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Original article

Detection and simulation of wildfire smoke impacting a Mediterranean urban atmosphere



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ABSTRACT

The combined use of chemical analysis of organic molecules in atmospheric aerosols (PM₁) collected in situ in Barcelona and optical measurements with a light detection and ranging (LIDAR) instrument allowed the characterization of the smoke plume from a wildfire that reached the city in July 2012. Analysis of the chemical composition of the aerosols collected on 23 July 2012 confirmed the large effect of biomass burning on urban air quality during a period of several hours. Typical biomass burning tracers, such as levoglucosan, dehydroabietic acid and polycyclic aromatic hydrocarbons (PAH) were enhanced at the same time as the aerosol concentrations in the boundary layer increased. According to air-mass trajectory modeling, the biomass burning particles originated from a severe wildfire burning 120 km northeast of the city. On the following days, no significant contribution of wildfire smoke was found in the urban air, although the lidar detected particles aloft. A Lagrangian particle dispersion model (FLEXPART) was used to simulate the transport of aerosols (PM_{2.5}) and carbon monoxide (CO), and the simulated concentrations in Barcelona were compared to in-situ measurements. FLEXPART simulated the onset of the wildfire smoke plume event in the urban center in the early morning of 23 July successfully; by contrast, the fast passage of the plume at the surface and the decoupling of the cleaner boundary layer from the persistent smoke plume aloft was not well captured. This was attributed to the fact that the model did not capture the local sea-breeze circulation well enough.

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1. Introduction

Aerosols have adverse effects on human health (Pérez et al., 2009; Pope et al., 2002) and influence the Earth's radiative balance (Forster et al., 2007). In urban areas, and especially in the Mediterranean region, high background aerosol levels are often observed due to anthropogenic emissions (i.e. traffic, industry, etc.)

and stable atmospheric conditions with high solar insolation, resulting in accumulation of pollutants within the planetary boundary layer (PBL) (Millán et al., 1997; Pérez et al., 2010; Pey et al., 2008). Moreover, the Mediterranean area is often exposed to Saharan dust outbreaks that occur about 15 times per year. During these events, the background aerosol levels are increased by between two and four times in the Western Mediterranean and more than ten times in the Eastern Mediterranean (Querol et al., 2009). Wildfires are also common in the Mediterranean area in summer and constitute an additional pollution source that further increases the aerosol levels (Phuleria et al., 2005; Rodríguez et al., 2002; Verma et al., 2009). Exposure to aerosols from wildfires has been associated to toxic effects such as lung cell damage and airway inflammation (Barrett et al., 2006; Thoring et al., 1982). Although these effects are not exclusively linked to biomass burning

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particles, there is evidence that they are more toxic than those from other emission sources on an equal-dose basis (Wegesser et al., 2009).

Recent studies for the urban area of Barcelona (Catalonia, Spain) showed a low-to-moderate impact of regional wildfire smoke and Saharan dust on the urban aerosol, which is normally dominated by local fossil fuel combustion sources (van Drooge et al., 2012). Simultaneous measurements of the vertical distribution of the aerosols in the atmospheric column showed that Saharan dust and wildfire smoke layers were mainly situated and transported in the free troposphere above the PBL (Sicard et al., 2011, 2012), with low impact on the air quality at ground level.

The present study focuses on the impact of a wildfire event that affected the urban area of Barcelona during a short period of time in July 2012 (see chronicle of wildfire in SI.1). On Sunday July 22nd (22J) a wildfire started along a highly transited highway near the border between France and Spain, in the Alt Empordà region, a forested area 120 km northeast of Barcelona. The fire burned for the next few days and was officially controlled on 25 July and completely extinguished on 30 July. As a result of the wildfire, four persons died, approximately 14,000 ha of mainly forested areas were burnt, as well as several farms and houses, and one camping site.

This paper describes the influence of the smoke plume generated by the fire on the urban aerosol concentrations in Barcelona by analyzing PM₁ samples and remote sensing lidar (Light Detection and Ranging) measurements, as well as satellite imagery and air mass trajectory modeling. The Lagrangian particle dispersion model FLEXPART was used (Stohl et al., 1998, 2005) to study the pathways of sampled air masses to the measurement station and to identify the contribution of the wildfire event.

2. Materials and methods

2.1. PM₁ filter sampling and organic tracer compound speciation

Atmospheric particulate matter with an aerodynamic diameter less than 1 µm (PM₁) was collected in the center of Barcelona (41°23′01.6″N; 2°10′45.8″E; 50 m above ground level (agl)) between 19 July and 24 July on pre-fired quartz filters (2500QAT-UP; Pallflex, Pall Corporation, USA) with 12 h time resolution (08:00 to 20:00 UT and 20:00 to 08:00 UT) using a Digitel-DH80 Hivol-sampler (Digitel Elektronik AG, Switzerland).

A detailed description of the applied analytical procedure is given in Fontal et al. (2015). Briefly, PM₁ filter samples were extracted using a mixture of dichloromethane and methanol (2:1 (v/v) (Merck, Germany)). The sample extracts were filtered over 0.45 µm teflon membrane filter (Whatman, USA) in order to remove particles and concentrated by vacuum rotary evaporation to 1 mL. Aliquots of 25 µL of the extract were evaporated under a gentle stream of N₂. Then, 25 µL of bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) (Supelco, USA) and 10 µL of pyridine (Merck, Germany) were added for derivatization of the saccharides, acids and polyols to their trimethylsilyl esters at 70 °C during 1 h. Samples were injected in a gas-chromatograph (GC) coupled to a mass spectrometer (MS) (Thermo Trace GC Ultra – DSQ II, Thermo Scientific, USA) equipped with a 60 m fused capillary column (RXi® 5Si MS 0.25 mm × 0.25 µm film thickness; Restek, USA). A MS selective detector was operated in full scan (*m/z* 50–650) and electron impact (70 eV) modes. The applied method allows quantitative determination of carboxylic acids, dicarboxylic acids (and derivatives), saccharides, aliphatic hydrocarbons (n-alkanes), polycyclic aromatic hydrocarbons (PAH) and hopanes. Method efficiency was assessed from recoveries of surrogate standards added to the filters

prior to extraction. Mean recoveries were higher than 70% for all compounds. Field blank levels were low, always below 30% of the levels found in the samples. All reported concentrations were corrected by surrogate recovery and blank levels. Limit of quantification of the individual organic compounds was 0.06 ng/m³ for sugars, 0.03 ng/m³ for n-alkanes and 0.001 ng/m³ for PAH and hopanes.

All statistical calculations were performed using the SPSS v.17 package (SPSS Inc., Chicago, Ill.). Unless otherwise noted, significance levels of the log–log correlations were set at *p* < 0.01.

2.2. Lidar measurements

Profiles of the aerosol stratification were obtained by the EARLINET (European Aerosol Research Lidar Network) lidar located in the center of Barcelona (41.39 N, 2.11 E, 115 m asl). The system employs a Nd:YAG laser emitting pulses at 355, 532 and 1064 nm at a repetition rate of 20 Hz. In reception, the backscattered elastic radiation and also the nitrogen (at 387 and 607 nm) and the water vapor (at 407 nm) Raman-shifted backscattered radiation is recorded. The vertical resolution is 3.75 m and the typical time resolution is 1 min.

A CIMEL sun-photometer, part of the Aerosol Robotic Network (AERONET), situated 600 m away from the lidar system was used to provide the aerosol optical depth (AOD) in the whole atmospheric column in the spectral bands of 440, 675, 870 and 1020 nm. On 23 July, the aerosol optical coefficient profiles (backscatter and extinction) were retrieved by averaging the two-components elastic lidar inversion algorithm (Fernald, 1984; Klett, 1985; Sasano and Nakane, 1984) using a constant lidar ratio of 50 sr. On 24 and 25 July, sun-photometer data were simultaneously available with the lidar measurements, so that the two-component elastic lidar inversion algorithm could be constrained with the sun-photometer-derived AOD (Reba et al., 2010). The retrieval of the PBL height was made using the gradient method (Sicard et al., 2006).

2.3. FLEXPART simulations

Forward simulations of the fire pollution plumes were made with the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998, 2005). The model was driven with ECMWF (European Centre for Medium-Range Weather Forecasts) operational analysis data with 0.18° × 0.18° latitude/longitude resolution, 91 vertical model levels and 3 h time resolution. Simulations were made both for a passive carbon monoxide (CO) tracer and a PM_{2.5} aerosol tracer undergoing dry deposition and scavenging by precipitation.

The emissions used for the simulations were taken from information available on the fire. The coordinates of the starting point of the wildfire and the consecutive chronicle of its evolution through time and space were obtained from the Fire Brigade reports (see SI.1 for the translation of the report). Based on the geographical position of the fire and satellite images (see SI.2), the surface area of the wildfire was estimated for the consecutive days (SI.3). The time resolution in relation to burnt area was not conclusive, especially on 22 July, when the fire was most active (SI.2). Accordingly, two scenarios (plume 1 and 2) were adapted with different burning areas on 22 July between 14:00 and 15:00 h (plume 1 and 2: 33 km² and 24 km²) and 15:00 and 17:00 h (plume 1 and 2: 9 km² and 19 km²) (SI.3). The areas burnt consisted of Mediterranean forests (76%) and agricultural fields (19%), and a mixture of different surfaces, including urbanized areas (5%). For Mediterranean vegetation types, Alves et al. (2011) estimated emission factors of 231 g CO/kg dry biomass burnt, and 9 g/kg for PM_{2.5}. The biomass of

Mediterranean vegetation per surface area was estimated to be 200 Mg/ha (Ruiz-Peinado et al., 2013).

2.4. Complementary data

Hourly NO, NO₂, O₃, CO, PM_{2.5} and PM₁₀ levels between July 19 and 24 were obtained from the Department of Territory and Sustainability of the Government of Catalonia. Satellite images were obtained from the MODIS (Moderate Resolution Imaging Spectroradiometer) (NASA, USA) instrument. Air mass trajectories were calculated using the HYSPLIT4 software from the NOAA-ARL (USA) (Draxler and Rolph, 2013; Rolph, 2013). Here GDAS data were used for the model calculation and the air-mass trajectories were based on isentropic surfaces. For the sampling sites the isentropic surfaces were related to the potential temperatures at 100, 1500 and 2500 m above ground level (agl).

3. Results and discussion

3.1. Remote sensing and in-situ urban air quality monitoring

A MODIS image (Fig. 1) shows that the wildfire smoke was transported in southerly direction on 23 July. The air quality parameters in the city center of Barcelona (station “Eixample” is situated in 41°23′7.40″N; 2°9′14.65″E) showed significantly ($p < 0.01$) higher daytime levels (08:00h–20:00 UT) on 23 July for CO (1.2 mg/m³) and PM₁₀ (71 µg/m³), compared to the concentrations averaged over the other days during the period 19–24 July (0.7 ± 0.2 mg/m³ and 33 ± 9 µg/m³, for CO and PM₁₀, respectively; Table S1, Fig. 2). Other air quality parameters, i.e. NO, NO₂ and O₃ did not show any significant difference on 23 July with respect to the other days (34 vs. 23 ± 13 µg/m³, 67 vs. 58 ± 16 µg/m³, 63 vs. 48 ± 11 µg/m³, respectively for NO, NO₂ and O₃; Table S1, Fig. 2). The relatively higher PM concentration on 23 July is even more pronounced if the period of the daily maximum concentrations is considered, between 07:00 UT and 14:00 UT. The highest measured concentrations at 10:00 UT were 1.8 mg/m³ and 189 µg/m³, respectively, for CO and PM₁₀. These peak concentrations of CO and PM₁₀ were not directly related to traffic emissions, since NO and NO₂ did not show any anomaly on 23 July. These results are in agreement with those found in other urban areas exposed to wildfire smoke, such as Los Angeles (Verma et al., 2009). However, besides increases of PM and

CO, an increase of NO was also detected in Los Angeles. In the present study, the monitoring station is, however, situated near busy streets, and traffic emissions of NO probably dominated even when the fire plume was observed. The PM₁₀ increase on 23 July was also observed at other urban stations in Barcelona, indicating that the PM event affected the entire urban area. Based on the PM concentrations on 23 July, the duration of this PM event was relatively short (approx. 5 h) resulting in a 24-h PM₁₀ concentration of 43 µg/m³, which is lower than the limit value of 50 µg/m³ set by the current legislation (Directive, 2008). Nevertheless, the high PM₁₀ peak concentration of 189 µg/m³ may have caused acute effects in part of the population that is most sensitive to particle exposure.

3.2. Aerosol organic tracer analysis

During the occurrence of the wildfires, PM₁ filter samples with 12-h sampling resolution were collected in Barcelona for studying the concentrations of organic tracer compounds, including those for biomass burning and fossil fuel combustion, in the urban air. The filters were collected on 19 and 22 July (before the wildfire event), on 23 July (during the wildfire event), and on 24 July (after the wildfire event). For the present study, results of chemical analysis of the filter samples collected on 19 July (day–night), 22 July (day–night), 23 July (night) and 24 July (day–night), when there was no influence of the wildfire plume, were compared to the results for the filter sample that was collected during the daytime on 23 July, when wildfire smoke influenced the city’s air quality (Table S1).

The chemical data (Table S1; Fig. 3) for 23 July (daytime) showed significantly higher concentrations of organic compounds that are typically strongly enhanced in biomass burning plumes, i.e. levoglucosan (1100 ng/m³), and its isomers, galactosan and mannosan, as well as xylitol, vanilic acid, syringic acid, and dehydroabietic acid (Fig. 3) (Vicente et al., 2012; Simoneit, 2002; Yan et al., 2008). The concentrations of these compounds were about two orders of magnitude higher than those observed during the other sampling periods, both before and after the wildfire event (e.g. levoglucosan = 8 ± 4 ng/m³; Fig. 3). The low levoglucosan concentrations of the samples not influenced by the fire plume were similar to the background levels found in previous studies in the same area (Alier et al., 2013; van Drooge et al., 2012; van Drooge and Grimalt, 2015), while the high daytime level (1100 ng/m³) on



Fig. 1. MODIS/TERRA image taken at 11:10 UT on 22 July imported into a Google Earth map and forward air mass trajectories starting at the site of the wildfire at 12:00, 16:00, 20:00, 00:00 and 04:00 UT.

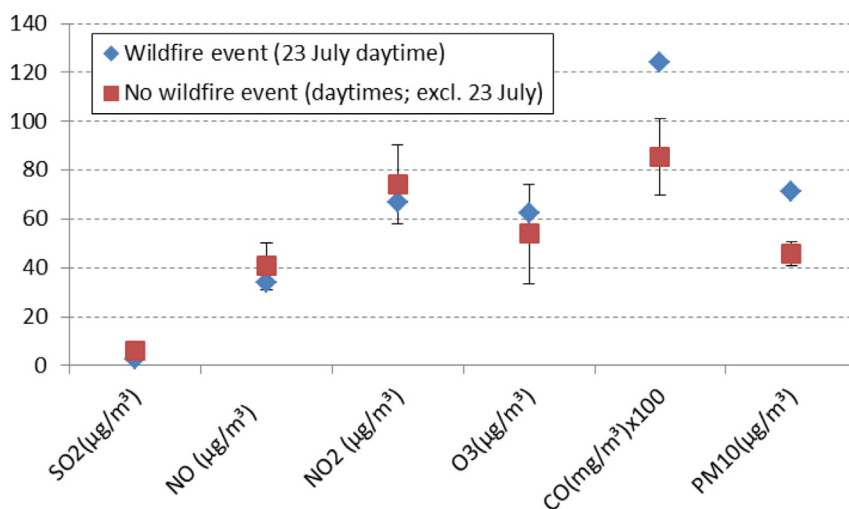


Fig. 2. Mean hourly concentrations of SO₂, NO, NO₂, O₃, CO and PM₁₀ at the urban site “Eixample” in Barcelona on 23 July (daytime: 8:00 to 20:00 h) (blue symbols). For comparison, mean values and corresponding standard deviations of the concentrations measured during the daytime on the other days before and after the wildfire event, are also shown (red symbols). The PM₁₀ and CO concentrations are significantly ($p < 0.01$) higher on 23 July during daytime than the other daytime concentration.

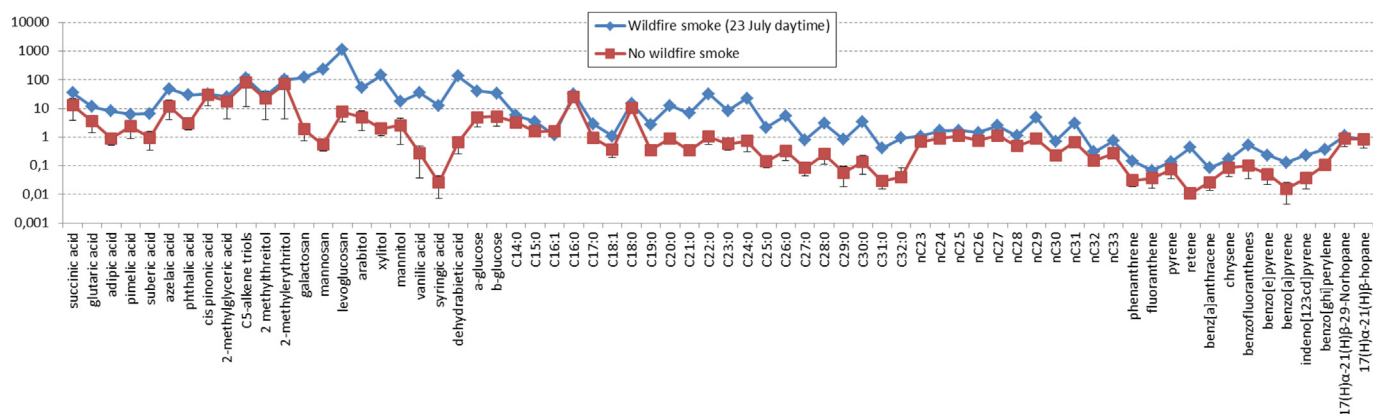


Fig. 3. Concentrations of organic compounds in PM₁ filter samples (ng/m³) on 23 July (daytime: 8:00 to 20:00 h) compared to the means and standard deviations of the concentrations measured on the other days before and after the wildfire event. Notice the logarithmic concentration scale.

23 July was in the range of the concentrations observed at sites that were directly exposed to biomass burning smoke (van Drooge and Grimalt, 2015; van Drooge and Pérez-Ballesta, 2009; Puxbaum et al., 2007).

Long-chain n-alkanes (carbon number > nC27) and long-chain carboxylic acids (carbon number > C19:0) showed 5 to 10 times higher concentrations on 23 July, respectively, than in the other samples, with even higher carbon number preference for the carboxylic acids and odd carbon number preference for the n-alkanes (Table S1; Fig. 3). However, these compounds with the observed carbon number preferences can also act as tracers of leaf detritus. Yan et al. (2008) related the occurrence of these compounds in biomass burning plumes to the volatilization of plant waxes from the leaves at high temperatures, which is confirmed in the present study.

Other tracer compounds, such as C₄–C₉ dicarboxylic acids and phthalic acid, also increased on 23 July (Table S1; Fig. 3). The highest increase was observed for phthalic acid (10 times), while other dicarboxylic acid concentrations showed a three-fold increase. Phthalic acid could be linked to the oxidation of naphthalene (Kautzman et al., 2010) in the atmosphere. Naphthalene itself was not detected in the filter samples. Due to its high volatility it is

exclusively in the atmospheric gas phase, and cannot be analyzed with the used analytical method (Fontal et al., 2015). Higher molecular weight and particle-bound PAHs between phenanthrene and benzo[ghi]perylene were found in the filters collected on July 23 at concentrations three-fold higher than those found for the other days (Σ PAH = 2.5 ng/m³ vs. 0.3–0.8 ng/m³; respectively; Table S1; Fig. 3). PAHs are generated during the incomplete combustion of organic matter, including fossil fuel and biomass (Schauer et al., 2007). The observed PAH increase on 23 July during daytime was not related to increases of traffic emissions, since other markers of this source, such as hopanes (Rogge et al., 1993), did not increase, as is normally observed in the area (Alier et al., 2013). The observed increase of PAH on 23 July was therefore related to the wildfire smoke. Accordingly, some PAH, such as retene, are tracers of wood combustion, specifically pine wood (Ramdahl, 1983). Indeed, retene concentrations on 23 July were 0.43 ng/m³ while they were only 0.01 ng/m³ on average in the other samples (Table S1; Fig. 3). Nevertheless, the overall observed increase of the PAH concentrations on 23 July was moderate. For instance, the concentrations of benzo[a]pyrene, one of the PAH with highest carcinogenic activity, was 0.13 ng/m³ in the daytime sample of 23 July (and 0.02 ± 0.01 ng/m³ on the other days), while

the annual limit value is 1 ng/m^3 , which would correspond to a small impact on public health (Boström et al., 2002; Olivares et al., 2011).

Concentration ratios of PAH isomers, such as benzo[a]anthracene vs. chrysene ($\text{Baan}/(\text{Baan} + \text{Chrys})$), benzo[a]pyrene vs. benzo[e]pyrene ($\text{BaP}/(\text{BaP} + \text{BeP})$), and indeno[1,2,3-cd]pyrene vs. benzo[ghi]perylene ($\text{IP}/(\text{IP} + \text{BgP})$), can be used as indicators for emission sources (Galarneau, 2008). However, these isomer ratios cannot stand alone as source apportionment tools due to the different sensitivity to photo-chemical degradation of the compounds (Esteve et al., 2006; Galarneau, 2008). Nevertheless, $\text{Baan}/(\text{Baan} + \text{Chrys})$, $\text{BaP}/(\text{BaP} + \text{BeP})$, and $\text{IP}/(\text{IP} + \text{BgP})$ ratios were 0.34, 0.35, and 0.38, respectively, on 23 July, and were higher than the mean isomeric ratios observed in the other samples (0.25 ± 0.06 , 0.23 ± 0.05 , and 0.24 ± 0.05). This suggests a change of PAH composition on 23 July compared to the other days. Higher ratios of these isomeric pairs have also been observed in other studies of biomass (wood) burning plumes (van Drooge and Grimalt, 2015), while the overall lower ratios, such as $\text{IP}/(\text{IP} + \text{BgP})$, have been related to the presence of fossil-fuel combustions (Schauer et al., 2007). Therefore, the isomeric ratios indicate influence of biomass burning on the urban air quality on 23 July.

The observed increases in organic compounds in Barcelona at the time of the wildfires are consistent with the increases in organic aerosol constituents observed during other such episodes. For example, the organic compounds in smoke from wildfires in Mediterranean Biomes, such as those in summer 2009 in the Iberian Peninsula (Vicente et al., 2012), or those in Southern California in 2007 (Verma et al., 2009), showed large emissions of water-soluble organic compounds, such as levoglucosan and isomers, due to thermal alteration of celluloses, as well as vanilic acid, syringic acid and dehydroabietic acid. Increases in the emissions of long chain carboxylic acid and aliphatic hydrocarbons were observed during these episodes but the increases associated to PAH were generally 2 or 3 orders of magnitude lower compared to the aforementioned compounds. Retene was an exception to this general PAH variation. The increase in the concentration of this compound accounted for about 40% of all PAHs detected (Vicente et al., 2012). In these previous studies, the observed concentration increases of dicarboxylic acid were relatively low (Vicente et al., 2012). However, a substantial proportion of these and other oxygenated compounds are formed during the atmospheric transport via oxidation of volatile organic compounds (Yan et al., 2008; Yee et al., 2013). These oxidation processes may also lead to significant transformation of the primary emitted organic compounds, including levoglucosan (Hennigan et al., 2010). In the present study, considering the relatively fast transport of the air mass to the city and the period of the day in which it occurred (early morning), the sampled wildfire smoke was still relatively fresh. The high levoglucosan levels and the relatively small increase of oxygenated compounds are in agreement with limited transformation during atmospheric transport.

Comparison of the chemical composition of the aerosols sequentially collected in Barcelona prior and after July 23 (see Fig. 3) indicates that the influence of wildfire smoke on air quality was only significant during the daytime on 23 July. In the subsequent sample taken during the night from 23 to 24 July, the levels of the biomass burning tracer compounds were very similar to those observed on 19 and 22 July. These results indicate that the influence of wildfire smoke on the air concentration of organic compounds at the surface was decreasing to background levels within hours after the occurrence of the concentration peak.

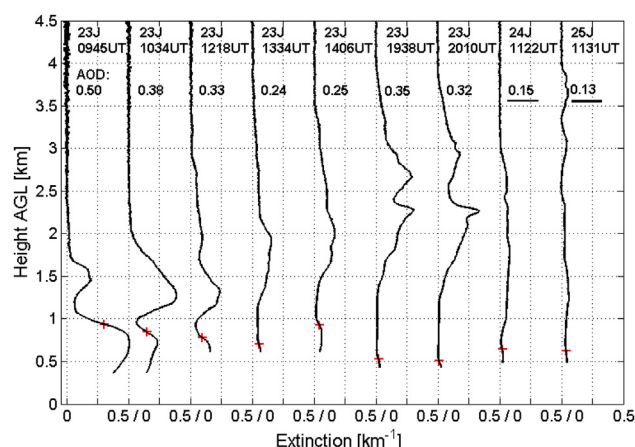


Fig. 4. Extinction coefficient profiles at 532 nm on 23, 24 and 25 July. The AOD is the lidar-retrieved AOD unless it is underlined, in which case it is the sun-photometer AOD. The boundary layer height is indicated by a red cross.

3.3. Aerosol stratification by lidar

Lidar extinction coefficient profiles taken between 09:45 and 20:10 UT on 23 July are shown in Fig. 4. For comparison, the profiles on 24 and 25 July around 12:00 UT are also shown. On 23 July at 09:45 UT the AOD value, 0.50, was high and most of the aerosol load was residing in the PBL. The extinction coefficient reached values in the PBL as high as 0.5 km^{-1} , which was about 5 times higher than the typical seasonal value in Barcelona (Sicard et al., 2011). During the rest of the morning the AOD slowly decreased to ~ 0.25 around 14:00 UT. That decrease was associated with a continuous decrease of the extinction coefficient in the PBL (on the order of 0.25 km^{-1} at 10:34 UT and 0.06 km^{-1} at 14:06 UT), indicating a decrease of the aerosol concentrations. This is in agreement with the PM_{10} concentration variation during the same time period. However, while the extinction coefficient decreased in the PBL, the extinction above the PBL increased. From 10:34 UT onward most of the aerosol load was no longer confined in the PBL but in a layer just above. At 10:34 UT this layer was rather thin ($\sim 1.3 \text{ km}$) while the extinction coefficient was high (peak at 0.39 km^{-1}). At 14:06 UT the layer aloft was much wider ($\sim 2.5 \text{ km}$) but the extinction coefficient had decreased (peak at 0.17 km^{-1}). These results indicate that the biomass burning particles detected in large quantity at ground level and in the PBL at $\sim 10:00 \text{ UT}$ were observed aloft shortly after. In the evening, at 19:38 and 20:10 UT, the elevated layer was even more pronounced with a center of mass around 2.5 km, a thickness of $\sim 2.7 \text{ km}$ and peaks of extinction coefficient greater than 0.25 km^{-1} . The AOD had also increased. Subsequently, on 24 and 25 July, the AOD decreased. On 24 July, the biomass burning layer was still clearly visible (center of mass around 1.8 km, thickness of $\sim 2.2 \text{ km}$ and peaks of extinction coefficient of $\sim 0.08 \text{ km}^{-1}$) while on 25 July a multi-layer structure appeared up to 4 km. It is however, uncertain whether the layers observed on 25 July still contain biomass burning particles.

The Hysplit (Draxler and Rolph, 2013) air mass back trajectories from Barcelona (Fig. 5) were consistent with the northern (wildfire) origin of the air-mass at 12:00 UT on 23 July at all altitudes (100, 1500 and 2500 m), while the air-mass arriving on 24 July at ground level (100 m) was no longer coming from the North but rather from the East. These observations explain why no significant biomass burning signal was found at ground level (or in the PBL) after 23 July. On the other hand, the air-mass trajectories arriving in Barcelona at 1500 and 2500 m altitude on 24 July were still coming from the North. It is possible that wildfire smoke particles were transported towards Barcelona; although the air masses are coming

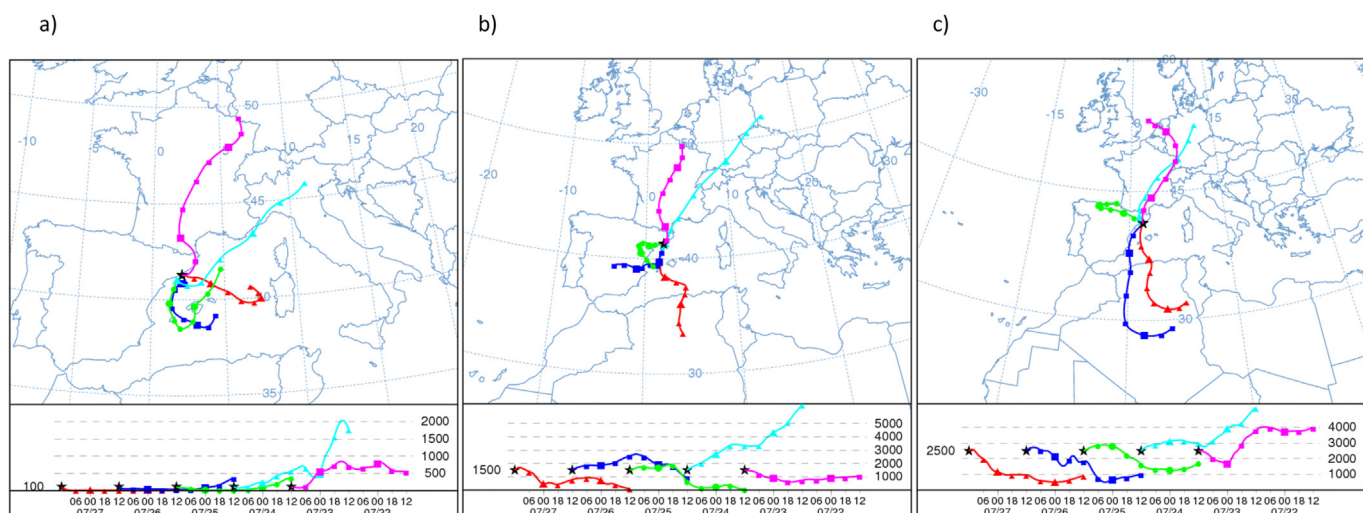


Fig. 5. 48-hour back-trajectories started every 24 h from Barcelona between 23 July and 27 July at 12:00 UT at an altitude of a) 100 m (ground level), b) 1500 m and c) 2500 m.

from higher altitude (Fig. 5b). On 25 July, the trajectories were rather short and circular indicating a possible re-circulation of air masses within the region. It is therefore possible that the multi-layer structure observed on 25 July was the result of mixing wild-fire smoke particles with aerosols of other origin.

Our interpretation of the biomass burning plume transport is the following: At the beginning of the event, at midday on 22 July, the early fire ejected particles into the PBL. This plume was transported in southerly direction to the coast, following the synoptic winds. During the night, the land breeze pushed the plume further out over the Mediterranean Sea. Since convection at night is limited, the plume was confined to the lowest few hundreds of meters above the sea. At sunrise, the circulation reversed and the smoke plume was transported back to the land. The trajectories in Figs. 1 and 5a are parallel to the coast at 09:00 UT and start to bend towards land at 10:00 UT. It is around that time that the maximum PM levels are reached. At midday the sea-breeze regime carried the plume further inland and at higher elevation which cleared the air of Barcelona from the smoke particles.

3.4. FLEXPART simulation of the wildfire event

The aforementioned data showed that the observed atmospheric particles were linked to the smoke plume that was transported towards the metropolitan area of Barcelona in the morning of 23 July. FLEXPART was used to investigate the transport of the biomass burning plume and determine the consistency between measured aerosol concentrations and simulated biomass burning plume.

Fig. 6 shows the simulation of the smoke plumes of the two slightly different scenarios at the surface at 12:00 UT on 23 July, i.e. when smoke was observed in the urban area. In both cases, the smoke plume travels in southerly direction over the sea and then turns towards the land, where it reaches the city of Barcelona. The simulated $\text{PM}_{2.5}$ concentrations are between 100 and 200 $\mu\text{g}/\text{m}^3$. These values are in the range of the maximum PM_{10} concentrations measured in this period (189 $\mu\text{g}/\text{m}^3$). Although there are no measured hourly $\text{PM}_{2.5}$ concentrations available, the comparison of measured $\text{PM}_{2.5}$ and PM_{10} on 24-h resolution shows that 77% of the PM_{10} is $\text{PM}_{2.5}$ on 23 July. This contribution of $\text{PM}_{2.5}$ was significantly higher ($p < 0.01$) than the mean contribution on the other days ($60\% \pm 4\%$), indicating that the measured PM concentrations during the wildfire event are indeed in the range of the simulated ones.

The simulated CO concentrations at 12:00 UT were 2.1 mg/m^3 , which is close to the maximum concentration measured (1.8 mg/m^3). Despite this general agreement, detailed comparison of the measured and simulated time series of CO and PM show considerable differences (Fig. 7). The measured PM values reached their maximum concentrations around 10:00 on 23 July and decreased rapidly afterwards to background levels at 14:00, while the estimated values peaked around 12:00 (i.e., about two hours after the measured peak) and then slowly decreased until the evening of the next day (24 July; i.e., when the fire was almost extinct). The measured CO in the urban area also decreased more rapidly than the simulated CO, confirming that the duration of the smoke episode at the surface was overestimated by the model.

The too long persistence of simulated fire influence near the surface probably arises from a strong coupling in FLEXPART between the surface and the air mass just above the PBL. As we have seen from the lidar measurements, the biomass burning plume is indeed present above the city during the period that FLEXPART simulates fire influence; however, while in reality the pollution aloft is decoupled from the surface, FLEXPART mixes the pollution down to the surface. The modeling problems are likely related to the sea breeze circulation. The influence of the sea breeze circulation system can be large in coastal areas, especially in the Mediterranean region (Millán et al., 1997), and it cannot be fully captured at the resolution of the ECMWF input data used by FLEXPART. This difficulty may lead to errors in both the horizontal as well as vertical position of the biomass burning plume. In particular, it seems that the decoupling of the elevated pollution layer from the surface during transport over the sea was not captured and may contribute to the modeling problems.

4. Conclusions

Smoke particles originating from a wildfire that started in the Alt Empordà region on 22 July 2012, about 120 km north of Barcelona, impacted the atmosphere of the city of Barcelona on 23 July. High aerosol loadings during the daytime of 23 July were found at ground level by PM_{10} on-line monitoring stations ($\text{PM}_{10} = 71 \mu\text{g}/\text{m}^3$ with a peak at 189 $\mu\text{g}/\text{m}^3$) and in the PBL by lidar measurements (extinction coefficient $\sim 0.5 \text{ km}^{-1}$). The aerosol organic chemical composition confirmed the large contribution of biomass burning (e.g. levoglucosan concentration of 1100 ng/m^3 on 23 July vs. only $8 \pm 4 \text{ ng}/\text{m}^3$ in other samples), together with a moderate increase of

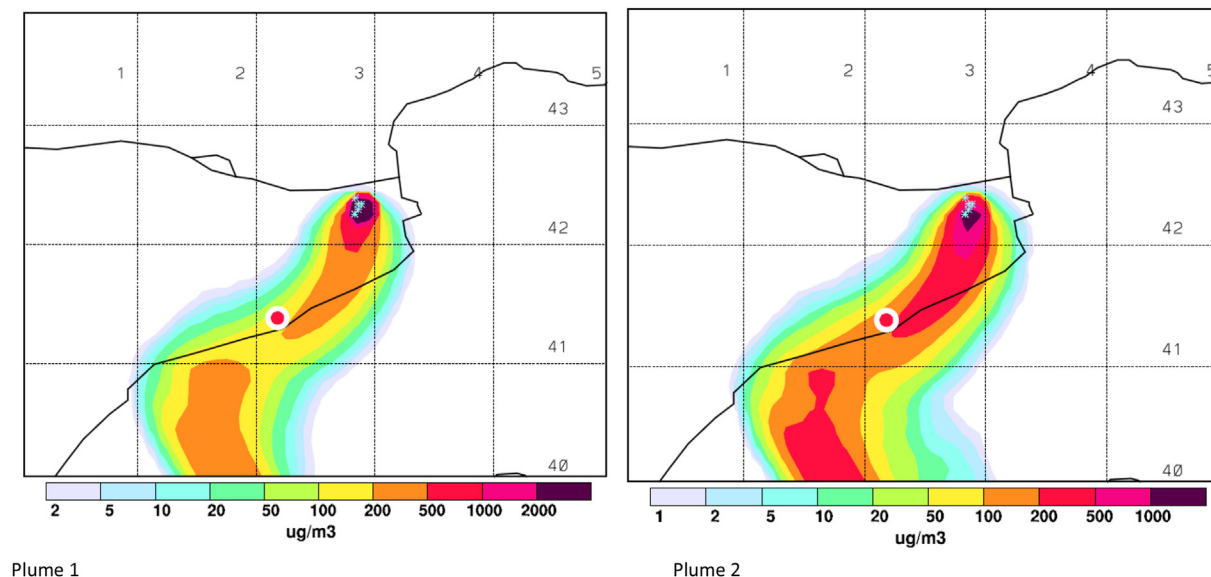


Fig. 6. FLEXPART smoke plume simulation of $\text{PM}_{2.5}$, starting on 22 July at 10.00 UT and showing the situation on 23 July at 12.00 UT. $\text{PM}_{2.5}$ particles from the wildfire are transported towards the urban area of Barcelona (red dot). Plume 1 and plume 2 differ slightly in burnt areas between 15:00 h and 19:00 h on 22 July but the total burnt area and $\text{PM}_{2.5}$ emissions are the same in both scenarios (see SI.3).

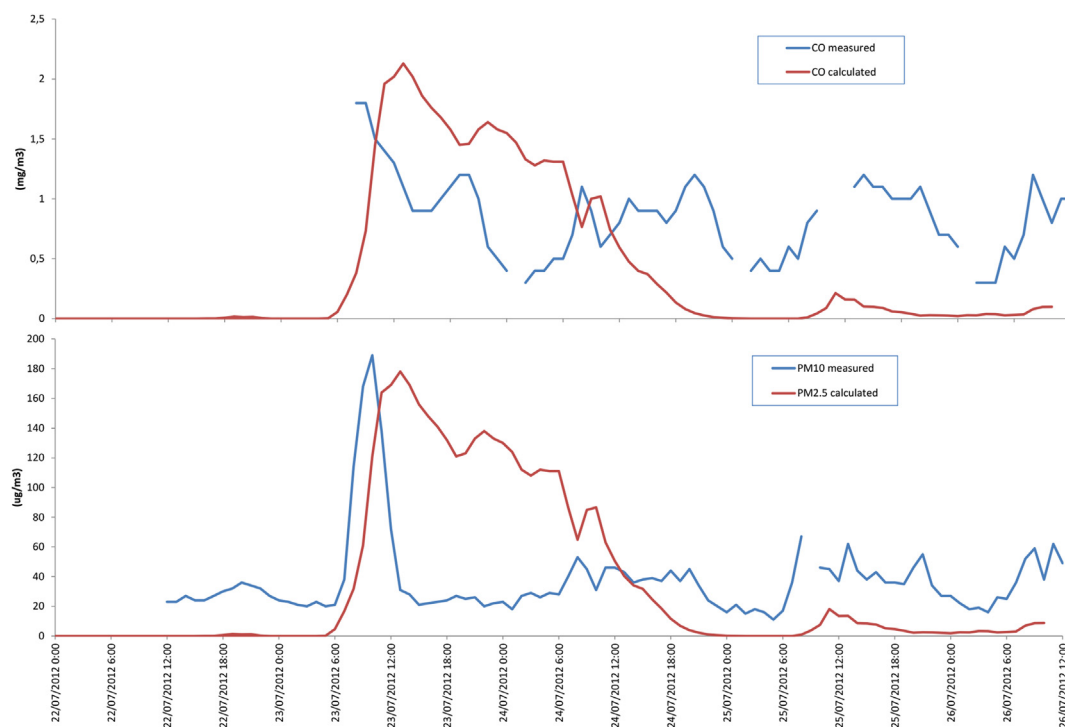


Fig. 7. Measured and estimated (FLEXPART) CO (mg/m^3) and PM_{10} (or 2.5) ($\mu\text{g}/\text{m}^3$) concentrations at the urban sampling site. No hourly data on $\text{PM}_{2.5}$ was available, so the estimated values were compared with PM_{10} . Note that about 50% of the PM_{10} is $\text{PM}_{2.5}$ in the 12 h samples of the studied period. The hourly time intervals are in UT.

toxic compounds, such as PAH ($2.5 \text{ ng}/\text{m}^3$ on 23 July vs. $0.6 \pm 0.3 \text{ ng}/\text{m}^3$ in other samples).

Satellite images, air-mass trajectories and Lagrangian particle dispersion model simulations confirmed that the origin of the biomass burning particles was the severe wildfire in Alt Empordà. On subsequent days, no significant contribution of smoke particles was found in the urban air at the surface, but the lidar found particles just above the urban PBL, the origin of which was confirmed by air-mass trajectory analyses.

FLEXPART model simulations were able to quantify the contributions of air pollutants from the wildfire in the city, but failed to reproduce the observed decoupling of surface concentrations from the pollution plume aloft from 23 July in the afternoon, hence producing a too persistent influence of the biomass burning plume at the surface.

The findings of the present study show different smoke trajectories from those observed in an earlier PM event in 2009. In that event, even though the wildfire smoke particles were concentrated

in an aerosol layer at 3 km above the city (Sicard et al., 2012), the influence on the air quality at ground level in the city was small (van Drooge et al., 2012). However, the biomass burning plume of the present study indeed reached the city of Barcelona at ground level and thus significantly influenced the urban air quality for several hours.

Conflict of interest

The authors report no conflict of interest. There are not previous publications submitted for publication on the present data.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2015.12.003>.

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