Atmospheric Environment 141 (2016) 139–152

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Summer atmospheric composition over the Mediterranean basin: Investigation on transport processes and pollutant export to the free troposphere by observations at the WMO/GAW Mt. Cimone global station (Italy, 2165 m a.s.l.)

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HIGHLIGHTS

- Mt. Cimone (Italy) is strategic to study Mediterranean summer atmospheric composition.
- We investigate processes affecting summer trace gas and aerosols at Mt. Cimone.
- Impact of different atmospheric regimes was investigated.
- 77% of observations can be tagged to aged emissions or background conditions.
- Tracer probability density functions are able to detect specific event.

ARTICLE INFO

Article history:
Received 3 December 2015
Received in revised form
30 May 2016
Accepted 18 June 2016
Available online 22 June 2016

Keywords:
Mediterranean basin
Po basin
Short-lived climate forcers/pollutants
Air-mass age
Air-mass transport

ABSTRACT

In this work, we analysed reactive gases (O_3, CO, NO_x) and aerosol properties (eqBC, σ_s and particle number concentration) collected at the WMO/GAW Mt. Cimone station (2165 m a.s.l., Italy) during the summer of 2012 in the framework of PEGASOS project. The major aim of this experiment is providing a characterization of the variability of summer atmospheric composition over the central Mediterranean basin, which is considered as a global "hot-spot" for atmospheric pollution and climate change.

The atmospheric tracers have been analysed as a function of (i) meteorological parameters, (ii) synoptic-scale circulation and (iii) anthropogenic emission source proximity as estimated by O_3/NO_x ratio variability. In particular, we identified three O_3/NO_x regimes which tagged the distance of anthropogenic sources: near outflow (23% of hourly data), far-outflow (38% of data) and background (39% of data). The highest levels of anthropogenic pollutants (e.g. O_3, CO, eqBC, accumulation particles) were concomitant with fresh emissions from northern Italy under near-outflow conditions: once injected to the free troposphere, these air-masses, rich in pollutants and climate-forcers (i.e. O_3, eqBC) and soil dust, can be spread over a large region, thus significantly affecting regional climate. Moreover, based on the anthropogenic source proximity, atmospheric tracer variability and synoptic-scale atmospheric circulation, we categorized and characterised four types of atmospheric regimes associated with (1) air-mass transport from the free troposphere, (2) transport of fresh emitted pollutants from the PBL, (3) transport at regional/continental scale of aged anthropogenic (4) transport of air-mass rich in mineral dust from northern Africa (i.e. coming from more than 1000 km).

Lastly, by analysing the probability density functions (PDFs) of trace gases and aerosol properties, "fingerprints" of the mentioned atmospheric regimes were pointed out. Such information is useful for the implementation of early-warning services, for the timely detection of event occurrence as well as for the definition of observation-based diagnostic for model verifications.

1. Introduction

The Mediterranean Basin is considered a hot-spot region in terms of air-quality (Monks et al., 2009) and climate change (Giorgi

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http://dx.doi.org/10.1016/j.atmosenv.2016.06.048
1352-2310/

and Lionello, 2008), due to the impact of anthropogenic and natural processes (Lelieveld et al., 2002; Kanakidou et al., 2011). During the warm season, events of ozone (O_3) photochemical production frequently occur in this region favored by high pressure conditions (e.g. Vautard et al., 2005) and anthropogenic pollutants can be vented up to mid-troposphere by vertical thermal processes (i.e. Henne et al., 2004; Monks et al., 2009). Kalabokas et al. (2007), pointed out that during summertime enhanced O_3 frequently exceeded the 8-h EU air quality standard (60 ppb) in the lower troposphere over the Eastern Mediterranean basin, while Safieddinne et al. (2014) showed that the central Mediterranean basin (i.e. from 5°E to 20°E) is the region were surface O_3 is maximized in summer. As reported by Richards et al. (2013), local anthropogenic NO_x emissions result in the overall largest sensitivity to near-surface and lower troposphere (below 700 hPa) summertime O_3 distribution over the Mediterranean basin. Over the eastern Mediterranean basin, the presence of an O_3 pool in the middle troposphere has been noticed (Zanis et al., 2014) which has been mainly related to stratosphere-troposphere exchange and subsidence from the upper troposphere. In addition, Saharan dust outbreaks from northern Africa (Querol et al., 2009) as well as widespread open biomass burning (Turquety et al., 2014) further exacerbate air-quality and the impact of anthropogenic emissions on the regional climate (Mallet et al., 2013). Because of the impact of these processes on air-quality and regional climate, ultimately on population health and ecosystem integrity, in the recent years experimental forecast and near-real time event detection services were launched for a suite of atmospheric compounds and disruptive events (e.g. Basart et al., 2012; Wagner et al., 2015 and references therein).

In this study, we provide an almost comprehensive characterization of the summer atmospheric composition over the central Mediterranean basin, by using a wide set of continuous observations at the high mountain station of Mt. Cimone (CMN, 44°12′ N, 10°42′ E; 2165 m a.s.l.), which is located in the Italian northern Apennines. Due to its elevation, this research site is typically exposed to air-masses from the planetary boundary layer (PBL) of the northern Italy (encompassing also the Po basin) during summer day-time, while it is representative of free troposphere during night-time (see e.g. Fischer et al., 2003; Rinaldi et al., 2015). Therefore, CMN represents a strategic site to investigate the impact of PBL air-mass export on the atmospheric composition of the Mediterranean free troposphere as well as to characterize its background conditions.

In this paper, we present and discuss variability of reactive gases (ozone, carbon monoxide, nitrogen oxides) and aerosol properties (number concentration and size distribution, aerosol scattering, equivalent black carbon concentration) observed during an intensive field campaign (2015, 10th June – 10th July) carried out in the framework of the EU project PEGASOS (Pan-European Gas-AeroSOls Climate Interaction Study, see Rinaldi et al., 2015). Besides providing an overall characterization of the PEGASOS measurement period at CMN, we used qualitative information about the proximity of emission sources, combined with analysis of synoptic-scale atmospheric circulation regimes and atmospheric tracer variability for discriminating the occurrence of different classes of air-masses transport (fresh pollution, aged pollution, dust transport, upper tropospheric air-mass transport). Nitrogen oxides ($NOx = NO + NO_2$) influence tropospheric radical chemistry, O_3 formation and secondary aerosol by oxidation to aerosol nitrate. Carbon monoxide (CO) is emitted from combustion processes, but it is also formed by the oxidation of methane (CH_4) and volatile organic compounds (VOCs). CO is also a major O_3 precursor. O_3 is a short-lived climate forcers/pollutants (SLCF/P) as being a greenhouse gas and a tropospheric oxidizing agent, thus affecting photochemical processes. Atmospheric aerosols (pollution particles, smoke, mineral dust, marine particles) exert a highly uncertain effect on radiative climate forcing and can have serious impacts on human health, especially in the Mediterranean basin (e.g. Mallet et al., 2013). In particular, black carbon (BC) is also recognized as an important SLCF/P due to its impact on solar and thermal radiation and on human health (UNEP and WMO, 2011).

Several studies in Europe have been carried out to investigate the impact of air-mass transport to atmospheric composition variability in the free troposphere as deduced by observations at high mountain observatories. As an instance, Cuevas et al. (2013) investigated the impact of long-range transport processes to long-term surface O_3 at the subtropical high mountain station Izaña (Canaries, 2373 m a.s.l.). By using air-mass back-trajectories and by analysing the O_3-CO relationship, these authors suggested significant impact of anthropogenic emissions from North America to O_3 variability. Similarly, Balzani Lőöv et al. (2008) estimated background concentrations of trace gases at the Jungfraujoch Alpine station (Switzerland, 3580 m a.s.l.) by using backward trajectories and atmospheric compound variabilities, showing that “primary” compounds appeared to be greatly influenced by long range transport during winter, while “secondary” compound levels and photochemistry impact increase until summer. For the same site, Collaud-Coen et al. (2011) investigated 14 years of meteorological parameters, aerosol variables (absorption and scattering coefficients, aerosol number concentration) and trace gases (CO, NO_x,SO_2) as a function of different synoptic weather types providing a quantification of air-mass export to the free troposphere. Moreover, Herrmann et al. (2015) investigated the influence of free troposphere and boundary layer on aerosol size distribution at Jungfraujoch, by analyzing the last contact of air-masses with PBL (by using the FLEXPART dispersion model) and variability of NOy/CO ratio used to estimate the “age” of air masses. They found that number concentration of particles larger than 90 nm were strongly affected by PBL which influences the measurement site especially during summer. During the Pic 2005 field campaign (13 June – 7 July 2005), Gheusi et al. (2011) investigated the question of the vertical layering of O_3 in a mountain area by an experimental set-up combining in situ ground-based observations at the high mountain station Puy du Midi (2875 m a.s.l., French Pyrenees) with O_3 lidar at two lower sites in close vicinity. They provided evidences that mixing with free-tropospheric air, photochemistry and surface deposition in the valleys should be considered for accounting quantitatively for the observed O_3 variations.

Through PEGASOS intensive field campaign, it was possible to shed light on the typical level and variability of trace gases and aerosol properties as a function of transport regimes and proximity with emission sources, thus offering new insights into the sources of atmospheric pollutants and climate forcers above the central Mediterranean Basin during summer season. In particular, for the first time, NO_x measurements have been used to disentangling the proximity of emission sources related to anthropogenic pollution observed at CMN. We also provide a set of information useful for the implementation of early-warning services based on background in-situ observations as well as for the definition of observation-based diagnostics for model validation, by identifying a set of “optimal” parameters useful for detection of different air-mass transport processes at CMN.

2. Material and methods

The measurements analysed in this paper were carried out at the Italian Climate Observatory “O. Vittori”, a research infrastructure which is part of the Mt. Cimone GAW/WMO Global Station (GAW ID: CMN, see www.isac.cnr.it/cimone). For all the observed