla, E., Kallos, G., 1997. Photo-oxidant dynamics in the Mediterranean basin in summer: results from European research projects. Journal of Geophysical Research 102, 8811–8823.

Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Ruiz, C.R., Cots, N., Massagué, G., Puig, O., 2001. PM10 and PM2.5 source apportionment in the Barcelona Metropolitan Area, Catalonia, Spain. Atmospheric Environment 35, 6407–6419.

Querol, X., Alastuey, A., Viana, M.M., Rodríguez, S., Artíñano, B., Salvador, P., Santos, S.G.D., Patier, R.F., Ruiz, C.R., Rosa, J.D.L., Campa, A.S.D.L., Menedez, M., Gil, J.I., 2004. Speciation and origin of PM10 and PM2.5 in Spain. Journal of Aerosol Science 35, 1151–1172.

Rodríguez, S., 2002. Sources and processes affecting levels and composition of atmospheric particulate matter in the Western Mediterranean. Ph.D. Thesis, Universitat Politècnica de Catalunya.

Rodríguez, S., Querol, X., Alastuey, A., Viana, M.M., Mantilla, E., 2003. Events affecting levels and seasonal evolution of airborne particulate matter concentrations in the Western Mediterranean. Environmental Science and Technology 37, 216–222.

Ruellan, S., Cachier, H., 2001. Characterisation of fresh particulate vehicular exhausts near a Paris high flow road. Atmospheric Environment 35, 453–468.

Salma, I., Chi, X., Maenhaut, W., 2004. Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary. Atmospheric Environment 38, 27–36.

Salvador, P., Artíñano, B., Alonso, D.G., Querol, X., Alastuey, A., 2004. Identification and characterisation of sources of PM10 in Madrid (Spain) by statistical methods. Atmospheric Environment 38, 435–447.

Saxena, P., Hildemann, L.M., McMurry, P.H., Seinfeld, J.H., 1995. Organics alter hygroscopic behavior of atmospheric particles. Journal of Geophysical Research 100, 18755–18770.

Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.M., Giesen, K.P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H., 2001. Results of the "carbon conference" international aerosol carbon round robin test stage I. Atmospheric Environment 35, 2111–2121.

Sternbeck, J., Sjödin, A., Andréasson, K., 2002. Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. Atmospheric Environment 36, 4735–4744.

Turpin, B.J., Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantisation of primary and secondary organic aerosol concentrations during SCAQS. Atmospheric Environment 29, 3527–3544.

Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmospheric Environment 34, 2983–3013.

Vallius, M., Janssen, N.A.H., Heinrich, J., Ruuskanen, G.H., Cyrys, J., Van Grieken, R., Hartog, J.J., Kreyling, W.G., Pekkanen, J., 2005. Sources and elemental composition of ambient PM2.5 in three European cities. Science of the Total Environment 337, 147–162.

Viana, M., Chi, X., Cafmeyer, J., Querol, X., Alastuey, A., Mikuška, P., Večeřa, Z., Maenhaut, W., 2006. Influence of sampling artefacts on measured PM, OC and EC levels in an urban area. Aerosol Science and Technology, in press.

Weckwerth, G., 2001. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). Atmospheric Environment 35, 5525–5536.

Yang, H., Yu, J.Z., Ho, S.S.H., Xu, J., Wu, W., Wan, C.H., Wang, X., Wang, X., Wang, L., 2005. The chemical composition of inorganic and carbonaceous materials in PM2.5 in Nanjing, China. Atmospheric Environment 39, 3735–3749.