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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 particle volumes), as well as high scattering coefficient (σ_p) values, were recorded at the regional GAW-WMO station of Mt. Cimone (CMN, 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 enhancement 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 volume: 3.00 μm^3 cm^{-3}, σ_p: 84.5 Mm^{-1}) were even higher than during the pollution event (CO: 138 ppbv, BC: 733 ng/m^3, fine particles volume: 1.58 μm^3 cm^{-3}, σ_p: 44.9 Mm^{-1}). Moreover, despite the presence of mineral dust able to affect significantly 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 CMN. In particular, the calculated O_3/CO ERs (0.10–0.17 ppbv/ppbv) were in the range of values found in literature for relatively aged (2–4 days) BB plumes and suggested significant photochemical O_3 production during the air-mass transport. For fine particles and σ_p, the calculated ERs was higher in the BB plumes than during the anthropogenic pollution events, stressing the importance of the identified BB event as a source of atmospheric aerosol able to affect the atmospheric radiation budget. These results suggest that episodes of mineral dust mobilization and wildfire emissions over North Africa could significantly influence radiative properties (as deduced from σ_p observations at CMN) and air quality over the Mediterranean basin and northern Italy.

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 (e.g. Crutzen and Andreae, 1990; Goode at al., 2000; Simmonds et al., 2005). In particular, boreal 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). 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 strongly involved in photochemical reactions (Crutzen et al., 1999; Volz-Thomas et al., 2002) and in determining the oxidation capacity of the

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troposphere (Gauss et al., 2003). Moreover it is a dangerous pollutant (Brunekreef and Holgate, 2002) and an efficient greenhouse gas (Forster et al., 2007). Due to chemical and photo-chemical processes and mixing with air-masses of different origin, the O_3 levels in the BB plumes can strongly vary during the export from the emission regions (Real 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). Even if important year-to-year variability affect global fire activity and thus wildfire emissions (van der Werf et al., 2006; Le Page et al., 2008), significant increasing trend in fire activity were observed during the recent decades over specific regions like Europe, Africa and US (Mouillot and Fields, 2005; Westerling et al. 2006).

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. Val Martin et al., 2006 and references therein). 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 influenced trace gas composition and aerosol properties both in the boundary layer and the free troposphere (Pace et al., 2006; Cristofanelli et al., 2007). However, during summer, large amounts of anthropogenic pollutants from the European boundary layer are also transported towards the Mediterranean basin/South Europe free troposphere (e.g. Henne et al., 2004; Henne et al., 2005a). 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 (e.g. Papayannis et al., 2008). 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; 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 volume, 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.

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 (CMN; 44°11′ N, 10°42′ E, 2165 m a.s.l.). The CMN 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 system (Fischer et al., 2003; Van Dingenen, 2005). At CMN, 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 less than ±2 ppbv in the range 1–100 ppbv) and sampling procedures are guaranteed within the GAW requirements (WMO, 2002). In particular, the O_3 analyser working at CMN was traced back to EMPA (Swiss Federal Laboratories for Materials Testing and Research) SRP#15 Standard Reference Photometer. 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 $0.3\,\mu\mathrm{m} \le \mathrm{Dp} \le 20\,\mu\mathrm{m}$. The instrument is based on the quantification 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 ($0.3\,\mu\mathrm{m} \le \mathrm{Dp} < 1\,\mu\mathrm{m}$) and coarse ($1\,\mu\mathrm{m} \ge \mathrm{Dp} > 20\,\mu\mathrm{m}$) aerosol fractions with a 1 min time resolution. OPC size distribution was used to derive aerosol volume for fine (V_{fine}) and coarse (V_{coarse}) particles. In particular, large increases in coarse particle volume 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 CMN, 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_p, 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 $<1\,\mu$m (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_web/) 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 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. Briefly, the method is based on direct analysis of WSOM in $\mathrm{D_2O}$ solution with identification and quantification of levoglucosan on the basis of the signal of its anomeric proton at 5.4 ppm of chemical shift. Inorganic ions ($\mathrm{NH_4^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Mg_2^+}$, $\mathrm{Ca_2^+}$, $\mathrm{Cl^-}$, $\mathrm{NO_2^-}$, $\mathrm{NO_3^-}$, $\mathrm{SO_4^{2-}}$) 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:

$$\begin{aligned}\text{Crustal matter} &= 1.12 \times \big[1.658 \times \mathrm{Mg} + 1.889 \times \mathrm{Al} \\ &+2.139 \times \mathrm{Si} + 1.204 \times \mathrm{K} + 1.399 \times \mathrm{Ca} + 1.668 \times \mathrm{Ti} \\ &+1.582 \times \mathrm{Mn} + (0.5 \times 1.286 + 0.5 \times 1.429) \times \mathrm{Fe}\big] \qquad (1)\end{aligned}$$

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

2.3 BOLAM model and back-trajectory calculations

In order to determine the origin of air masses reaching CMN, 3-D air mass back-trajectories (with 1 hour 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 (1224 m a.s.l. for the location of CMN) 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 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 CMN 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 CMN, 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 volumes, σ_p 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 h for the CMN endpoint, based on the ECMWF wind field (1°×1° 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 CMN 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 CMN 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, V_{fine} and V_{coarse} as well as σ_p, 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; V_{fine}: 1.93±0.99 μm^3 cm^{-3}; V_{coarse}: 13.11±6.25 μm^3 cm^{-3}; σ_p: 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, V_{fine} and V_{coarse} particles, as well as σ_p 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 an marked increase of the upper quartiles (+5.6 ppbv for the 75th percentile; +6.2 ppbv or 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

Table 1. Comparison of O_3, CO, BC, fine and coarse particle volumes, and total scattering coefficient (σ_p) 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	61 (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 %
V_{fine} ($\mu m^3\,cm^{-3}$)	$<10^{-3}$–5.80	0.82 (0.80; 3832)	0.05–1.83	0.63 (0.48; 39)	0.83–3.16	1.58 (0.54; 41)	0.27–4.59	3.00 (0.80; 73)	72%
V_{coarse} ($\mu m^3\,cm^{-3}$)	$<10^{-3}$–46.16	2.53 (4.58; 3832)	0.09–9.98	2.14 (2.49; 39)	3.19–9.09	9.09 (4.77; 41)	0.05–31.57	15.54 (6.08; 73)	72%
σ_p (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%

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 CMN.

These conditions favoured the transport of mineral dust from the Sahara, as confirmed by the high V_{coarse} ($>10.0\,\mu m^3\,cm^{-3}$) recorded at CMN (Fig. 1) from 25 to 30 August 2007. Although OPC measurements were not available 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 mobilization of mineral dust over Sahara desert was confirmed also by the OMI (Ozone Monitoring Instrument) measurements, showing high values of Aerosol Index over this area (Fig. 4).

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, 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. 5), 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 obtained 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; 35° N<Lat.<37° N) wildfires started on 25 August 2007 with a peak from 28 to 30 August 2007 (Fig. 4).

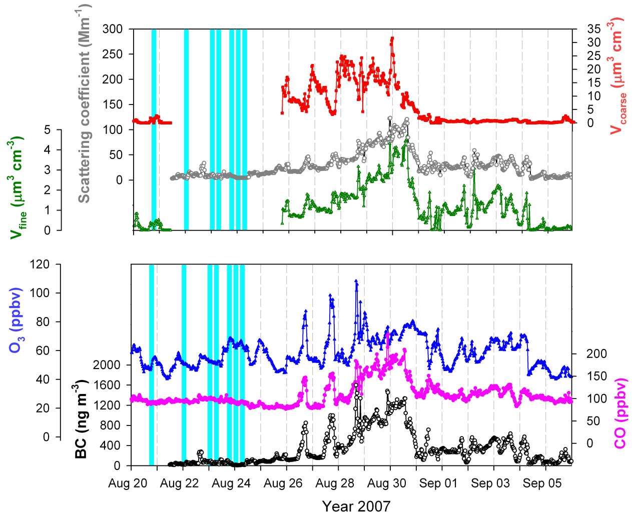

Fig. 1. Mt. Cimone: 20 August–5 September 2007. Upper plate: 30 min averaged values for V_{coarse} (red), V_{fine} (green) and σ_p (grey). Bottom plate: 30 min averaged concentrations of O_3 (blue), BC (black) and CO concentrations (purple). The cyan bars indicate the periods characterised by summer background conditions as defined in the Sect. 2.4.

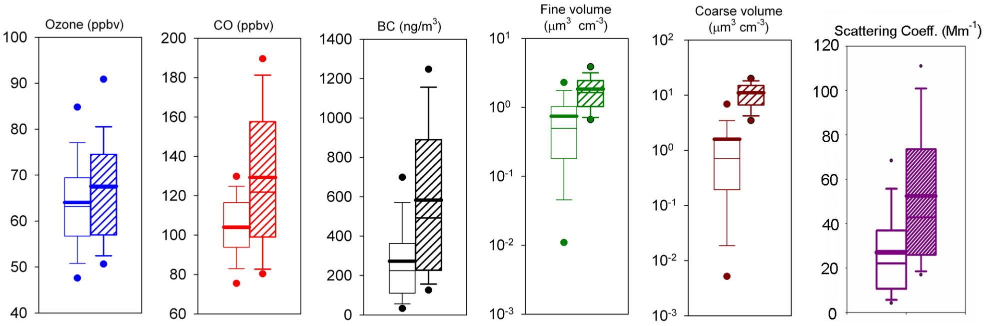

Fig. 2. Box-and-whiskers plot of 30 min averaged values for O_3 (blue), CO (red), BC (black), V_{fine} (green), V_{coarse} (brown) and σ_p (purple) at Mt. Cimone in June–August 2007 (on the left) and for 26–30 August 2007 (on the right, bold). The box and whiskers denote the 10th, 25th, 50th, 75th and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

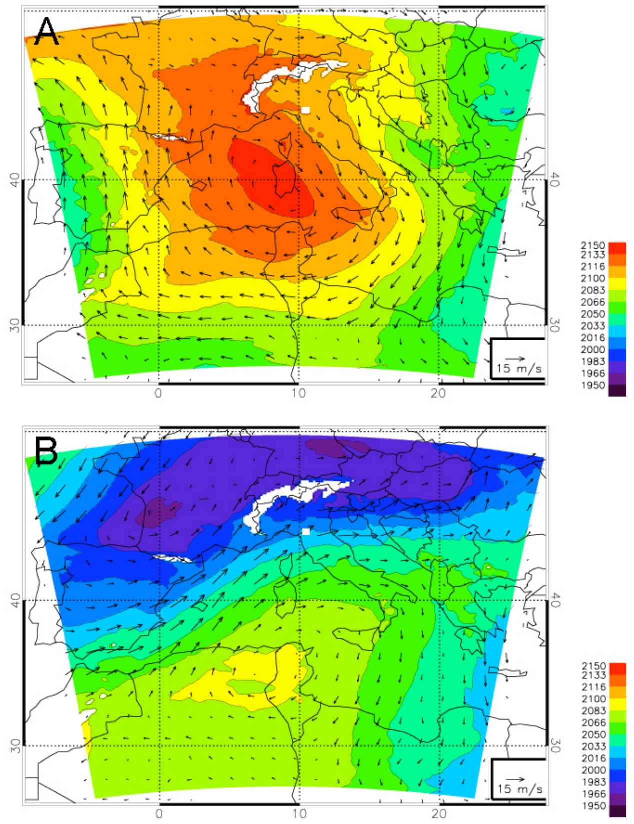

Fig. 3. Geopotential height (expressed in meters, coloured scale) and wind vectors at 800 hPa, deduced by BOLAM analysis on 26 August 2007 12:00 UTC **(A)** and 29 August 2007 12:00 UTC **(B)**. The white square denotes the CMN location.

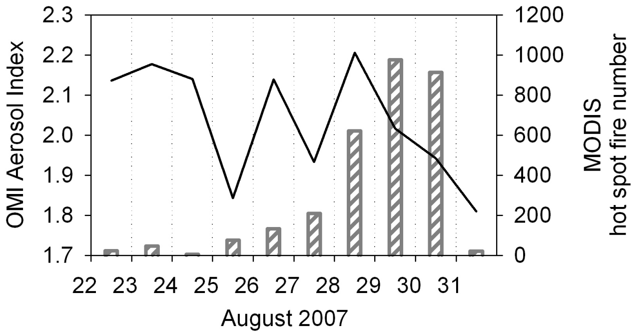

Fig. 4. Daily values of OMI Aerosol Index averaged over the Sahara desert (continuous line, left y-axis) and daily number of MODIS hot spot fire (bars, right y-axis) detected over the North African coastlines (Lat: 0° E–10° E ; Lon: 37° N–35° N) during August 2007 (data courtesy by NASA/GSFC and University of Maryland, Goddard Earth Sciences Data and Information Services Center and KNMI).

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 levels were recorded at CMN (Fig. 6). Compared to the average conditions at CMN for summer 2007, the levels of O_3, CO, BC, V_{fine} and σ_p, 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 CMN 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 speeds (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 CMN, 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

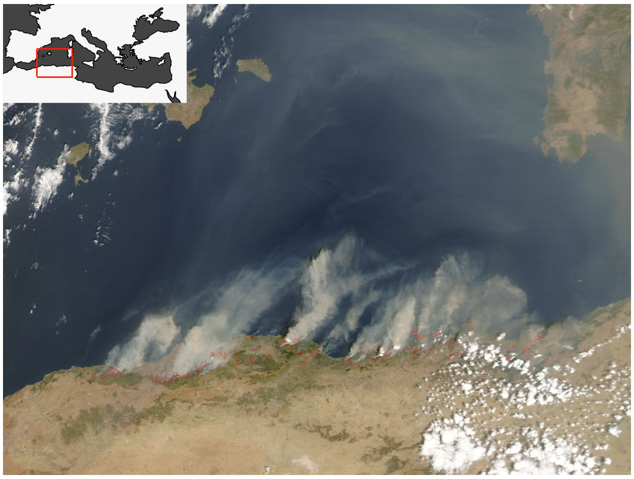

Fig. 5. True colour image detected over North Africa by MODIS (Moderate Resolution Imaging Spectroradiometer) on NASA's Aqua satellite on 29 August 2007 (courtesy of http://earthobservatory.nasa.gov/).

systems are often observed in mountain areas (Vergeiner and Dreiseitl, 1987; Zaveri et al., 1995; Henne et al., 2005b). Together with entrainment processes related to diurnal PBL growth (Beck et al., 1997; Tressol et al., 2008) and topographic venting (Henne et al., 2004), such wind systems can efficiently contribute to the export of pollutants to the free troposphere during daytime as observed at alpine stations (Baltensperger et al., 1997; Scheel et al., 1997; Carnuth et al., 2002; Schuepbach et al., 2001; Zellweger et al., 2000) and at CMN as well (Fischer et al., 2003; van Dingenen et al., 2005).

The presence of air masses transported from the PBL is also supported by the analysis of coarse particle variations (Fig. 6) which at CMN are greatly influenced by Saharan dust transport events (Marinoni et al., 2008). In fact, on 26–28 August 2007, the V_{coarse} showed a diurnal cycle with high values during night-time (up to 36.00 $\mu\mathrm{m}^3\ \mathrm{cm}^{-3}$) and lower values (below 2.60 $\mu\mathrm{m}^3\ \mathrm{cm}^{-3}$) during day-time, when the highest values of pollutant tracers (O_3, CO, BC, V_{fine}, σ_p) were recorded. This indicated that during night-time, when high wind speeds (>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 CMN, 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.

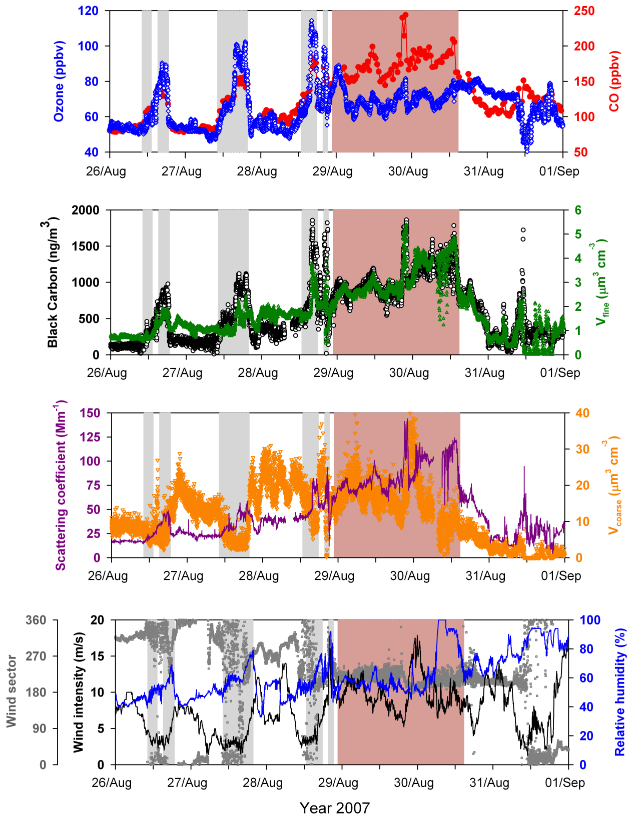

Fig. 6. Time series of 1 min O_3 and CO (blue and red dots, plate **(a)**, BC and V_{fine} (black and green dots, plate **(b)**, V_{coarse} and σ_p (orange dots and purple line, plate **(c)**, wind speed, direction and relative humidity (black line, grey dots and blue line, plate **(d)** during 26–31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

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. For σ_p and O_3, the ERs calculated by the "scatterplot" technique method are higher than those calculated with the "enhancement" method, thus indicating the large uncertainties 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=0.89), V_{fine} (R^2=0.66), σ_p (R^2=0.78) and O_3 (R^2=0.89) suggested the possibility that strong transport

Table 2. Comparison of BC (ΔBC/ΔCO), fine particle volume ($\Delta V_{\mathrm{fine}}/\Delta$CO), σ_p ($\Delta\sigma_p/\Delta$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
$\Delta V_{\mathrm{fine}}/\Delta$CO (($\mu m^3$ cm^{-3})/ppbv)	0.024±0.005	0.020±0.002	0.030±0.002	0.026±0.003
$\Delta\sigma_p/\Delta$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

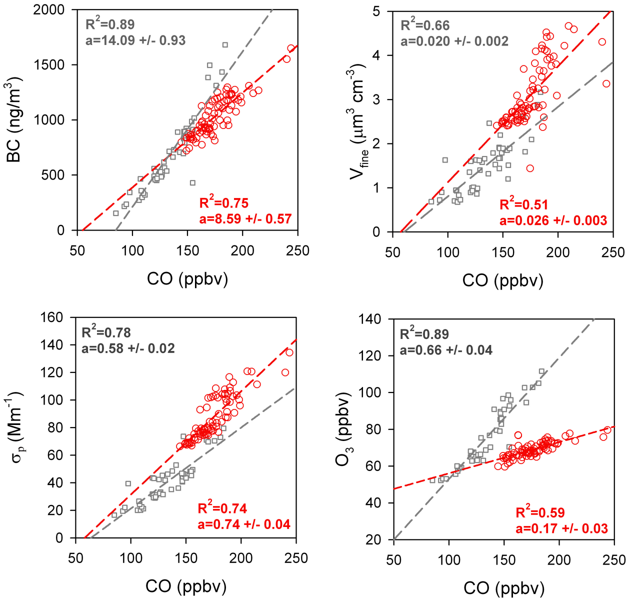

Fig. 7. Relationship between CO and BC, V_{fine}, σ_p and O_3 for the anthropogenic pollution (grey) and the BB events (red). Linear interpolations together with their fitting parameters (linear correlation coefficient "R^2" and the slope "a") are also reported basing on 30 min data.

of pollutants on regional scale 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 (about 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 V_{fine} and σ_p (Table 2) are in the upper range of, or higher than those obtained for "anthropogenic" pollution products in previous studies. In fact, Price et al. (2004) and Weiss-Penzias et al. (2006) recorded σ_p/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. Please note that considering the number of fine particles instead of V_{fine}, ERs of (0.60±0.08) cm^{-3}/ppbv and (0.82±0.06) cm^{-3}/ppbv were obtained for "enhancement" and the "scatter" technique (R^2=0.82), respectively. However, bearing in mind that OPC only detects particles with radii greater that 0.3 μm, great caution should be deserved in considering these results as representative of submicron particle number.

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 CMN 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

Starting in the evening of 28 August 2007, high trace gas and aerosol concentrations were continuously observed at CMN for about 36 h (until midday on 30 August 2007, see Fig. 1). 30 min averages of O_3, CO, BC, V_{fine} and σ_p peaked at 77 ppbv, 243 ppbv, 1483 ng m^{-3}, 4.59 μm^3 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 V_{coarse} were recorded at the measurement site (average value: 15.54±6.08 μm^3 cm^{-3}), indicating the presence of mineral dust. In fact, the 3-D back-trajectory ensembles calculated by BOLAM (Fig. 8) showed

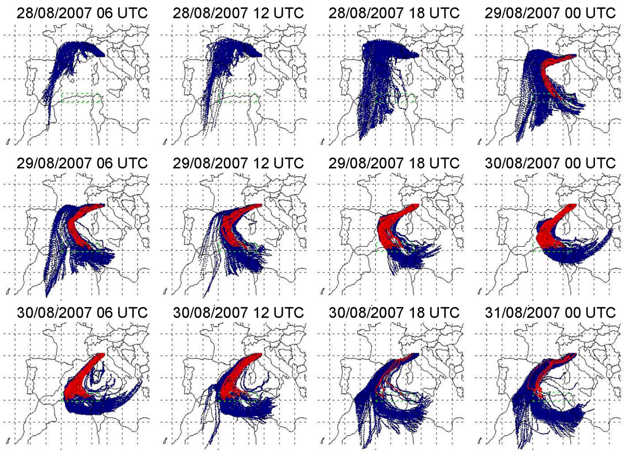

Fig. 8. Back-trajectory ensemble for CMN from 28 August 2007 06:00 UTC to 31 August 2007 00:00 UTC. The back-trajectories which "intercepted" the active MODIS hot spot fires are highlighted in red.

that North African air masses reached CMN 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 CMN, 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 CMN (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). Note that the increase in CO and BC concentrations observed in the afternoon-evening on 28 August 2007, was not directly related with the BB product transport but with the advection of polluted air-masses from North Italy, as shown in the Sect. 3.2. 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 CMN.

The presence of mineral dust and BB products in air masses arriving at CMN 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) 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 μg/m^3; NO_3^-: 0.06 μg/m^3; SO_4^{2}: 0.85 μg/m^3), were in the lower range of summer average CMN 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 μg/m^3), while those in the fine fraction (PM_1) underwent a significant increase, peaking on 29 August 2007 (10.69 μg/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 μg/m^3, more than double the value on the first sampling day, as well as the summer background

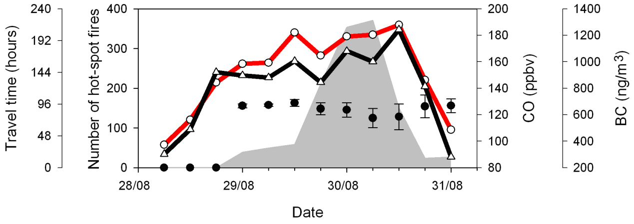

Fig. 9. Comparison of the time series of 3 h measured CO and BC concentration at CMN (red and black lines, respectively) with the number of MODIS hot-spot fires (grey areas) intercepted by back-trajectories arriving at CMN at each 6 h time step. The average back-trajectory travel times (black dots) to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

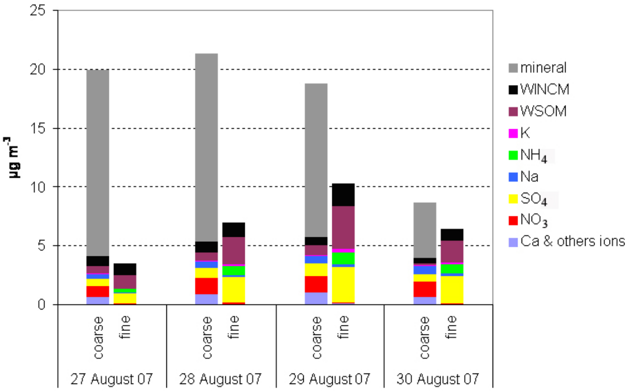

Fig. 10a. Chemical composition of coarse (PM_{1-10}) and fine (PM_1) fractions of aerosol at CMN from 27 to 30 August 2007. Dates in the x-axis denote the starting day of each sampling. Note that on the fine fractions the analysis for mineral aerosol determination was not performed.

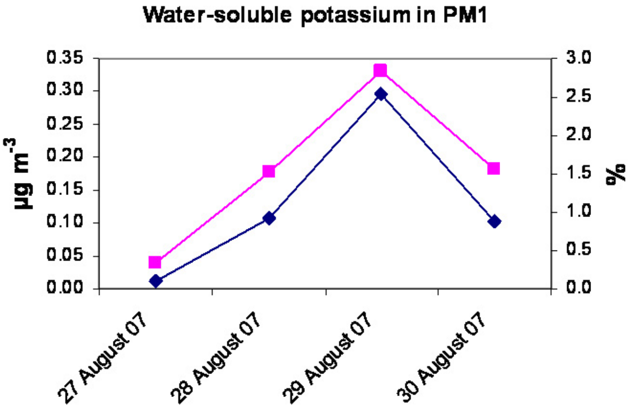

Fig. 10b. Concentration of water-soluble potassium in PM_1 (blue line) and its contribution to the total PM_1 mass reconstructed by the chemical analysis (purple line).

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 μg/m^3) to 29 August 2007 (5.0 μg/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 CMN the potassium average concentration was 0.036±0.025 μg/m^3. On 27 August 2007 K^+ mass concentration was 0.012 μg/m^3 whereas there was a large increase in potassium (up to ten times) in the subsequent three samples, reaching 0.297 μg/m^3 on 29 August 2007. These results indicate that aerosol properties at CMN 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 CMN 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, analysis was performed of the measurement period in which BOLAM showed at CMN 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 transport (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 CMN for the North African BB plume suggest that the observed BC experienced very little removal during the 3–4 days of transport.

V_{fine} and σ_p 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. In this case, considering the number of fine particles instead of V_{fine}, ERs of (0.87±0.04) cm^{-3}/ppbv and (1.15±0.09) cm^{-3}/ppbv were obtained for "enhancement" and the "scatter" technique (R^2=0.65), respectively. The σ_p/CO ER at CMN 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 enhancement 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 CMN 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 CMN, 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 CMN 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 CMN, 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 (equivalent BC, V_{fine} and V_{coarse}) and scattering coefficient were recorded at the regional GAW-WMO station of CMN (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 CMN 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. Even if BB transport to CMN were already observed during summer 2003 (Cristofanelli et al., 2006), this North African BB event constitutes the first investigation concerning an episode of wildfire product transport mixed with mineral dust at this measurement site, often 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 of mineral dust from the Sahara strongly affected the V_{coarse}(+610% with respect to the summer 2007 average levels, 2.53 $\mu\mathrm{m}^3\,\mathrm{cm}^{-3}$), the products related to the BB event significantly increased the concentrations of O_3 (+11%), CO (+63%), BC (+271%), V_{fine}(+365%) and σ_p coefficient (+212%), as compared with the average summer 2007 levels (64 ppbv, 107 ppbv, 273 $\mathrm{ng/m}^3$, 0.82 $\mu\mathrm{m}^3\,\mathrm{cm}^{-3}$, 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%, V_{fine}: +189%, σ_p: +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 CMN), on 29 August 2007 PM_{10} increased by 260% with respect to the August 2007 mean value (9.6 $\mu\mathrm{g/m}^3$). 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 CMN. Even if, due to the large emission variations between wildfires, caution should be deserved in directly relating BB plume ages and O_3/CO ERs, this appears to be 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. However, following Henne et al. (2008), it should be noted that since the regression slopes deduced by the "scatter technique" were obtained by applying a least squares regression, the obtained ERs can be underestimated. For this reason, we also calculated regression slopes by using the Reduced Major Axis (RMA) techniques, accounting for errors in both the x and the y-variable. Nevertheless, due to the rather high R^2 observed only slight increases of regression slopes (and ERs) were calculated both for the pollution and the BB events. In particular, by considering the RMA technique, the O_3/CO ER calculated by the "scatter" technique increase to 0.22 ppbv/ppbv.

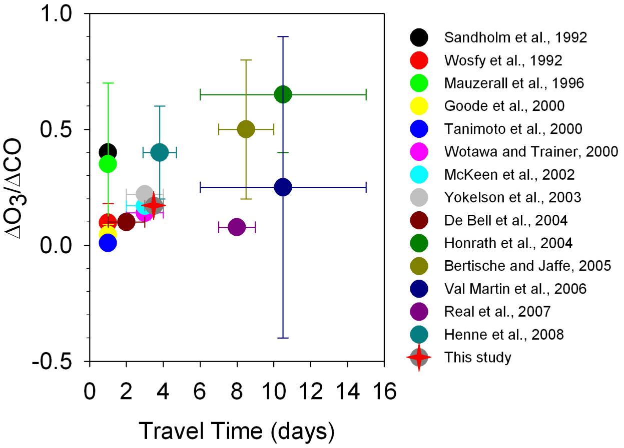

Fig. 11. ERs of O_3 (relative to CO) observed in previous investigations of BB plumes. Vertical bars denote the range of observed ERs. Horizontal bars denote the travel time for the observed BB plume.

The O_3/CO ER values obtained at CMN 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 photochemical O_3 production occurred in the BB plume during transport towards CMN. 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). Even if the low O_3 mixing ratios usually observed at CMN during Saharan dust events may be also related to the chemical properties of air-masses originating from North Atlantic and North Africa (Bonasoni et al., 2004), significant heterogeneous O_3destruction 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 CMN. By applying this constant scaling factor to O_3 during the BB event, an O_3/CO ER of 0.16–0.19 ppbv/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).

During the drought periods that frequently affect the Mediterranean basin (particularly during the summer months), BB products can be often found to affect the Mediterranean basin (Sciare et al., 2003; Pace et al., 2005, 2006; Cristofanelli et al., 2006). In particular, by analysing the behaviour of fine light-absorbing aerosol in the central Mediterranean during summer 2003, Pace et al. (2005) estimated that the particles emitted by the forest fires over South Europe produced an increase of heating rate as large as 2.8 K/day at the altitude of the aerosol layer, thus probably affecting also the atmospheric circulation by increasing the atmospheric stability. Moreover, it is well known that also mineral dust plays important role on the climatic system (e.g. Forster et al., 2007) and the importance of Saharan dust as source of mineral aerosol for the Mediterranean basin is indicated by several investigations. In fact, during a 11-year period (1983–1994) Moulin et al. (1997) reported 16 Saharan dust events per year over western Mediterranean, while recent results from EARLINET (European Aerosol Research Lidar Network) activity showed that, depending on the geographical location, over the Mediterranean basin from 12 to 35 days per year can be affected by Saharan dust outbreaks (Papayannis et al., 2008). Similar results were presented by Marinoni et al. (2008) who identified an average of 40 days per year as influenced by Saharan dust events at CMN and by Collaud Coen et al. (2004) who found 48 dust events from March 2001–December 2002 at the Jungfraujoch alpine station. Because it is expected that North Africa and Mediterranean basin will probably experience more frequent and severe droughts in the near future (Christensen et al., 2007; Solomon et al., 2007), such events might gain further 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.

Thus, since tropospheric O_3 and aerosol particles strongly influence the radiative budget of the atmosphere (Forster et al., 2007), the present results suggest that episodes of wildfire product and mineral dust emissions from North Africa can play a significant role in influencing radiative properties (as also suggested by the BC and σ_p measurements at CMN) and air quality over the Mediterranean basin. However, to better clarify the potential role of these classes of events (mineral dust transport, BB product transport as well as concurring BB product and mineral dust transport) in influencing systematically the composition of the troposphere over the Mediterranean region, a multi-year climatological investigation appears as an important step.

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