

1 **Detection and simulation of wildfire smoke impacting a Mediterranean urban atmosphere**

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20 **Abstract**

21 The combined use of chemical analysis of organic molecules in atmospheric aerosols (PM₁)

22 collected in situ in Barcelona and optical measurements with a light detection and ranging

23 (LIDAR) instrument allowed the characterization of the smoke plume from a wildfire that

24 reached the city in July 2012. A Lagrangian particle dispersion model (FLEXPART) was applied

25 to simulate the smoke plume and to compare the results with in-situ data.

26 The chemical composition of the aerosols collected on 23 July 2012 confirmed the large

27 contribution of biomass burning in the urban air during several hours by the increase of

28 compounds, such as levoglucosan, dehydroabietic acid and polycyclic aromatic hydrocarbons

29 (PAH), which was coincident with an increase of the aerosol density in the boundary layer (BL).

30 According to air-mass trajectory modelling, the origin of the biomass burning particles was

1 related to the severe wildfire occurring 120 km northeast of the city. On the following days, no
2 significant contribution of wildfire smoke was found in the urban air (i.e. in the BL), although the
3 lidar detected particles aloft. The FLEXPART model was able to simulate the onset of the
4 wildfire smoke plume event in the urban center in the early morning of 23 July, but not the fast
5 transition of the plume at the surface, indicating that small-scale meteorological phenomena,
6 such as an intensive local sea-breeze was not fully characterized by this model, resulting to
7 simulated behavior of particles at the surface which was more representative of the conditions
8 aloft.

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10 **Keywords:** Urban organic aerosol; levoglucosan; polycyclic aromatic hydrocarbons; regional
11 wildfire smoke; LIDAR; FLEXPART

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1 **Introduction**

2 Aerosols have adverse effects on human health (Pérez et al., 2009; Pope et al., 2002) and
3 influence on the Earth's radiative balance (Forster et al., 2007). In urban areas, and especially
4 in the Mediterranean region, high background aerosol levels are often observed due to
5 anthropogenic emission (i.e. traffic, industry, etc.) and stable atmospheric conditions with high
6 solar insolation, resulting in accumulation of pollutants within the planetary boundary layer
7 (boundary layer) (Millán et al., 1997; Pérez et al., 2010; Pey et al., 2008). Moreover, the
8 Mediterranean area is often exposed to Saharan dust outbreaks that occur about 15 times per
9 year and cause two to four and up to ten time increases of the annual aerosol levels in the
10 Western and Eastern Mediterranean, respectively (Querol et al., 2009). Wildfires are common in
11 summer and constitute an additional contribution that further increases the aerosol levels
12 (Phuleria et al., 2005; Rodríguez et al., 2002; Verma et al. 2009). Exposure to aerosols from
13 wildfires has been associated to toxic effects such as lung cell damage and airway inflammation
14 (Barrett et al. 2006; Thoring et al. 1982). Although these effects are not exclusively linked to
15 biomass burning particles, there is evidence that they are more toxic than those from other
16 emission sources on an equal-dose basis (Wegesser et al. 2009).

17 Recent studies on the influence of these natural emission sources on the organic aerosol in the
18 urban area of Barcelona (Catalonia, Spain) showed a low-to-moderate impact of regional
19 wildfire smoke and Saharan dust on the urban aerosol, which is normally dominated by local
20 fossil fuel combustion sources (van Drooge et al., 2012). Simultaneous measurements of the
21 optical properties of the aerosols in the atmospheric column showed that Saharan dust and
22 wildfire smoke layers were mainly situated and transported in the free troposphere above the
23 boundary layer (Sicard et al., 2011; 2012), with low impact on the air quality at ground level.

24 The present study focuses on the impact of a wildfire event that affected the urban area of
25 Barcelona during a short period of time in July 2012 (see chronicle of wildfire in SI.1). On
26 Sunday July 22nd (22J) a wildfire started along a highly transited highway near the border
27 between France and Spain, in the Alt Empordà region, a forested area 120 km northeast of
28 Barcelona. The fire was active during the next few days and was officially controlled on 25 July
29 and completely extinguished on 30 July. As a result of the wildfire, four persons died,

1 approximately 14000 ha of mainly forested areas were burnt, as well as several farms and
2 houses, and one camping site.

3 This paper describes the influence of the smoke plume on the urban aerosol concentrations in
4 Barcelona by means of chemical analysis of PM₁ samples and remote sensing lidar (Light
5 Detection and Ranging) measurements, as well as satellite imagery and air mass trajectory
6 modeling. The Lagrangian particle dispersion model FLEXPART was used (Stohl et al., 1998,
7 2005) to study the pathways of sampled air masses to the measurement station and to identify
8 the contribution of the wildfire event.

9

10 **2. Materials and Methods**

11 **2.1. PM₁ filter sampling and organic tracer compound speciation**

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

17 A detailed description of the applied analytical procedure is given elsewhere (Fontal et al.
18 2015). Briefly, PM₁ filter samples were extracted using a mixture of dichloromethane and
19 methanol (2:1 (v/v) (Merck, Germany). The extracts were filtered over 0.45 µm teflon membrane
20 filter (Whatman, USA) in order to remove particles and concentrated by vacuum rotary
21 evaporation to 1 mL. Aliquots of 25 µL of the extract were evaporated under a gentle stream of
22 N₂. Then, 25 µL of bis(trimethylsilyl)trifluoroacetamide (BSFTA) + 1% trimethylchlorosilane
23 (TMCS) (Supelco, USA) and 10 µL of pyridine (Merck, Germany) were added for derivatization
24 of the saccharides, acids and polyols to their trimethylsilyl esters at 70° C during 1 h. Samples
25 were injected in a Thermo gas-chromatograph (GC) coupled to a mass spectrometer (MS)
26 (Thermo Trace GC Ultra – DSQ II, Thermo Scientific, USA) equipped with a 60 m fused
27 capillary column (RXi® 5Si MS 0.25 mm x 0.25 µm film thickness; Restek, USA). A MS
28 selective detector was operating in full scan (*m/z* 50 – 650) and electron impact (70 eV) modes.
29 The applied method allows quantitative determination of carboxylic acids, dicarboxylic acids
30 (and derivates), saccharides, aliphatic hydrocarbons (n-alkanes), polycyclic aromatic

1 hydrocarbons (PAH) and hopanes. Method efficiency was assessed from recoveries of
2 surrogate standards added to the filters prior to extraction. Mean recoveries were higher than
3 70% for all compounds. Field blank levels were low, always below 30% of the levels found in
4 the samples. All reported concentrations were corrected by surrogate recovery and blank levels.
5 Limit of quantification of the individual organic compounds was 0.06 ng/m³ for sugars, 0.03
6 ng/m³ for n-alkanes and 0.001 ng/m³ for PAH and hopanes.

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

9

10 **2.2. Lidar measurements**

11 Profiles of the aerosol stratification were obtained by the EARLINET (European Aerosol
12 Research Lidar Network) lidar located in the center of Barcelona (41.39N, 2.11E, 115 m asl).
13 The system employs a Nd:YAG laser emitting pulses at 355, 532 and 1064 nm at a repetition
14 rate of 20 Hz. In reception, the backscattered elastic radiation and also the nitrogen (at 387 and
15 607 nm) and the water vapor (at 407 nm) Raman-shifted backscattered radiation is recorded.
16 The vertical resolution is 3.75 m and the typical time resolution is 1 minute.

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

27

28 **2.3. FLEXPART simulations**

29 Forward simulations of the fire pollution plumes were made with the Lagrangian particle
30 dispersion model FLEXPART (Stohl et al., 1998, 2005). The model was driven with ECMWF

1 (European Centre for Medium-Range Weather Forecasts) operational analysis data with 0.18° x
2 0.18° latitude/longitude resolution, 91 vertical model levels and 3 hour time resolution.
3 Simulations were made both for a passive carbon monoxide (CO) tracer and a PM_{2.5} aerosol
4 tracer undergoing dry deposition and scavenging by precipitation.
5 The emissions used for the simulations were taken from information available on the fire. The
6 coordinates of the starting point of the wildfire and the consecutive chronicle of its evolution
7 through time and space were obtained from the Fire Brigade reports (see SI.1 for the translation
8 of the report). Based on the geographical position of the fire and satellite imaging (see SI.2), the
9 surface area of the wildfire was estimated for the consecutive days (SI.3). The time resolution in
10 relation to burnt area was not conclusive, especially on 22 July, when the fire was most active
11 (SI.2). Accordingly, two scenarios (plume 1 and 2) were adapted with different burning areas on
12 22 July between 14:00 and 15:00h (plume 1 and 2: 33 km² and 24 km²) and 15:00 and 17:00h
13 (plume 1 and 2: 9 km² and 19 km²) (SI.3). The large surface areas that were burnt consisted of
14 Mediterranean forests (76 %) and agricultural fields (19 %), while 5 % was a mixture of different
15 surfaces, including urbanized areas. Alves et al. (2011) estimated an emission factor of 231 g
16 CO/kg Mediterranean vegetation burnt, while this was 9 g/kg for PM_{2.5}. The mass of
17 Mediterranean vegetation per surface area was estimated to be 200 Mg/ha (Ruiz-Peinado,
18 2013).

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20 **2.4. Complementary data**

21 Meteorological data (temperature, relative humidity, wind speed, and wind direction) for the
22 sampling period were obtained from the meteorological station near the sampling site run by the
23 Department of Territory and Sustainability of the Government of Catalonia. Hourly NO, NO₂, O₃,
24 CO, PM_{2.5} and PM₁₀ levels between July 19 and 24 were also obtained from the same
25 department. Satellite images were obtained from the MODIS (Moderate Resolution Imaging
26 Spectroradiometer) (NASA, USA) instrument. Air mass trajectories were calculated using the
27 HYSPLIT4 software from the NOAA-ARL (USA) (Draxler and Rolph, 2013; Rolph 2013). Here
28 GDAS1 data were used for the model calculation and the air-mass trajectories were based on
29 isentropic surfaces. For the sampling sites the isentropic surfaces were related to the potential
30 temperature at 100, 1500 and 2500 m above ground level (agl).

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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 southern direction on 23 July. The air quality parameters in the city centre (station “Eixample”) during the period 19 until 24 July showed significantly ($p < 0.01$) higher daytime levels (08:00h-20:00 UT) on 23 July for CO ($1.2 \mu\text{g}/\text{m}^3$) and PM₁₀ ($71 \mu\text{g}/\text{m}^3$), compared to the concentrations averaged over the other sampling periods ($0.7 \pm 0.2 \text{ mg}/\text{m}^3$ and $33 \pm 9 \mu\text{g}/\text{m}^3$, 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 sampling periods (34 vs. $23 \pm 13 \mu\text{g}/\text{m}^3$, 67 vs. $58 \pm 16 \mu\text{g}/\text{m}^3$, 63 vs. $48 \pm 11 \mu\text{g}/\text{m}^3$, respectively for NO, NO₂ and O₃; Table S1, Fig. 2). The higher PM concentration on 23 July is emphasized if the period of maximum daily concentrations is considered; between 07:00 UT and 14:00 UT, with the maximum concentration at 10:00 UT for CO and PM₁₀ of $1.8 \text{ mg}/\text{m}^3$ and $189 \mu\text{g}/\text{m}^3$, respectively. These peak concentrations of CO and PM₁₀ were not directly related to traffic emissions, since NO and NO₂ did not show any difference on 23 July in comparison to the other weekdays. Moreover, the CO and PM₁₀ concentrations on 23 July are 40% and 80% higher than the maximum levels observed on the other days during the week. These results are in agreement with those found in other urban areas that were exposed to wildfire smoke, such as Los Angeles (Verma et al. 2009). Nevertheless, besides an increase 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 emission of NO are probably dominating the influence of the wildfire NO contributions, especially since the wildfires occurred more than 100 km away. The PM₁₀ increase on 23 July was also observed in other urban stations, 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 hours) resulting in a 24-h PM₁₀ concentration of $43 \mu\text{g}/\text{m}^3$, which is lower than the limit value of $50 \mu\text{g}/\text{m}^3$.

3.2. Aerosol organic tracer analysis

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

10 The chemical data (Table S1; Fig.3) for 23 July (daytime) showed significantly higher
11 concentrations of biomass burning organic tracer compounds, i.e. levoglucosan (1100 ng/m³),
12 and its isomers, galactosan and mannosan, as well as xylitol, vanilic acid, syringic acid, and
13 dehydrabietic acid (Fig. 3) (Vicente et al., 2012, Simoneit, 2002; Yan et al. 2008). The
14 concentrations of these compounds were about two orders of magnitude higher than those
15 observed during the other sampling periods, both before and after the wildfire event (e.g.
16 levoglucosan = 8 ± 4 ng/m³; Fig. 4). The low levoglucosan concentrations of the samples not
17 influenced by the fire plume were similar to the background levels found in previous studies in
18 the same area (Alier et al., 2013; van Drooge et al., 2012; van Drooge and Grimalt, 2015), while
19 the high daytime level (~1000 ng/m³) on 23 July was in the range of the concentrations
20 observed at sites that were directly exposed to biomass burning (van Drooge and Grimalt, 2015;
21 van Drooge & Pérez-Ballesta, 2009; Puxbaum et al., 2007).

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

29 Other tracer compounds, such as C₄-C₉ dicarboxylic acids and phthalic acid, also increased on
30 the day that wildfire smoke affected the air quality in the city (Table S1; Fig.3). The highest

1 increase was observed for phthalic acid (7-10 times), while other dicarboxylic acid
2 concentrations showed a three-fold increase. Phthalic acid could be linked to the oxidation of
3 naphthalene (Kautzman et al. 2010) after atmospheric transport. Naphthalene itself was not
4 detected in the filter samples. Due to its high volatility it is exclusively in the atmospheric gas
5 phase, and cannot be analyzed with the used analytical method (Fontal et al. 2015). Higher
6 molecular weight and particle-bounded PAHs between phenanthrene and benzo[ghi]perylene
7 were found in the filters collected on July 23 at concentrations three-fold higher than in those of
8 the other days (Σ PAH = 2.5 ng/m³ vs. 0.3 to 0.8 ng/m³; respectively; Table S1; Fig. 3). PAHs
9 are generated during the incomplete combustion of organic matter, including fossil fuel or
10 biomass (Schauer et al. 2007). The observed PAH increase in the 23 July during daytime was
11 not related to increases of traffic emissions, since other markers of this source, such as
12 hopanes (Rogge et al., 1993), did not increase, as is normally observed in the area (Alier et al.
13 2013). The observed increase of PAH on 23 July was related to the wildfire smoke. Accordingly,
14 some PAH, such as retene, are tracers of wood combustion, specifically pine wood (Ramdahl,
15 1983). This compound concentration increased in the city at the time of the wildfire, e.g. 0.43
16 ng/m³ vs. 0.01 in other samples (Table S1; Fig. 3). Nevertheless, the overall observed increase
17 of the PAH concentrations on 23 July was moderate. For instance, the concentrations of
18 benzo[a]pyrene, one of the PAH with highest carcinogenic activity, was 0.13 ng/m³ in the
19 daytime sample of 23 July (and 0.02 ± 0.01 ng/m³ on the other days), while the annual limit
20 value is 1 ng/m³, involving a moderate impact on public health as consequence of the exposure
21 to these compounds (Boström et al., 2002; Olivares et al., 2011). The relative composition of
22 PAH isomers, such benzo[a]anthracene vs. chrysene (Baan/(Baan+Chrys), benzo[a]pyrene vs.
23 benzo[e]pyrene (BaP/(BaP+BeP), and inden[123cd]pyrene vs. benzo[ghi]perylene (IP/(IP+BgP),
24 can be used as indicators for emission sources (Galarneau, 2008), although these isomers
25 ratios cannot stand alone as source apportionment tools due to the different sensitivity to photo-
26 chemical degradation of the compounds (Esteve et al., 2006; Galarneau, 2008). Nevertheless,
27 Baan/(Baan+Chrys), BaP/(BaP+BeP), and IP/(IP+BgP) ratios were 0.34, 0.35, and 0.38,
28 respectively, on 23 July, and were higher than the mean isomeric ratios observed in the other
29 samples (0.25 ± 0.06, 0.23 ± 0.05, and 0.24 + 0.05). These differences of relative PAH
30 composition shows a change of PAH composition on 23 July with respect the other days, and

1 higher ratios of these isomeric pairs has been observed in other studies where the atmosphere
2 was influenced by biomass (wood) burning (Van Drooge and Grimalt, 2015), while the overall
3 lower ratios, such as the dominance of BgP over IP (resulting in lower IP/(IP+BgP) ratio) has
4 been related to the presence of fossil-fuel combustions (Schauer et al. 2007). Therefore, the
5 isomeric ratios indicate influence of biomass burning on the urban air quality on 23 July.

6 The observed increases in organic compounds in Barcelona at the time of the wildfires are
7 consistent with the increases in organic aerosol constituents observed in other episodes. Thus,
8 the organic compounds in smoke from wildfires in Mediterranean Biomes, such as those in
9 summer 2009 in the Iberian Peninsula (Vicente et al., 2012), or those in Southern California in
10 2007 (Verma et al. 2009), showed large emissions of water-soluble organic compounds, such
11 as levoglucosan and isomers, due to thermal alteration of celluloses, as well as vanilic acid,
12 syringic acid and dehydroabietic acid. Increases in the emissions of long chain carboxylic acid
13 and aliphatic hydrocarbons were observed on occasion of these episodes but the increases
14 associated to PAH were generally 2 or 3 orders of magnitude lower compared to the
15 aforementioned compounds. Retene was an exception to this general PAH variation. The
16 increase in the concentration of this compound accounted for about 40% of all PAHs detected
17 (Vicente et al. 2012). In these previous studies, the observed concentration increases of
18 dicarboxylic acid were relatively low (Vicente et al. 2012). However, a substantial proportion of
19 these and other oxygenated compounds are formed during the atmospheric transport after
20 oxidation of volatile organic compounds (Yan et al. 2008; Yee et al., 2013). These oxidation
21 processes may also lead to significant transformation of the primary emitted organic
22 compounds, including levoglucosan (Hennigan et al. 2010). In the Barcelona samples,
23 considering the relative fast transport of the air mass to the city and the period of the day in
24 which it occurred (early morning), the sampled wildfire smoke was still relatively fresh. The high
25 levoglucosan levels and the relatively small increase of oxygenated compounds are in
26 agreement with limited transformation during atmospheric transport.

27 Comparison of the chemical composition of the aerosols sequentially collected in Barcelona
28 prior and after July 23 (see Fig. 3) indicates that there the influence of wildfire smoke on air
29 quality was only significant during the daytime on 23 July. In the consecutive samples from the
30 nighttime of 23 to 24 July, the levels of the biomass burning tracer compounds were very similar

1 to those observed on 19 and 22 July. These results indicate that the influence of wildfire smoke
2 on the air concentrations of organic compounds at the surface (i.e. in the boundary layer) was
3 decreasing to background levels within hours after the maximum concentration episode.

4 5 **3.3. Aerosol stratification by lidar**

6 The temporal series of extinction coefficient profiles on 23 July between 09:45 and 20:10 UT is
7 shown in Fig. 4. For comparison, the profiles on 24 and 25 July around 12:00 UT are also
8 shown. On 23 July at 09:45 UT the AOD value, 0.50, was high and most of the aerosol load was
9 confined in the boundary layer. The extinction coefficient reached values in the boundary layer
10 as high as 0.5 km^{-1} , which was about 5 times higher than the typical seasonal value in
11 Barcelona (Sicard et al., 2011). During the rest of the morning the AOD slowly decreased to
12 ~ 0.25 around 14:00 UT. That decrease was associated with a continuous decrease of the
13 extinction coefficient in the boundary layer (on the order of 0.25 km^{-1} at 10:34 UT and 0.06 km^{-1}
14 at 14:06 UT) which indicated a decrease of the aerosol concentrations. This result was in
15 agreement with the PM_{10} measurements at the same period. In contrast, while the extinction
16 coefficient decreased in the boundary layer, the AOD of the aloft layer increased. From 10:34
17 UT onward most of the aerosol load was no longer confined in the boundary layer but in a layer
18 just above. Thus, at 10:34 UT this layer was rather thin ($\sim 1.3 \text{ km}$) while the extinction
19 coefficient was strong (peak at 0.39 km^{-1}), at 14:06 UT the layer aloft was much wider (~ 2.5
20 km) and the extinction coefficient had decreased (peak at 0.17 km^{-1}). These results indicate that
21 the biomass burning particles detected in large quantity at ground level or in the boundary layer
22 at $\sim 10:00$ UT were observed aloft shortly after. In the evening, at 19:38 and 20:10 UT, the
23 elevated layer was even more pronounced with a center of mass around 2.5 km, a thickness of
24 $\sim 2.7 \text{ km}$ and peaks of extinction coefficient greater than 0.25 km^{-1} . The AOD had also
25 increased. Then, on 24 and 25 July, the AOD decreased. On 24 July, the biomass burning layer
26 was still clearly visible (center of mass around 1.8 km, thickness of $\sim 2.2 \text{ km}$ and peaks of
27 extinction coefficient of $\sim 0.08 \text{ km}^{-1}$) while on 25 July a multi-layer structure appeared up to 4
28 km. At this point of the study we cannot conclude whether the layers observed on 25 July still
29 contain biomass burning particles.

1 The Hysplit (Draxler and Rolph, 2013) air mass trajectories (Fig. 5) were consistent with the
2 northern (wildfire) origin of the air-mass at 12:00 UT on 23 July at all altitudes (100, 1500 and
3 2500 m), while the air-mass arriving on 24 July at ground level (100 m) was no longer from the
4 North but rather from the East. These observations explain why no significant biomass burning
5 signal was found at ground level (boundary layer) after 23 July. On the other hand, the air-mass
6 trajectories arriving to Barcelona at 1500 and 2500 m altitude on 24 July were still from the
7 North, possibly transporting wildfire smoke particles. On 25 July, the trajectories were rather
8 short and circular indicating a possible re-circulation of air masses within the region. It is
9 therefore possible that the multi-layer structure observed on 25 July was the result of mixing
10 wildfire smoke particles with other aerosols.

11 Accordingly, the presence of wildfire smoke in the urban center of Barcelona was consequence
12 of the combination of two main factors: the synoptic situation and the start time of the fire. At the
13 beginning of the event, at midday on 22J, the early fire ejected particles into the lower layer of
14 the atmosphere. This plume was transported southerly to the coast, following the synoptic
15 winds. There, when the night has settled, the land breeze pushed the plume further out over the
16 Mediterranean Sea. Since no thermal advection occurs at night, the plume was not advected
17 and probably travelled at a stable altitude in the first hundreds of meters above the sea. At
18 sunrise, the breeze started its inversion, and slowly turned from a land to a sea breeze. The
19 trajectories in Fig.5 are parallel to the coast at 09:00 UT and start to bend towards land at 10:00
20 UT. It is around that time that the maximum PM levels are reached. At midday the sea-breeze
21 regime carried the plume further inland and at higher elevation which cleared the air of
22 Barcelona from the smoke particles.

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24 **3.4. FLEXPART simulation of wildfire event**

25 The aforementioned data showed that the observed atmospheric particles were linked to the
26 smoke plume that was transported towards the metropolitan area of Barcelona in the morning of
27 23 July. FLEXPART was used to investigate the transport of the biomass burning plume and
28 determine the consistency between measured aerosol concentrations and fire smoke.

29 Fig. 6 shows the simulation of the smoke plumes of the two slightly different scenarios at the
30 surface at 12:00 UT on 23 July, i.e. when smoke was chemically detected in the urban area. In

1 both cases, the smoke plume travels in southerly direction over the sea and then turns towards
2 the land, where it reaches the city of Barcelona. The estimated PM_{2.5} concentrations are around
3 between 100 and 200 µg/m³. These values are in the range of the maximum PM₁₀
4 concentrations measured in this period (189 µg/m³). Although there are not measured hourly
5 PM_{2.5} concentrations available, the comparison of measured PM_{2.5} and PM₁₀ on 24-hour
6 resolution shows that 77% of the PM₁₀ is PM_{2.5} on 23 July in the urban area. This contribution of
7 PM_{2.5} was significantly higher ($p < 0.01$) than the mean contribution of the other days (60 % ± 4
8 %), indicating that the measured PM concentrations during the wildfire event are indeed in the
9 range of the simulated ones. The simulated CO concentrations at 12:00 UT were 2.1 mg/m³,
10 which is close to the maximum concentration measured (1.8 mg/m³). Despite this general
11 agreement, detailed comparison of the measured and simulated time series of CO and PM
12 show considerable differences (Fig. 7). The measured PM values reached their maximum
13 concentrations around 10:00 on 23 July and decreased rapidly afterwards to background levels
14 at 14:00, while the estimated values peaked around 12:00 (i.e., about two hours after the
15 measured peak) and then slowly decreased until the evening of the next day (24 July; i.e., when
16 the fire was almost extinct). The measured CO in the urban area also decreased more rapidly
17 than the estimated CO, although not as fast as the measured PM, which is due to the large
18 contribution of local sources (especially traffic emissions) to the measured CO.

19 The too long persistence of simulated fire influence near the surface probably arises from a
20 strong coupling in FLEXPART between the surface and the air mass just above the boundary
21 layer. As we have seen from the lidar measurements, the biomass burning plume is indeed
22 present above the city during the period that FLEXPART simulates fire influence; however, in
23 contrast to the FLEXPART simulation, the pollution is not brought down to the surface. The
24 modeling problems may be related to the sea breeze circulation. The influence of the sea
25 breeze circulation system can be large in coastal areas, especially in the Mediterranean region
26 (Millán et al., 1997), and it is likely not fully captured at the resolution of the ECMWF input data
27 used by FLEXPART. This difficulty may lead to errors in both the horizontal as well as vertical
28 position of the biomass burning plume. In particular, decoupling of an elevated pollution layer
29 from the surface during transport over the sea is probably not captured and may contribute to
30 the modeling problems.

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4. Conclusions

Smoke particles originating from a wildfire that started in the Alt Empordà region on 22 July 2012, about 120 km north, impacted in 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 on-line PM₁₀ monitoring stations (PM₁₀ = 71 µg/m³ with peak at 189 µg/m³) and in the boundary layer by lidar measurements (extinction coefficient ~ 0.5 km⁻¹). The aerosol chemical organic composition confirmed the large contribution of biomass burning (e.g. levoglucosan concentration of 1100 ng/m³ on 23 July vs. only 8 ± 4 ng/m³ in regular samples), together with a moderate increase of toxic compounds, such as PAH (2.5 ng/m³ on 23 July vs. 0.6 ± 0.3 ng/m³ in regular samples).

Satellite images, air-mass trajectories and Lagrangian particle dispersion 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 boundary layer, 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 elevation of surface concentrations.

The findings of the present study show different smoke trajectories from those observed in a former PM event in 2009. In that event, despite that the wildfire smoke particles were concentrated in an aerosol layer at 3 km above the city (Sicard et al., 2012), small influence of the smoke particles was identified on the air quality at ground level in the city (van Drooge et al., 2012). However, the wildfire episode of the present study indeed reached the city of Barcelona at ground level and thus significantly influenced the air quality for several hours.

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1 Figure captions.

2 Figure 1. MODIS/TERRA image taken at 11:10 UT on 23 July introduced to Google Earth map,
3 as well as the sites where the wildfire was active in posterior hours (see SI.1-SI.3).

4

5 Figure 2. Mean hourly concentrations of air quality parameter at the urban site “Eixample” in
6 Barcelona on 23 July (daytime: 8:00 to 20:00h) with respect the mean \pm sd of the concentrations
7 measured during the daytime on the other days before and after the wildfire event. The PM₁₀
8 and CO concentrations are significantly ($p < 0.01$) higher on 23 July daytime than the other
9 daytime concentration which is indicated by *.

10

11 Figure 3. Log-concentrations of organic compounds in PM₁ filter samples (ng/m³) on 23 July
12 (daytime: 8:00 to 20:00h) with respect the mean \pm sd of the concentrations measured on the
13 other days before and after the wildfire event.

14

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

18

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

21

22 Figure 6. FLEXPART smoke plume simulation of PM_{2.5}, starting on 22J at 10.00 UT and
23 showing the situation on 23 July at 12.00 UT. PM_{2.5} particles from the wildfire are transported
24 towards the urban area of Barcelona (red dote). Plume 1 and plume 2 differ slightly in burnt
25 areas between 15:00h, 17:00 and 19:00h although the total burnt area and PM_{2.5} emissions are
26 the same in both scenarios (see SI.2).

27

28 Figure 7. Measured and estimated (FLEXPART) CO (mg/m³) and PM₁₀ (or 2.5) (μ g/m³)
29 concentrations in the urban sampling site. No hourly data on PM_{2.5} was available, so the

- 1 estimated values were compared with PM_{10} . Note that about 50 % of the PM_{10} is $PM_{2.5}$ in the 12
- 2 hour samples of the studied period. The hourly time intervals are in UT.
- 3