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Significant variations of trace gas composition and aerosol properties at Mt. Cimone during air mass transport from North Africa – contributions from wildfire emissions and mineral dust

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Abstract

High levels of trace gas (O_3 and CO) and aerosol (BC, fine and coarse particles) concentrations, as well as high scattering coefficient (σ_s) values, were recorded at the regional GAW-WMO station of Mt. Cimone (MTC, 2165 m a.s.l., Italy) during the period 26–30 August 2007. Analysis of air-mass circulation, aerosol chemical characterization and trace gas and aerosol emission ratios (ERs), showed that high O_3 and aerosol levels were likely linked to (i) the transport of anthropogenic pollution from Northern Italy, and (ii) the advection of air masses rich in mineral dust and biomass burning (BB) products from North Africa. In particular, during the advection of air masses from North Africa, the CO and aerosol levels (CO: 175 ppbv, BC: 1015 ng/m^3, fine particle: 83.8 cm^{-3}, σ_s: 84.5 Mm^{-1}) were even higher than during the pollution event (CO: 138 ppbv, BC: 733 ng/m^3, fine particles: 41.5 cm^{-3}, σ_s: 44.9 Mm^{-1}). Moreover, despite the presence of mineral dust able to significantly affect the O_3 concentration, the analysis of ERs showed that the BB event represented an efficient source of fine aerosol particles (e.g. BC), but also of the O_3 recorded at MTC. The results suggest that events of mineral dust mobilization and wildfire emissions over North Africa could significantly influence radiative properties (as deduced from σ_s observations at MTC) and air quality over the Mediterranean basin and Northern Italy. Since in the future it is expected that wildfire and Saharan dust transport frequency could increase in the Mediterranean basin due to more frequent and severe droughts, similar events will possibly play an important role in influencing the climate and the tropospheric composition over South Europe.

1 Introduction

In the troposphere, among the major sources of atmospheric pollutants and climate altering species, an important role is played by biomass burning (BB) events (Crutzen and Andreae, 1990; Goode at al., 2000; Simmonds et al., 2005). In particular, boreal

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forest wildfires have a considerable impact on the variability of tropospheric CO and O_3 in the Northern Hemisphere (e.g. Novelli et al., 2003; Kasische et al., 2005; Lapina et al., 2006). CO strongly influences the abundance of the OH radical and initiates several important chemical reactions involving climate altering compounds and chemically active gases (e.g., Seinfeld and Pandis, 1998; Forster et al., 2007). O_3 is one of the most prominent atmospheric gases involved in photochemical reactions (Crutzen et al., 1999; Volz-Thomas et al., 2002), and is a key agent determining the oxidation capacity of the troposphere (Gauss et al., 2003). Owing to its oxidizing properties, O_3 is also a dangerous pollutant in the lower troposphere, causing harm to human health (Hoek et al., 1993; Conti et al., 2005) and ecosystems (e.g., Brunekreef and Holgate, 2002; Paoletti et al., 2006). Moreover, O_3 plays a central role in the radiative budget of the troposphere: beside CO_2 and CH_4, it has been recognised as the third anthropogenic greenhouse gas in terms of atmospheric radiative forcing (Forster et al., 2007). Large wildfires can also emit large amounts of aerosol particles (Hsu et al., 1999; Christopher et al., 2000). In particular, the black carbon (BC) produced by boreal wildfires accounts for 10% of the annual anthropogenic BC emissions in the Northern Hemisphere (Bond et al., 2004). Due to its direct impact on solar and thermal radiation, BC was recognised as a contributing factor in global warming (Andreae and Gelencsèr, 2006 and references therein). Additionally, BB aerosols are responsible for an indirect radiative forcing by modifying the concentration and size spectrum of cloud droplets (e.g. Lohmann et al., 2000; Forster et al., 2007).

Previous studies have shown that the atmospheric compounds directly emitted by BB or produced by photochemical processes occurring within BB plumes can be transported over long distances, thus affecting both air quality and climate on the regional to global scales (e.g. Forster et al., 2001; Galanter et al., 2000; Wotawa and Trainer, 2000; Jaffe et al., 2001; Duncan et al., 2003; Val Martin et al., 2006; Stohl et al., 2006; Real et al., 2007). In Europe the Mediterranean basin is affected by large wildfire events, especially during summer. As an example, during the extreme dry and hot summer of 2003, the large forest fires in Spain, Portugal, Greece and Italy, significantly

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influenced trace gas composition and aerosol properties both in the boundary layer and the free troposphere (Pace et al., 2006; Cristofanelli et al., 2007; Hodzic et al., 2007; Solberg et al., 2008). However, during summer, large amounts of anthropogenic pollutants from the European boundary layer are also transported towards the Mediterranean basin/South Europe free troposphere (Wotawa et al., 2000; Bonasoni et al., 2000; Henne et al., 2004). Moreover, Saharan dust mobilization over African deserts represent a significant natural source of mineral aerosols for the Mediterranean basin, as well as Southern and Continental Europe (d'Almeida, 1986; Franzen et al., 1994; Rodriguez et al., 2001; Ryall et al., 2002; Marenco et al., 2006). As mineral dust constitutes a good surface for promoting heterogeneous chemistry (e.g. Zhang et al., 1994) and modifying actinic fluxes (e.g. Dentener and Crutzen, 1993; He and Carmichael, 1999), the background O_3 balance in the Mediterranean basin can be strongly affected by the transport of dust particles from North Africa (e.g. Dentener et al., 1996; Bauer et al., 2004; Bonasoni et al., 2004). Therefore, the Mediterranean basin and South Europe can be strongly impacted both by mineral dust from North Africa and by natural and anthropogenic pollutant emissions, thus confirming this area to be a major crossroad of different air mass transport processes (Lelieveld et al., 2002; Millàn, 2006; Duncan et al., 2008).

During late August 2007, at the GAW-WMO Station of Mt Cimone (Italy), high levels of trace gases (O_3 and CO) were recorded, together with significant variations in the aerosol properties (equivalent BC contents, particle number concentrations, scattering coefficient, chemical composition). The present paper shows that such variations were probably related to a pollution event over Northern Italy, combined with event of mineral dust and BB product transport from North Africa. Since Mt. Cimone is located on the northern Mediterranean basin and south of Continental Europe, the observations carried out there can provide useful information for better evaluating the role of different transport processes in modifying the tropospheric background conditions in this crucial area.

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2 Experimental and methodologies

2.1 Site and measurement descriptions

Measurements of surface O_3 and CO concentrations, along with aerosol physical (size distribution, equivalent BC concentration, scattering coefficient) and chemical properties (organic and inorganic composition) were carried out at the regional GAW-WMO Station of Mt. Cimone (MTC; 44°11′ N, 10°42′ E, 2165 m a.s.l.). The MTC measurements are considered representative for the baseline conditions of the Mediterranean free troposphere (Bonasoni et al., 2000; Fischer et al., 2003), even if during the warm months an influence of boundary layer air can be detected due to convective processes and mountain breeze regime (Fischer et al., 2003; Van Dingenen, 2005). At MTC, tropospheric O_3 measurements have been carried out continuously since 1996 using a UV-photometric analyser (Dasibi 1108). The accuracy and quality of measurements (sampling time: 1 min, combined standard uncertainty lesser than ±2 ppbv in the range 1–100 ppbv) are guaranteed within the GAW requirements. The CO concentrations are measured by a GC-RGD set up, consisting of a custom gas chromatograph equipped with a reduction gas detector – Trace Analytical RGD2. The instrument has been running continuously since January 2007. Every 15 min an air sample is injected into the gas chromatograph for separation, and then analysed for CO concentration via mercury oxide reduction and detection of mercury vapours by UV absorption. Each sample for analysis is alternated with a calibration sample by means of real air working standards with concentrations representative for ambient air concentration for the Northern Hemispheric troposphere. The working standards were prepared at Max-Planck-Institute for Biogeochemistry in Jena and referenced against the CSIRO/1999 scale. This guarantees a continuous check of the detector calibration (Novelli, 1999) with an accuracy higher than ±0.5% on the recorded CO concentration values.

Concerning aerosol measurements, particle concentration and size distribution are obtained using an optical particle counter (OPC; Grimm, Particle Size Analyzer Mod. 1.108) in the size range 0.3 μm≤Dp≤20 μm. The instrument is based on the quantifi-

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cation of the 90° scattering of light by aerosol particles. According to the specifications, the reproducibility of the OPC in particle counting is ±2% (Putaud et al., 2004). Such measurements allow the determination of the fine (0.3 μm≤Dp<1 μm) and coarse (1 μm≥Dp>20 μm) aerosol fractions with a 1 min time resolution. In particular, large increases in coarse particle concentrations are usually considered indicative of the presence of mineral dust at this measurement site (Bonasoni et al., 2004; Van Dingenen et al., 2005; Marinoni et al., 2008). At MTC, continuous measurements of equivalent black carbon concentration (BC) is obtained by a multi-angle absorption photometer (MAAP 5012, Thermo Electron Corporation). This instrument measures the absorption coefficient of aerosol deposited on a glass fibre filter tape, with removal of the scattering effect (at different angles) that can interfere with optical absorption measurements. The reduction of light transmission at 670 nm, multiple reflection intensities, and air sample volume are continuously integrated over the sample run period to provide a real time data output (1 min resolution, variable integration time) of BC concentration (Petzold et al., 2002). Finally, an integrating nephelometer (Ecotech M9003) continuously determines σ_s, i.e. the scattering coefficient of light at 520 nm due to atmospheric particles.

2.2 Aerosol Chemistry

Atmospheric aerosols in the 1–10 μm (PM_{1-10}) and <1 μm (PM_1) size fractions were collected on quartz-fiber filters using a dichotomous sampler from MSP Corporation (Universal Air Sampler, model 310) at a constant nominal air flow rate of 300 lt/min. Based on the aerosol emission and transport forecast provided by the NAAPS – Navy Aerosol Analysis and Prediction System (Hogan et al., 1991, 1993; http://www.nrlmry.navy.mil/aerosol/) showing an incoming Saharan dust transport episode to North Italy, daily samples were collected from 27 to 30 August 2007. Sampling times varied approximately from 22 to 24 h, starting at around 11:00 a.m. until approximately the same time on the following day. After sampling, the filters were analyzed for their carbon content and concentration of water-soluble inorganic ions. The coarse (PM_{1-10}) aerosol samples also underwent analysis of mineral oxides. The study of the carbonaceous

material in both size fractions included the determinations of total carbon (TC) by evolved gas analysis, and of water-soluble organic carbon (WSOC) and carbonate carbon by liquid TOC. Both methods were carried out using a Multi N/C 2100 total organic carbon analyser. The difference between TC and WSOC and carbonate carbon (Matta et al., 2003; Rinaldi et al., 2007) resulted in the water-insoluble carbon (WINC). Water-soluble organic matter (WSOM) and water-insoluble carbonaceous matter (WINCM) were derived from WSOC and WINC using conversion factors of 1.8 and 1.2, respectively. The WSOM chemical composition of PM_1 samples was investigated using HNMR spectroscopy (Decesari et al., 2006), with the aim of determining the concentration of levoglucosan (Schkolnik and Rudich, 2006), a major biomass burning tracer. Inorganic ions (NH_4^+, Na^+, K^+, Mg_2^+, Ca_2^+, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and light organic ions (acetate, formate, oxalate and methansulfonate) concentrations were determined by ion chromatography (IC). Finally, mineral dust elements in the coarse aerosol fraction, including Mg, Al, Ca, K, Ti, Mn and Fe, were simultaneously detected by means of Particle-Induced X-ray Emission (PIXE), while Al was detected by Particle Induced Gamma-ray Emission (PIGE) with 3.06 MeV protons using the external beam facility at the 3 MV Tandetron accelerator of LABEC laboratory of INFN in Florence (Calzolai et al., 2006). Quantitative concentrations were deduced by a sensitivity curve obtained by analyzing thin reference standards from Micromatter of known elemental composition (uncertainty ±5%), at the same experimental conditions as for real samples. The mass of total mineral material was reconstructed from the elemental composition using the following equation:

$$\text{Crustal matter} = 1.12^{*}[1.658^{*}\text{Mg} + 1.889^{*}\text{Al} + 2.139^{*}\text{Si} + 1.204^{*}\text{K} + 1.399^{*}\text{Ca} + 1.668^{*}\text{Ti} + 1.582^{*}\text{Mn} + (0.5 \times 1.286 \times 0.5 \times 1.429) \times \text{Fe}] \quad (1)$$

where the concentrations of Ca, Mg and K were those of the insoluble fractions (=total element concentrations minus the amount determined by ion chromatography). The Si concentration, which cannot be determined in aerosol samples collected on quartz-fiber filters, was derived from that of Al, using an average factor Si/Al=2.31, typical for

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the dust outbreaks at MTC (Marenco et al., 2006).

2.3 BOLAM model and back-trajectory calculations

In order to determine the origin of air masses reaching MTC, 3-D air mass back-trajectories (with 1-h resolution along their path) were calculated every one hour using the BOLAM (BOlogna Limited Area Model) mesoscale meteorological model (Buzzi and Foschini, 2000). BOLAM is a meteorological model based on the primitive equations in the hydrostatic approximation. The 3-D variables are defined on vertical hybrid coordinates and are distributed on a non-uniformly spaced Lorenz grid. The horizontal discretization is based on geographical coordinates with latitudinal rotation on an Arakawa C-grid. The initial and lateral boundary conditions were supplied from ECMWF analyses at 0.5°×0.5° resolution, distributed by the MAP (Mesoscale Alpine Programme) Data Centre. Gridded data are available every 6 h on 91 vertical hybrid levels of the ECMWF. The simulation, run from 24 August 00:00 UTC to 31 August 00:00 UTC, covers an area centred over the western Mediterranean basin (251×231 grid points), with 0.1°×0.1° horizontal resolution and 40 vertical hybrid levels extending from the ground level to the top of the atmosphere defined as 0.1 hPa.

Clusters of back-trajectories were calculated using the approach proposed by Gheusi and Stein (2002) and applied by Fierli et al. (2008). The air parcel position is transported as a passive tracer, experiencing advection, transport by subgrid turbulence, convection and vertical diffusion. Compared to the usual Lagrangian trajectory calculations, this technique has the advantage of avoiding any time or spatial interpolation of the model wind field, because the transport processes are calculated at every time step and at every grid point. Moreover, since the subgrid transport processes are taken into account, the motions captured by the Lagrangian tracers correspond exactly to the model dynamics. Gheusi and Stein (2002) have demonstrated that the Lagrangian evolution can be studied on a qualitative basis for relatively large trajectory clusters. In the present paper, this method was applied off-line and a total of 12 clusters (one every 6 h) was calculated during the period 28 August 2007 06:00 UTC–31 August 2007

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00:00 UTC. Each single trajectory (starting at a fixed time and extending backward to 24 August 2007 00:00 UTC) originated from the model grid points included in a box centred over the MTC position (longitude: 9.4° E–11.4° E, latitude: 44.0° N–44.5° N) and ranging between 750 hPa and the ground height, thus leading to the advection of about 260 parcels.

2.4 Enhancement ratios (ER)

For the purpose of attaining a better characterisation of the pollution and BB products affecting MTC, the enhancement ratios (ER) for aerosol and O_3 were calculated. According to Andreae and Merlet (2001), the excess of a trace species "X" normalized by the increase of CO concentrations can provide an estimation of the species "X" production by combustion processes. CO is considered the reference species because it is one of the principal compounds emitted by combustion (Andreae and Merlet, 2001) and has a relatively long lifetime in the troposphere (Novelli et al., 1992). Usually, two methods are used to evaluate ERs. The so-called "enhancement technique" (e.g. Pfister et al., 2006 and references therein) determines ERs by evaluating CO and "X" species mixing ratio increases with respect to "background" conditions. The so-called "scatter-technique" determines ERs by calculating the slope of the linear fit between "X" species and CO concentrations (e.g. Parrish et al., 1998). As each one of these methods has specific strengths and weaknesses (see for more details Bertische and Jaffe, 2005 or Pfister et al., 2006), in this work both were applied to anthropogenic pollution and BB tracers (i.e. BC, fine particle numbers, σ_s and O_3). In particular, for the "enhancement technique" analysis the background levels of trace gas and aerosol were evaluated by analysing the 7-day FLEXTRA 3-D back-trajectories (Stohl et al., 1995), which were calculated every 6 hours for the MTC endpoint, based on the ECMWF wind field (1.25°×1.25° geographical resolution). As shown in previous works (e.g. Wotawa et al., 2000; Fischer et al., 2003), in spite of the coarse meteorological data resolution driving FLEXTRA, the model revealed remarkable skill in simulating the transport of air masses towards mountain sites. In particular, to exclude air masses possibly

influenced by wildfire emissions and experiencing direct mixing within the PBL, it was decided to select the back-trajectories that travelled above 2000 m a.s.l before reaching MTC and that originated over a pristine area (i.e. the North Atlantic region). This led to a very restrictive definition of trace gas and aerosol background levels at MTC for the summer 2007 (Table 1). In fact, by applying this filter, only 5% of the 368 calculated back-trajectories were selected.

3 Results

3.1 Data overview

Time series of 30 min averages for O_3, CO, BC, fine and coarse particles as well as σ_s, are shown in Fig. 1. During the period 26–30 August 2007, high average levels of trace gases (O_3: 67±10 ppbv; CO: 129±25 ppbv; mean±1−σ) and aerosols (BC: 615±223 ng/m^3; fine particles: 48.89±26.82 cm^{-3}; coarse particles: 1.23±0.37 cm^{-3}; σ_s: 46.6±14.7 Mm^{-1}) were recorded. They are presented against average values for the whole of summer 2007 in Table 1. In particular, as shown by the analysis of box-and-whiskers plots (Fig. 2), the concentrations of CO, BC, fine and coarse particles, as well as σ_s values, were characterised by a median exceeding the 75th percentile of the summer 2007. During the same period, the O_3 distribution was also characterised by a marked increase of the upper quartiles (+5.6 ppbv for the 75th percentile; +6.2 for the 95th percentile).

3.2 Meteorology and air mass circulation over the Mediterranean basin

The BOLAM simulation for 24 August 2007 (here not shown) highlighted that the passage of a trough over West Europe favoured the transport of air masses from North Africa to the Central Mediterranean and Italy. From 25 to 28 August 2007 the low tropospheric circulation over the central Mediterranean basin was instead determined by

a high-pressure ridge centred over Sardinia, favouring the transport of air masses from North Africa towards Northern Italy, as shown by the BOLAM analyses (Fig. 3a). Subsequently the high-pressure system weakened and moved southward over the Algerian coast. From 28 August 2007 a low-pressure trough affected Western Europe (Fig. 3b), again favouring air mass transport from North Africa toward Northern and Central Italy. The end of air mass advection from North Africa, around 31 August 2007, was related to the eastward displacement of the low-pressure system (not shown), which induced a westerly flow over Northern Italy and MTC.

These conditions favoured the transport of mineral dust from the Sahara, as confirmed by the high coarse particle concentrations (>1.0 cm^{-3}) recorded at MTC (Fig. 1) from 25 to 30 August 2007. Although OPC measurements were not available at MTC for the onset of the transport event, the NAAPS simulations (not shown) indicated that dust mobilized over Algeria, Morocco and Mauritania reached Southern Europe and Northern Italy, starting from 23 August 2007.

The same high pressure area which favoured the transport of mineral dust from North Africa to Northern Italy, also promoted very dry and hot meteorological conditions over South Europe and North Africa (WMO, 2008). In particular, from 24 to 28 August 2007, the geopotential height at the 500 hPa surface showed very high values (from 592 to 600 dam) over a large area, extending from North Africa to Eastern Europe, with surface temperature higher than 40°C over Southern Italy, Algeria and Tunisia. Over the Po Basin (Northern Italy), these meteorological conditions favoured the onset of photochemical smog episodes. In fact, data recorded by the Regional Agency for Environmental Protection of Emilia-Romagna (ARPA-ER) showed increasing daily O_3 maxima from 25 to 28 August 2007, when the population information threshold (i.e. 180 $\mu g/m^3$) was exceeded.

The hot and dry meteorological conditions associated with the extensive high pressure system also favoured the onset of several wildfires over Greece, Southern Italy and North Africa (Kaiser et al., 2008; Turquety et al., 2008). In particular, diffuse fire events affected the Atlas region. According to news reports, several people died,

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dozens of families had to evacuate their homes, and the number of people seeking medical attention for respiratory and allergy problems dramatically increased as a result of the fires. As evidenced by the image captured by the Moderate Resolution Imaging Spectroradiometer (MODIS) on board NASA's Aqua satellite (Fig. 4), a thick haze of brownish-grey smoke was emitted by these fires and transported across the Mediterranean Sea. As deduced by the analysis of the daily total number of MODIS hot spot fires (Fig. 5), according to the method reported by Justice et al. (2002) and Giglio et al. (2003), over North African coastlines (defined as the geographical box: 0° E<Lon.<10° E; 37° N<Lat.<35° N), wildfires started on 25 August 2007, with a peak from 28 to 30 August 2007 (Fig. 5).

3.3 26–28 August 2007: pollution event over Northern Italy

As shown by the analysis of 1 min average values, during 26–28 August 2007, three consecutive episodes of elevated trace gas and fine aerosol concentrations were recorded at MTC (Fig. 6). Compared to the average conditions at MTC for summer 2007, the levels of O_3, CO, BC, fine particles and σ_s, appeared extremely enhanced on these days (Table 1). In particular, the O_3 peak (116 ppbv) recorded during the late afternoon/evening on 28 August 2007 was the highest O_3 concentration recorded at MTC during the whole of 2007. All the above pollutants showed similar strong diurnal cycles peaking in the late afternoon/evening, suggesting common driving processes and sources. As also shown in Fig. 6, the periods characterised by enhanced pollution levels were also characterised by rather low wind intensities (median value: 3.4 m/s), scattered wind directions (mostly ranging from SW to NE with 85% of occurrences from the North sector), and increased relative humidity (up to 70–80%). Even if no measurements of vertical wind velocity were performed at MTC, it is likely that daytime valley breezes and convective processes transported humid and polluted air masses from the planetary boundary layer (PBL) to the measurement site. In fact, during typical anticyclonic conditions, thermal wind systems are often observed in mountain areas (Henne et al., 2004). Together with entrainment processes related to diurnal PBL growth (Beck

et al., 1997; Tressol et al., 2008), such wind systems can efficiently contribute to the export of pollutants to the free troposphere during daytime (Baltensberger et al., 1997; Schuepbach et al., 2001; Zellweger et al., 2000).

The presence of air masses transported from the PBL is also supported by the analysis of coarse particle variations (Fig. 6), which, despite to urban areas, at MTC are greatly influenced by Saharan dust transport events (Marinoni et al., 2008). In fact, on 26–28 August 2007, the coarse-particle concentrations showed a diurnal cycle with high values during night-time (up to 2.50 cm^{-3}) and lower values (below 0.54 cm^{-3}) during day-time, when the highest values of pollutant tracers (O_3, CO, BC, fine particles, σ_s) were recorded. This indicated that during night-time, when high wind speed (>8.0 m/s) were recorded, the measurement site was probably affected by air masses originating over North African deserts. Previous investigations (Bonasoni et al., 2004; Bauer et al., 2004) showed that when mineral dust affected MTC, O_3 decreases were recorded due to the interaction of dust particles with solar radiation, and heterogeneous chemical processes. This might also be the case of night-time (00:00–05:00 UTC+1) periods from 26 to 28 August 2007, when average O_3 levels (54±2 ppbv) were significantly (at the 95% confidence level) lower than for the summer 2007 (−16%) and summer 2007 night-time (−13%) average values. During day-time and late evening, on the other hand, the local/regional breeze circulation (as also suggested by the light wind speed) transported air masses rich in anthropogenic pollutants and poor in mineral dust from the PBL to the measurement site and possibly to the free troposphere.

In order to analyse better the processes giving rise to such high aerosol and O_3 levels, their ERs in respect to CO were calculated. For each day, periods characterised by CO values above night-time levels and significant (at the 2-σ level) decreases of coarse particle concentrations, were considered (grey bars on Fig. 6). The ERs obtained by applying the "enhancement" and the "scatter" techniques (see Sect. 2.4) are shown in Table 2, while the scatterplots with their linear fits are reported in Fig. 7. With the exception of BC, the ERs calculated by the "scatterplot" technique method are higher than those calculated with the "enhancement" method, thus indicating the large un-

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certainties associated with the ER calculation (Pfister et al., 2006; Real et al., 2007). However, the strong correlations (Fig. 7) between CO and BC (R^2=0.92), fine particle (R^2=0.90), σ_s (R^2=0.90) and O_3 (R^2=0.92) suggested the possibility that strong pollutant sources not far off could have affected the measurement site (Chen et al., 2001), a hypothesis that is further supported by the high ERs obtained for BC/CO (about 11×10^{-3} , expressed as μg/m^3 BC versus μg/m^3 CO). Such values are more than double those reported at the baseline station of Mace Head for a long-range pollution event (~4.0 ng m^{-3}/ppbv, Jennings et al., 1996), although more in line with those observed in highly populated, industrialized areas (e.g., 6.7×10^{-3} μg m^{-3}/μg m^{-3}, Chen et al., 2001; 8.05×10^{-3} μg m^{-3}/μg m^{-3}, Li et al., 2006). The ERs observed for fine particles and σ_s (Table 2) are in the upper range of, or higher than those obtained for "anthropogenic" pollution products in previous studies. Price et al. (2004) and Weiss-Penzias et al. (2006) recorded σ_s/CO ratios of 0.5 Mm^{-1}/ppbv and 0.44 Mm^{-1}/ppbv within Asian pollution plumes detected over the Eastern North Pacific and at Mt. Bachelor (Oregon, USA, 2763 m a.s.l.), respectively.

The ERs obtained for O_3 (Table 2) were also higher than values usually recorded in middle and upper troposphere (e.g. Fischer et al., 2002; Wang et al., 2006), or at remote sites in the moderately polluted boundary layer air of North America (Chin et al., 1994), Canadian Atlantic coastlines (Parrish et al., 1993) and Central Atlantic Ocean during summer (Parrish et al., 1998). The retrieved O_3 ERs were also higher than the O_3/CO slope (0.25 ppbv/ppbv) observed by Fischer et al. (2003) at MTC during June 2000. This further stressed the strong influence played by photochemical O_3 production associated with reactive carbon (CO and hydrocarbon) emissions (Fishman et al., 1980) during the August 2007 episode.

3.4 29–30 August 2007: mineral dust and BB products from North Africa

In the evening of 28 August 2007, high trace gas and aerosol concentrations were continuously observed at MTC for about 36 h (until midday on 30 August 2007, see Fig. 1). 30 min averages of O_3, CO, BC, fine particles and σ_s peaked at 77 ppbv,

243 ppbv, 1483 ng m^{-3}, 143.1 cm^{-3} and 137.7 Mm^{-1}, at 23:00 UTC+1 on the 29 August 2007. Besides being much higher than average summer 2007 levels, the trace gas and aerosol concentrations were comparable with those recorded during the pollution event (Table 1). Moreover, high coarse aerosol concentrations were recorded at the measurement site (average value: 1.31±0.33 cm^{-3}), indicating the presence of mineral dust. In fact, the 3-D back-trajectory ensembles calculated by BOLAM (Fig. 8) showed that North African air masses reached MTC after travelling over potential source regions of mineral dust in the Sahara desert, as deduced by the analysis of OMI Aerosol Index gridded data (not shown). In the same period, several wildfires were also present along the North African coast line (see Sect. 3). To establish a possible source-receptor relationship between North African wildfires and trace gases and aerosol properties at MTC, we analysed BOLAM back-trajectories as a function of the geographic and temporal distribution of MODIS hot-spot fires. In particular, back-trajectories passing at less than 5 km (horizontal distance) from the locations of active MODIS hot-spot fires (red trajectories in Fig. 8), were selected as possibly influenced by BB products. In Fig. 9, the time series of the total number of intercepted MODIS hot-spot fires is reported together with the corresponding 3-h averages of BC and CO concentrations recorded at the measurement site. Starting from 29 August 2007 at 00:00 UTC, air masses which passed over MODIS hot-spot fires reached MTC (average transport times ranging from 75 to 93 h), where the concentrations of BB tracers (i.e. CO and BC) increased by about 50% in respect with values recorded on 28 August 2007 (Fig. 9). Starting from 30 August 2007 at 18:00 UTC, an evident decrease of CO and BC concentrations (−35%) was recorded when atmospheric circulation and meteorological conditions changed, and wildfire locations were no longer intercepted by air masses reaching MTC.

The presence of mineral dust and BB products in air masses arriving at MTC from 29 to 30 August 2007 were confirmed by the chemical composition of aerosol particles sampled during the event. As shown in Fig. 10a, in the first sampling period (27–28 August 2007), the PM_{1-10} chemical composition and mass concentration (19.9 μg/m^3)

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clearly reflects the transport of Saharan dust rich in insoluble mineral oxides and Ca salts, whereas the mass concentrations of the aerosol components originating from combustion sources, i.e. PM_1 particulate organic matter (WSOM+WINCM: 2.12 $\mu g/m^3$; NO_3^-: 0.06 $\mu g/m^3$; SO_4^2: 0.85 $\mu g/m^3$), were in the lower range of summer average MTC levels (Marenco et al., 2006). The concentration of the chemical components in the coarse fraction (PM_{1-10}) remained high until 29–30 August (18.7 $\mu g/m^3$), while those in the fine fraction (PM_1) underwent a significant increase, peaking on 29 August 2007 (10.69 $\mu g/m^3$). Such trends are in close agreement with the time evolution of coarse and fine aerosol number concentrations (Fig. 1), respectively. On 29–30 August 2007, the PM_1 particulate organic matter increased to 5.5 $\mu g/m^3$, more than double the value on the first sampling day, as well as the summer background levels reported by Marenco et al. (2006). In the same period (Fig. 9), the equivalent BC concentration also experienced a large increase (+124%), accounting for approximately half the water-insoluble carbonaceous matter (WINCM). However, the concentration increase of the more oxidised organic compounds was even more pronounced, so that the contribution of WSOM to total carbonaceous matter rose from 53% to 65%. This finding can be explained by the progressive substitution of organic material originating from fossil fuel combustion sources in the Po Valley on 27–28 August 2007 (see previous section), with BB aerosols enriched in WSOM (Decesari et al., 2006) on 29–30 August. The increase of the WSOM fraction could be partly due to aerosol ageing occurring during the transport of carbonaceous aerosols, which also supports the non-local source of the chemical components of PM_1 during the event.

Mass concentrations of water-soluble ionic species in the PM_1 fraction also exhibited an increasing trend starting from 27 (1.5 $\mu g/m^3$) to 29 August 2007 (5.0 $\mu g/m^3$), with NO_3^-, SO_4^2, NH_4^+ and K^+ as major contributing species (Fig. 10a). In particular, potassium in submicron particles, widely used as a tracer for BB plumes (Andreae, 1983; Ma et al., 2003), showed a significant increase in terms of both absolute concentrations and relative contribution to PM_1 (Fig. 10b). As shown by Marenco et al. (2006), in summer 2004 at MTC the potassium average concentration was 0.036±0.025 $\mu g/m^3$.

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On 27 August 2007 K^+ mass concentration was 0.012 $\mu g/m^3$ whereas there was a large increase in potassium (up to ten times) in the subsequent three samples, reaching 0.297 $\mu g/m^3$ on 29 August 2007. These results indicate that aerosol properties at MTC were strongly influenced by the North African BB products from 29 to 30 August 2007. Interestingly, the concentrations of another biomass smoke tracer, levoglucosan (Simoneit, 2002), fell under the detection limit (20 ng m^{-3}) for all samples, meaning that levoglucosan accounted for less than 1% of the carbonaceous organic matter during the expected peak of the BB event (on 29 August 2007), a finding in apparent contradiction with the potassium data. However, recent measurement of BB aerosol plumes in Africa (Capes et al., 2008) have revealed that levoglucosan accounted for a negligible fraction of organic matter in aged (4–8 days) wildfire plumes, and that the levoglucosan relative concentration to organic matter decreased progressively during transport. Therefore, the overall results of the chemical analyses strongly support the advection of aged BB aerosols mixed with mineral dust to MTC during 28–30 August 2007, with a peak of the BB contribution on 29 August 2007.

To evaluate the ERs of aerosol and O_3, we performed an analysis of the measurement period in which BOLAM showed at MTC the presence of air masses that had travelled over wildfires (i.e. 29 August 2007 23:00–30 August 2007 14:00). Excluded from the analysis were the data recorded on 29 August 2007 from 00:00 to 03:00 UTC+1, when high O_3 values (up to 88 ppbv) were observed, without marked variations of CO, suggesting possible mixing with other air masses.

The "scatterplot" analysis of aerosol properties and O_3 as a function of CO concentrations revealed lower values of correlation coefficient than for the anthropogenic pollution plumes (Fig. 7). This is not surprising, considering the greater mixing and dilution that the air masses affected by BB might have experienced during the 3–4 days transport from the North African coastline. As shown in Table 2, during the BB period, the BC/CO ERs were lower than those observed for the anthropogenic pollution. In literature, a broad range of BC/CO ERs are reported for BB plumes due to the various processes acting both on the emission (i.e. fuel type, combustion efficiency) and trans-

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port (washout processes, air mass mixing, air mass age). Observations of boreal BB products (from North America and Siberia) at baseline stations in the Azores (PICO-NARE – 2200 m a.s.l.; Val Martin et al., 2006), Ireland (Mace Head; Forster at al., 2001) and Japan (Mt. Fuji – 3776 m a.s.l.; Kaneyasu et al., 2007) have shown ERs ranging from 0.5 to 8.4 ng m^{-3}/ppbv. Compared with such values, the higher ERs recorded at MTC for the North African BB plume suggest that the observed BC experienced very little removal during the 3–4 days of transport.

Fine particle concentrations and σ_s also showed higher ERs than for the anthropogenic pollution plumes (Table 2), stressing the importance of the identified BB event as a source of atmospheric aerosol able to affect the atmospheric radiation budget. The σ_s/CO ER at MTC on 29–30 August 2007 was in the range of values reported by other authors for long-range transport of BB smoke. Bertschi at al. (2004) and Bertschi and Jaffe (2005) calculated ER ranging from 0.24 to 1.24 Mm^{-1}/ppbv for very aged (7–10 days) Asian boreal fires. Airborne measurements carried out over the Amazon Basin in dry season 2006, have pointed out for typical BB emitted aerosol ERs of 0.36–0.40 Mm^{-1}/ppbv in the PBL and around 1.00 Mm^{-1}/ppbv in the free troposphere, indicating that the ageing process has an important effect on the optical and physical properties of BB-emitted aerosols (Chand et al., 2006).

The $\Delta O_3/\Delta CO$ values (0.10–0.17 ppbv/ppbv) were significantly lower (by a factor 3–4) than those observed for the anthropogenic pollution plume (Table 2). This could be explained by the lower NO_x:CO emission ratio in BB than in industrial or urban emissions (Wofsy et al., 1992; Andreae et al., 1994; McKeen et al., 2002; Pfister et al., 2006; Real et al., 2007). Moreover, due to the long-range transport, the observed BB plumes could have experienced more dilution and mixing than the air masses transported to MTC by the pollution event originating from Northern Italy. The $\Delta O_3/\Delta CO$ values were obtained within the range of those reported by previous investigations for moderately aged (2–4 days) BB plumes (e.g. Wotawa and Trainer, 2000; McKeen et al., 2002; Yokelson et al., 2003; DeBell et al. 2004). Besides indicating the robustness of the identified plume origin, together with the enhanced O_3 levels recorded at

MTC, such ERs indicate a probable significant O_3 production occurred in the North African wildfire plume. However, it should be borne in mind that the presence of mineral dust could have partially hindered O_3 production. A rough estimate of the mineral dust influence in limiting the observed O_3 concentrations may be inferred from Bonasoni et al. (2004): for 12 Saharan dust events at MTC from June to December 2000, a −8% (median value) O_3 decrease with respect to monthly averages was observed. Assuming this value as representative for Saharan dust transport at MTC, it can be supposed that without mineral dust a mean O_3 concentration of 76 ppbv (+19% with respect to summer 2007 mean value) and a O_3/CO ERs of 0.16–0.19 ppbv/ppbv might characterise the detected BB plume.

4 Discussion and conclusions

By the end of August 2007, very high levels of trace gas (CO and O_3), aerosol concentrations (equivalent BC, fine and coarse particle), and scattering coefficient were recorded at the MTC GAW-WMO station (2165 m a.s.l., Italy). As deduced by air mass circulation analysis and aerosol chemical characterization, this was due to two different transport processes affecting the measurement site from 26 to 30 August 2007: transport of polluted air masses from Northern Italy and transport of a BB product plume with mineral dust from North Africa. In particular, the high aerosol and ozone levels recorded at MTC during the transport of polluted air masses further emphasised the role of Northern Italy as an efficient source region of anthropogenic pollution for the Mediterranean basin free troposphere. The North African BB event constitutes the strongest observation of wildfire product transport at MTC, usually considered representative for the background conditions of Southern Europe/Mediterranean basin (Bonasoni et al., 2000; Fischer et al., 2003). To our knowledge, the present work is the first investigation on BB emissions from North African coastlines and is, therefore an important contribution to improving the evaluation of sources of trace gases and aerosol over Southern Europe/Mediterranean basin. In particular, while the export

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of mineral dust from the Sahara strongly affected the coarse particle concentrations (+720% with respect to the summer 2007 average levels), the products related to the BB event significantly increased the concentrations of O_3 (+11%), CO (+63%), BC (+271%), fine particle number (+272%) and σ_s coefficient (+212%), as compared with the average summer 2007 levels (64 ppbv, 107 ppbv, 273 ng/m^3, 22.09 cm^{-3}, 0.18 cm^{-3}, 27.0 Mm^{-1}, respectively). Moreover, the CO and aerosol levels recorded during the BB event were higher than during the anthropogenic pollution event (CO: +26%, BC: +39%, fine particles: +101%, σ_s: +100%), indicating that in the considered period, North Africa represented a significant source of trace gas and aerosol particles over Southern Europe and Northern Italy. In fact, on 29–30 August 2007, high PM_{10} values were recorded over the Po Basin by ARPA-ER: at a rural station located at the edge of Bologna urban area (Mt. Cuccolino, 60 km North-East to MTC), on 29 August 2007 PM_{10} increased by 260% with respect to the August 2007 mean value (9.6 μg/m^3). Even if no information is available on the PM_{10} chemical composition in the Po Basin, this suggests that the BB products mixed with Saharan dust from North Africa could have significantly influenced the lower troposphere over Northern Italy.

As deduced from BOLAM three-dimensional back-trajectory analysis, during the BB event air masses travelled from 75 to 93 h from the wildfire area to MTC, in good agreement with the O_3/CO ER analysis. In fact, the calculated O_3/CO ERs (0.10–0.17 ppbv/ppbv) was within the range of those reported by previous investigations for relatively aged (2–4 days) BB plumes. The O_3/CO ER values obtained at MTC and other locations during episodes of BB product transport are plotted as a function of air mass ageing (expressed as travel time) in Fig. 11, showing how ER increases with the ageing of air masses, suggesting O_3 production within the BB plumes. Several investigators (e.g. Pfister et al., 2006; Val Martin et al., 2006; Real et al., 2007) have proposed that this could be the effect of the slow recycling of PAN, HNO_3 and organic nitrates, which favour the photochemical formation of O_3 in BB plumes by increasing the effective lifetime of NO_2. Thus, even if lower than those during the pollution event, the obtained ERs and the high O_3 levels support the hypothesis that significant pho-

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tochemical O_3 production occurred in the BB plume during transport towards MTC. However, it should be borne in mind that the mineral dust mixed within the BB plume could have partially hindered O_3 production (Bonasoni et al., 2004). Significant heterogeneous O_3 destruction can occur on the surface of dust aerosols (Hanisch and Crowley, 2003; Bauer et al., 2004), while HNO_3 and NO_3 depletion on dust particles can remove a fraction of O_3 precursors (Zhang and Carmichel, 1999; Harrison et al., 2001). In addition, mineral dust can cause a decrease in the photolysis rate throughout the troposphere, thus depressing the formation of O_3 in the lower troposphere (Dentener et al., 1996; He and Carmichel, 1999; Balis et al., 2000). The possible influence of mineral dust in limiting O_3 production within the BB plume was roughly inferred by considering the median O_3 decrease (−8%) observed by Bonasoni et al. (2004) during Saharan dust events at MTC. By applying this constant scaling factor to O_3 during the BB event, an O_3/CO ER of 0.16–0.19 ppbv was obtained, still lower than that obtained for the anthropogenic pollution episode and still in agreement with BB products 2–4 days old (Fig. 11).

Since tropospheric O_3 and aerosol particles strongly influence the radiative budget of the atmosphere (Forster et al., 2007), the present results suggest that North African wildfire products and mineral dust can play a significant role in influencing radiative properties (as also suggested by the σ_s MTC measurements) and air quality over the Mediterranean basin. Because it is expected that North Africa and the Mediterranean basin will probably experience more frequent and severe droughts in the near future (Christensen et al., 2007), such events might gain in importance, as sources of atmospheric compounds able to exert an influence on the regional climate and on the tropospheric composition over South Europe/Mediterranean basin.

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Table 1. Comparison of O_3, CO, BC, fine and coarse particle number, and total scattering coefficient (σ_s) 30 min values during the pollution event over northern Italy, with observations impacted by BB, with all observations during summer 2007 (JJA), and with observations carried out during clean background condition. σ and N indicate the standard deviation and the number of data, respectively.

	Summer 2007		Background Selection		North Italy Pollution		Biomass Burning		Summer 2007: data availability
Parameter	Min–Max	Mean (σ ; N)	Min–Max	Mean (σ; N)	Min–Max	Mean (σ; N)	Min–Max	Mean (σ; N)	
O_3 (ppbv)	30–126	64 (12; 4310)	42–79	6 (8; 46)	53–111	77 (15; 41)	60–77	70 (5; 74)	88%
CO (ppbv)	57–244	107 (19; 4251)	74–134	99 (11; 45)	94–184	138 (21; 41)	144–243	175 (18; 74)	91%
BC (ng/m^3)	<6–1411	273 (244; 4069)	<11–554	181 (119; 38)	234–1680	733 (334; 41)	521–1483	1015 (194;74)	81%
Fine particle (cm^{-3})	0.02–122.01	22.09 (24.9; 3832)	1.23–52.50	17.8 (12.1; 39)	14.9–110.4	41.5 (20.6; 41)	19.3–143.1	83.75 (28.47; 73)	72%
Coarse particle (cm^{-3})	<10−3−1.96	0.18 (0.33; 3832)	0.02–0.60	0.16 (0.14; 39)	0.30–1.99	0.81 (0.43; 41)	0.03–1.91	1.31 (0.31; 73)	72%
σ_s (Mm^{-1})	2.0–137.7	27.0 (21.58; 4083)	5.9–64.7	24.9 (16.0; 37)	22.1–79.4	44.9 (14.4; 41)	19.3–137.7	84.5 (18.6; 72)	92%

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Table 2. Comparison of BC (ΔBC/ΔCO), fine particle ($\Delta N_{fine}/\Delta CO$), σ_s ($\Delta\sigma_s/\Delta CO$) and O_3($\Delta O_3/\Delta CO$) enhancement ratios (ER) with respect to CO concentrations for the anthropogenic pollution event and the North African BB event. ERs obtained by "enhancement" and "scatter" techniques are both reported.

Enhancement Ratios	Anthropogenic Pollution		Biomass Burning	
	Enhancement technique	Scatter techniques	Enhancement technique	Scatter techniques
ΔBC/ΔCO (ng m^{-3}/ppbv)	14.00±3.94	14.09±0.93	10.40±0.26	8.59±0.57
$\Delta N_{fine}/\Delta CO$ (cm^{-3}/ppbv)	0.60±0.08	0.82±0.06	0.87±0.04	1.15±0.09
$\Delta\sigma_s/\Delta CO$ (Mm^{-1}/ppbv)	0.49±0.06	0.58±0.02	0.77±0.09	0.74±0.04
$\Delta O_3/\Delta CO$ (ppbv/ppbv)	0.44±0.06	0.66±0.04	0.10±0.04	0.17±0.03

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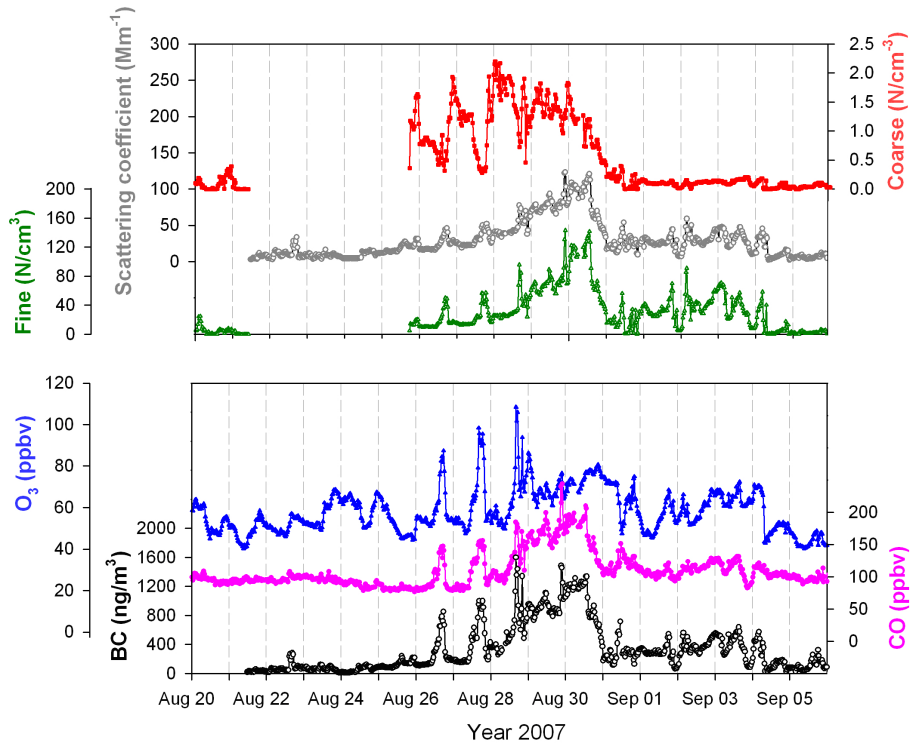

Fig. 1. Mt. Cimone: 20 August–5 September 2007. Upper plate: 30 min averaged values for coarse particle concentrations (red), fine aerosol concentrations (green) and σ_s (grey). Bottom plate: 30 min averaged concentrations of O_3 (blue), BC (black) and CO concentrations (purple).

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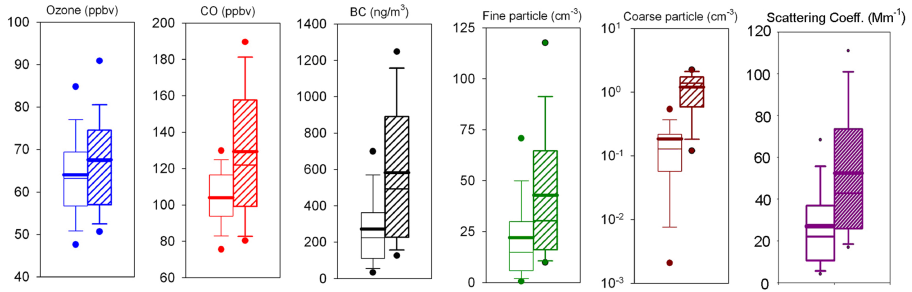

Fig. 2. Box-and-whiskers plot of 30 min averaged values for O_3 (blue), CO (red), BC (black), fine (green), coarse (brown) particles and σ_s (purple) at Mt. Cimone in June–August 2007 (on the left) and for 26–30 August 2007 (on the right, bold). The box and whiskers denote the 10th, 25th, 50th, 75th and 90th percentiles, the outliers the 5th and 95th percentiles and the bold lines the average values.

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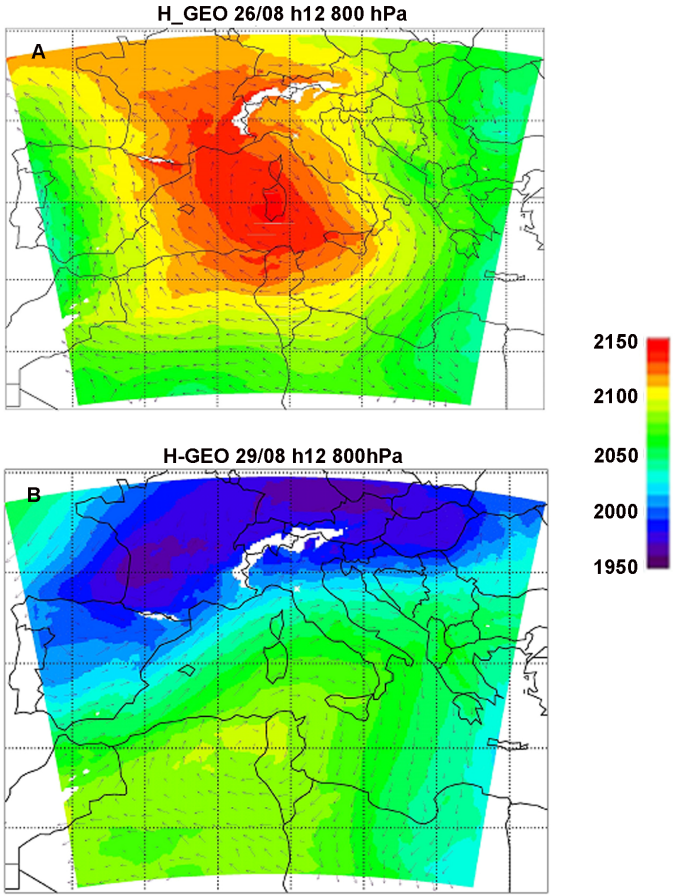

Fig. 3. Geopotential height (expressed in meters, coloured scale) and wind vectors at 800 hPa, deduced by BOLAM analysis on 26 August 2007 12:00 UTC **(A)** and 29 August 2007 12:00 UTC **(B)**. The white asterisks denote MTC location.

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Fig. 4. True colour image detected over North Africa by MODIS (Moderate Resolution Imaging Spectroradiometer) on NASA's Aqua satellite on 29 August 2007 (courtesy of http://earthobservatory.nasa.gov/).

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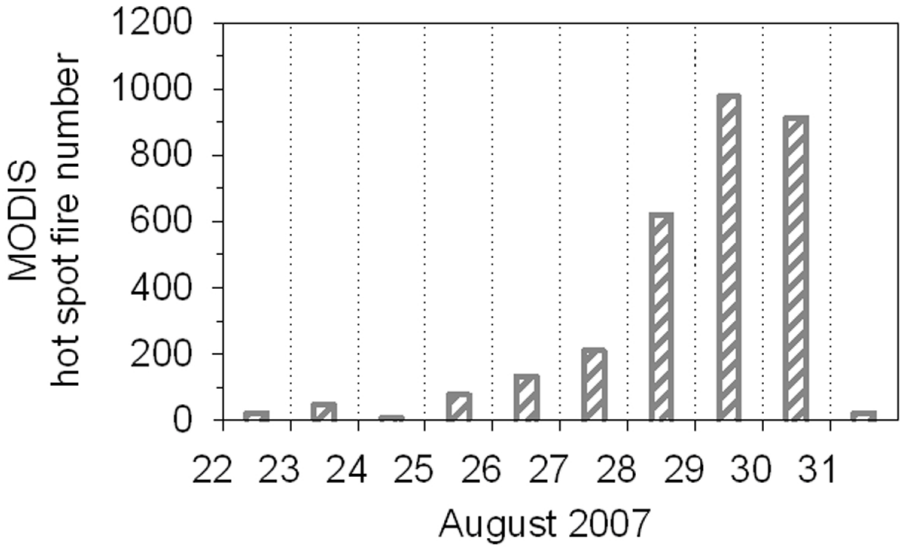

Fig. 5. Daily number of MODIS hot spot fire detected over the North African coastlines (Lat: 0° E–10° E ; Lon: 37° N–35° N) during August 2007 (data courtesy by NASA/GSFC and University of Maryland).

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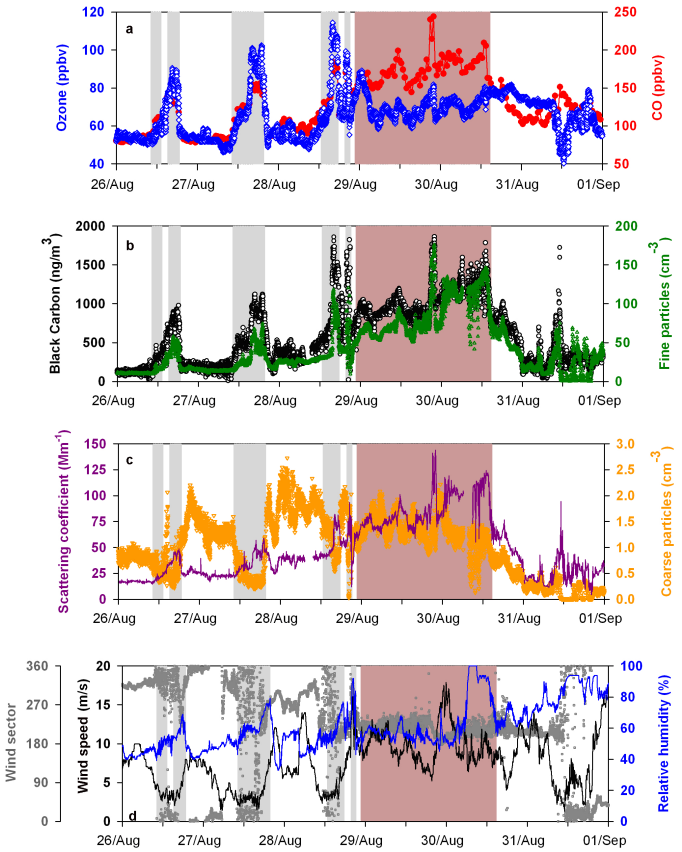

Fig. 6. Time series of 1-min O_3 and CO (blue and red dots, plate **a**), BC and fine particles (black and green dots, plate **b**), coarse particle and σ_s (orange dots and purple line, plate **c**), wind speed, direction and relative humidity (black line, grey dots and blue line, plate **d**) during 26–31 August 2007 at MTC. Grey bars denote the anthropogenic pollution event, red bar denote the BB event.

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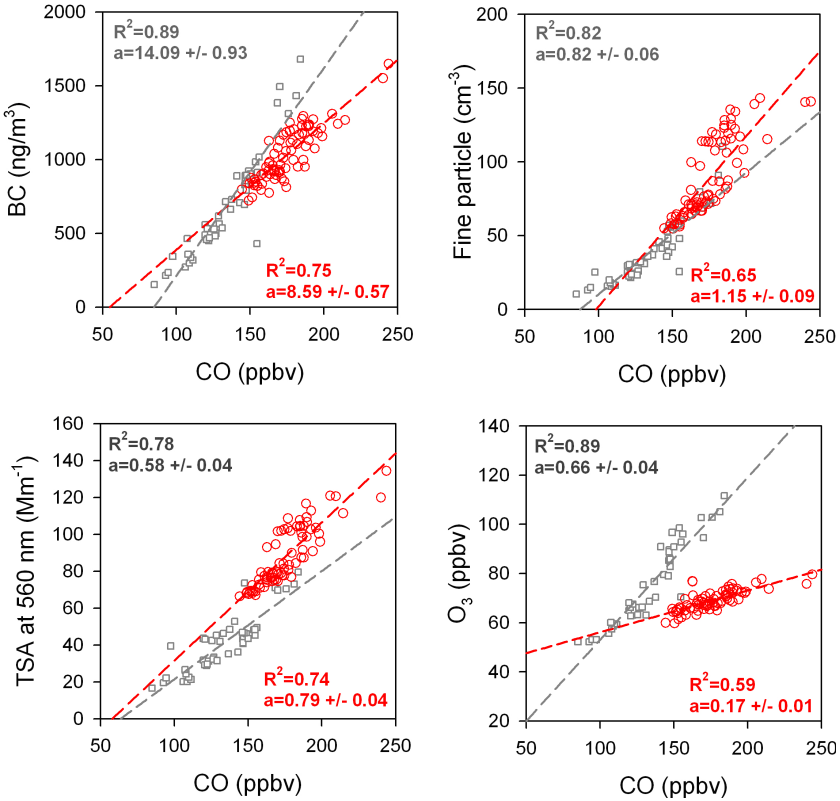

Fig. 7. Relationship between CO and BC, fine particle number, σ_s and O_3 for the anthropogenic pollution (grey) and the BB events (red). Linear interpolations together with their fitting parameters (linear correlation coefficient "R^2" and the slope "a") are also reported.

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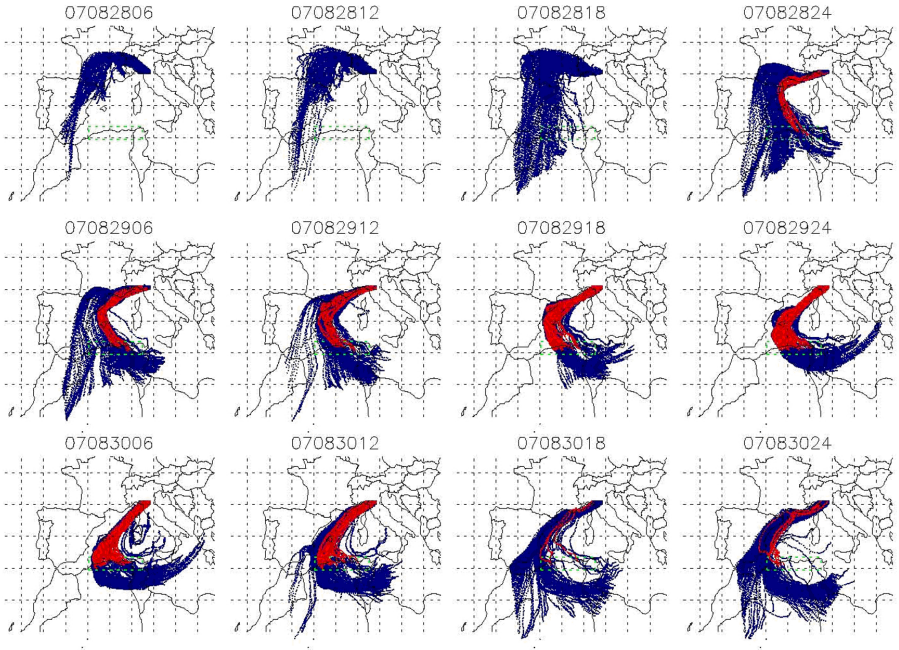

Fig. 8. Back-trajectory ensemble for MTC from 28 August 2007 06:00 UTC to 31 August 2007 00:00 UTC. The back-trajectories which "intercepted" the active MODIS hot spot fires are highlighted in red.

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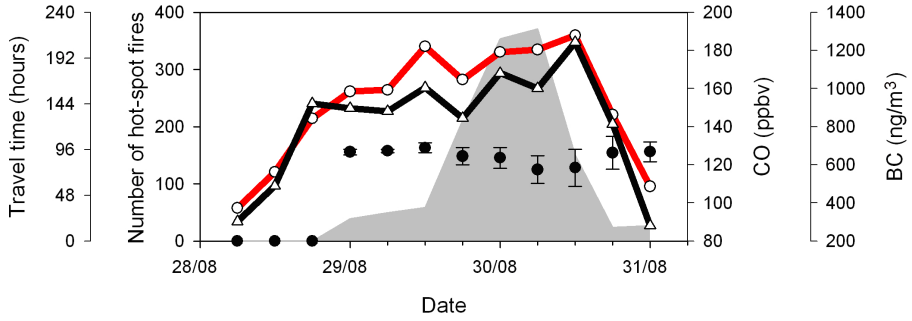

Fig. 9. Comparison of the time series of 3-h measured CO and BC concentration at MTC (red and black lines, respectively) with the number of MODIS hot-spot fires (grey areas) intercepted by back-trajectories arriving at MTC at each 6-h time step. The average back-trajectory travel times (black dots) to reach MTC from the previous active MODIS hot-spot fire are reported together with their standard deviations (error bars).

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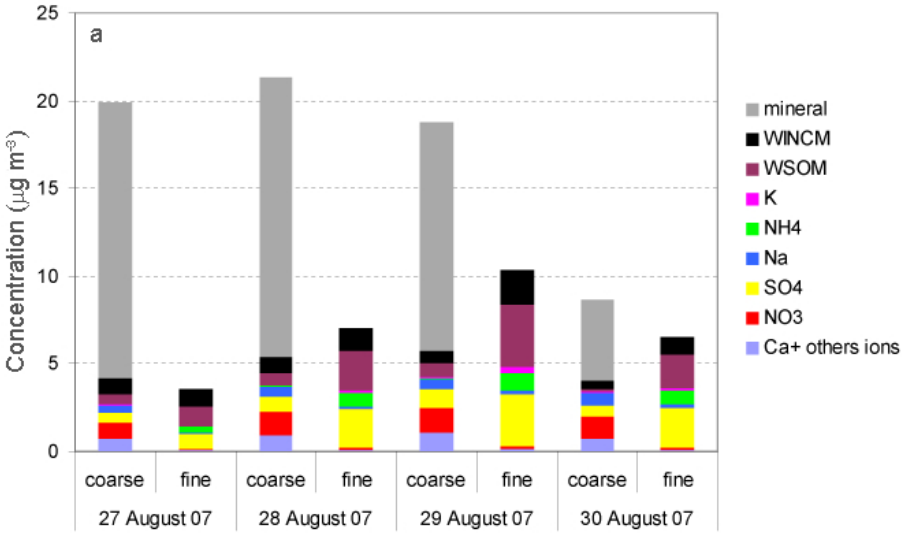

Fig. 10a. Chemical composition of coarse (PM_{1-10}) and fine (PM_1) fractions of aerosol at MTC from 27 to 30 August 2007. Dates in the x-axis denote the starting day of each sampling. Note that on the fine fractions the analysis for mineral aerosol determination was not performed.

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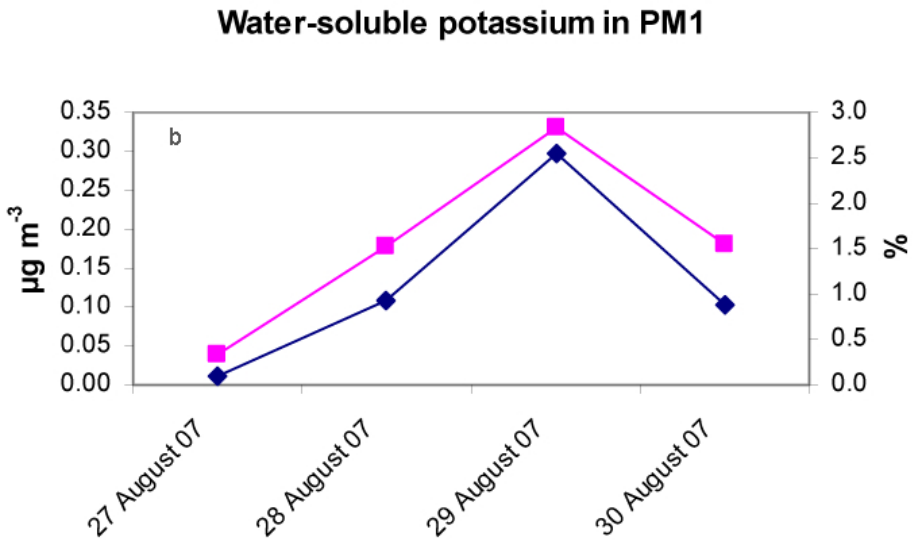

Fig. 10b. Concentration of water-soluble potassium in PM_1 (blue line) and its contribution to the total PM_1 mass reconstructed by the chemical analysis (purple line).

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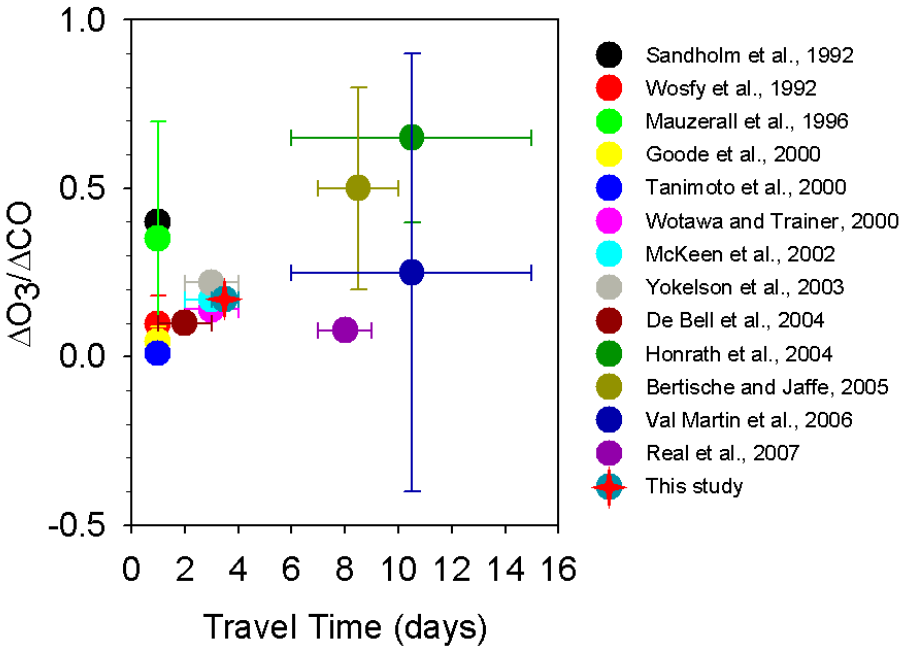

Fig. 11. ERs of O_3 (relative to CO) observed in previous investigations of BB plumes. Vertical bars denote the range of observed ERs. Horizontal bars denote the travel time for the observed BB plumes.

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