Atmospheric Environment 101 (2015) 23–33

Contents lists available at ScienceDirect

Atmospheric Environment

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

Long-term surface ozone variability at Mt. Cimone WMO/GAW global station (2165 m a.s.l., Italy)

P. Cristofanelli [a, *], H.-E. Scheel [b], M. Steinbacher [c], M. Saliba [d], F. Azzopardi [d], R. Ellul [d], M. Fröhlich [e], L. Tositti [f], E. Brattich [f], M. Maione [g], F. Calzolari [a], R. Duchi [a], T.C. Landi [a], A. Marinoni [a], P. Bonasoni [a]

[a] *National Research Council of Italy, Institute for Atmospheric Sciences and Climate, 40129 Bologna, Italy*
[b] *Karlsruhe Institute of Technology, IMK-IFU, 82467 Garmisch-Partenkirchen, Germany*
[c] *Laboratory for Air Pollution/Environmental Technology, Empa – Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland*
[d] *Atmospheric Research, Physics Department, University of Malta, Msida MSD 2080, Malta*
[e] *Luftreinhaltung & Klimaschutz, Umweltbundesamt GmbH, Spittelauer Lände 5, 1090 Wien, Austria*
[f] *Laboratory of Natural Radiochemistry, Chemistry Department, Bologna University, 40126 Bologna, Italy*
[g] *Dipartimento di Scienze di Base e Fondamenti (DiSBeF), University of Urbino "Carlo Bo", Urbino, Italy*

HIGHLIGHTS

- We analysed 19 years of surface O_3 data at the Mt. Cimone station (2165 m, Italy).
- High O_3 values were observed during summer in the Mediterranean region.
- NAO variability appeared to affect winter O_3, while heat-waves affected summer O_3.
- O_3 increased over 1991–2011 but no trends were detected for the 1996–2011.
- Summer O_3 growth-rates showed a slowing-down in recent years.

ARTICLE INFO

Article history:
Received 19 June 2014
Received in revised form
3 November 2014
Accepted 5 November 2014
Available online 6 November 2014

Keywords:
Ozone
Trends
Mediterranean basin
Heatwave
Italy

ABSTRACT

The Mediterranean basin represents a hot spot area for short-term O_3 distribution and anthropogenic contributions to it. This is why we analysed in this work the surface O_3 variability observed at Mt. Cimone WMO/GAW global station (CMN, 44°12′ N, 10°42′ E, 2165 m a.s.l., Italy) from 1991 to 2011. The measurements performed at this mountain observatory represent the longest surface O_3 record at a baseline site in the Mediterranean basin.

Monthly O_3 averages at CMN show a typical seasonal cycle characterised by a winter minimum and a spring – summer maxima. The shape of the mean annual variation of O_3 is well comparable with those observed at other four baseline sites in the Alps and in the Mediterranean region: Jungfraujoch – Swiss Alps, Sonnblick – Austrian Alps, Mt. Krvavec– Slovenia and Giordan Lightouse – Island of Gozo, Malta. In general, O_3 levels at CMN show higher values during warm months, which is likely to be related both to vertical transport of polluted air-masses at regional and continental scales and to enhanced photochemistry.

Here, we also investigate the influence of specific atmospheric processes (i.e. the occurrence of heat-waves, North Atlantic Oscillation, thermal transport of air-masses from the regional PBL and stratospheric intrusions) in affecting O_3 variability at CMN.

Overall, a significant positive (95% confidence level) linear trend in monthly O_3 mole fraction was observed over the period 1991–2011 (0.21 ± 0.10 nmol/mol yr^{-1}) while no trend (-0.02 ± 0.12 nmol/mol yr^{-1}) was detected for the 1996–2011, when measurements were carried out by an homogeneous

---

* Corresponding author.
E-mail address: p.cristofanelli@isac.cnr.it (P. Cristofanelli).

http://dx.doi.org/10.1016/j.atmosenv.2014.11.012

experimental set-up. On a seasonal basis, a positive trend has been observed for 1996–2011 (0.34 ± 0.32 nmol/mol yr^{-1}) only for spring. Significant decreases of the seasonal O_3 growth-rates have been detected at CMN during 1991–2011 from winter to spring and only for summer during 1996–2011.

1. Introduction

Tropospheric ozone (O_3) is an atmospheric key compound. It is recognised as a powerful greenhouse gas (Forster et al., 2007), it influences the oxidation capacity of the troposphere and it affects the population health as well as the ecosystem integrity and crop yields (The Royal Society, 2008). Levels of tropospheric O_3 at regional scale are strongly affected by anthropogenic emissions (UNEP and WMO, 2011). Stratosphere Troposphere Exchange (STE) and lightning production represent the main natural tropospheric O_3 sources (e.g. Wild, 2007); the intrusion of stratospheric air-masses into the troposphere (hereinafter SI) affect O_3 variability at mountain sites (e.g. Cui et al., 2009; Trickl et al., 2010). O_3 is also a short-lived climate forcer because it is an effective greenhouse gas. Thus, any action which leads to the decrease of O_3 precursor emissions, mainly methane, would represent a very effective action to mitigate the anthropogenic impacts on the Earth climate (UNEP and WMO, 2011).

The Mediterranean basin represents a hot spot area for short-term O_3 distribution and anthropogenic contributions to it (Lelieveld et al., 2002; Kanakidou et al., 2011). Because of the typical anticyclonic conditions of the Mediterranean basin, intensive O_3 photochemical production events frequently occur in this region during the warm season (Vautard et al., 2005). Recent investigations also pointed out the role of downward air-mass transport from the stratosphere/upper troposphere in affecting summertime free-tropospheric Mediterranean O_3 (e.g. Zanis et al., 2014).

In this work we present and analyse the long-term time series of surface O_3 observations carried out at Mt. Cimone World Meteorological Organization (WMO)/Global Atmosphere Watch (GAW) global station (Italy) from 1991 to 2011. The study aims at providing information on long-term surface O_3 variability at this high mountain site which, being located South of the Alps in the Apennines, can be considered as representative (especially during the cold months) of the Mediterranean basin/southern Europe (MB/SE) free troposphere.

2. Material and methods

2.1. Measurement site

Mt. Cimone (44.18 N, 10.70 E, 2165 m a.s.l.) is the highest peak of the Italian northern Apennines (Fig. S1 of the supplementary data). The surface O_3 measurements presented in this work have been mainly carried out at the “O. Vittori” Italian Climate Observatory (ICO-OV), an atmospheric observatory operated by the Institute of Atmospheric Sciences and Climate of the National Research Council of Italy (ISAC-CNR), part of the Mt. Cimone WMO/GAW global station (GAW ID: CMN). As reported by previous investigations the atmospheric observations carried out at CMN can be considered representative of the free tropospheric conditions of the MB/SE during the cold months (see e.g. Bonasoni et al., 2000; Henne et al., 2010). However, during warm periods throughout the year, the measurement site can be affected by “thermal” and convective transport of planetary boundary layer (PBL) air masses related with the development of daytime slope and valley winds as well as PBL growth and entrainment processes (Colombo et al., 2000; Cristofanelli et al., 2009).

2.2. Surface O_3 measurements

At CMN, the first surface O_3 measurements were carried out in the period 1991–1993 by ISAC-CNR at the Air Force Meteorological Observatory, which is located about 50 m higher than the current location of the measurement site (see the Supplementary Data for more details and Table S1 for a summary of major changes concerning the experimental set-up and calibration methodologies). The experimental set-up consisted of a UV-analyser Dasibi 1108 W/GEN, which continuously sampled ambient air from a non-heated Teflon sampling head.

After an interruption between 1993 and 1994, measurements of O_3 started on a regular basis in January 1996 and are still ongoing at the ICO-OV, using the same analyser but with an improved sampling system (see the Supplementary Data). Parallel measurements of O_3 at the two locations for comparison are unfortunately unavailable. Good practice and quality control protocols in O_3 measurement however support a reasonable comparability of data collected in the two periods in spite of the different measurement location. Moreover, station logbooks have been collected since 1991 and information on maintenance interventions, execution of calibration as well as major problems is available.

For both measurement periods a complete description of Quality Assurance and Quality Control (QA/QC) procedures, sampling systems, instrumental set-up and adopted reference scales are available in the Supplementary Data (Table S1). On September 2010, the QA/QC procedures, the measurement system and related protocols were successfully assessed by WMO World Calibration Centre WCC-Empa (Zelwegger et al., 2012). Surface O_3 data series for CMN (1-h average values) at the ICO-OV from 1996 to 2011 are available at the World Data Centre for Greenhouse Gases (http://ds.data.jma.go.jp/gmd/wdcgg/).

2.3. Heatwave identification

As reported by Cristofanelli et al. (2007), at CMN significant contributions to high O_3 can be traced back to heat waves (HWs) in combination with efficient transport of polluted air masses on both the regional and the continental scales. An HW is a prolonged period of excessively hot weather over a region and it is a well-known meteorological feature of the Mediterranean summer (Wang et al., 2011). These events are recognized to cause great costs in terms of human health and environmental hazard (e.g. EEA, 2012).

There is not a common accepted definition of HW. Thus to unambiguously identify HWs which affected the north of Italy, we analysed the time series of daily mean and maximum temperature at three ground level locations in the Po valley, i.e. Verona (45°23′N 10°53′E), Milano (45°26′N 9°17′E) and Bologna (44°32′ 11°18′). In particular, we categorized as being influenced by HWs the warm periods (April–September) when simultaneously identified by the following ECA&D (European Climate Assessment and Dataset) and WMO selection methodologies:

(1) ECA&D: a period of at least 6 days with daily mean temperature above the upper tenth percentile of the temperature distribution for each of the calendar days (Klein Tank et al., 2002);
(2) WMO: a period of at least 6 days with the daily maximum temperature greater than 5 °C above the climate normal (CliNo) maximum temperature.

In this work, CliNo was calculated over 1971–2000 reference period with the purpose of taking into account recent variations of the observed global air temperature (e.g. Brunetti et al., 2006). With the aim to minimize local influences and to consider only events at the regional scale, we considered the periods characterised by the simultaneous occurrence of HW at the 3 above-named low-land stations.

2.4. Stratospheric intrusion identification

In order to investigate the influence of SI on the long-term O_3 variability at CMN, we selected the days influenced by these events by analysing the behaviour of the following stratospheric tracers available at CMN (see Cristofanelli et al., 2006): in-situ Beryllium-7 (^{7}Be) and relative humidity (RH), equivalent potential vorticity (PV) of air-masses reaching the measurement site (as deduced by the analysis of 7-day 3D FLEXTRA back-trajectories) and total column O_3 (TCO) over CMN location (as deduced by TOMS and OMI overpass data). Based on the methodologies proposed in Cristofanelli et al. (2006) we identified days with likely influence by SI when these stratospheric tracers exceeded specific threshold values. More details about the determination of these stratospheric tracers and the algorithm to select SI-influenced days can be found in the Supplementary Data.

3. Results

3.1. Seasonal O_3 cycle at Mt. Cimone

O_3 monthly average values showed a typical seasonal cycle characterised by a winter minimum and a spring - summer maximum, often resulting in a broad spring-summer peak (Fig. 1). This is a typical continental annual cycle (Gilge at al., 2010; Tarasova et al., 2007) which differs from Northern hemisphere remote sites where a spring maximum in April/May is usually observed (Monks, 2000; Tarasova et al., 2007). The observed broad spring/summer maximum is considered to be a combination of background "hemispheric-scale" impact and photochemical production from regional emissions (e.g. Zanis et al., 2007; Monks et al., 2009), especially in summer: as recently assessed by Cristofanelli et al. (2013), 19% of O_3 variability at CMN during May–September can be attributed to anthropogenic precursor emissions and enhanced photochemistry.

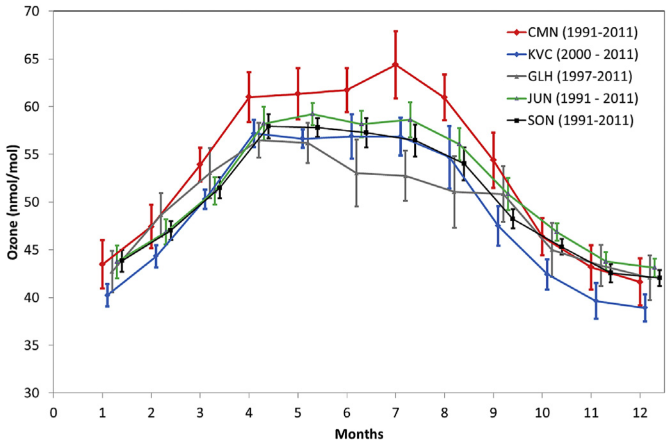

Fig. 1. Average O_3 monthly mean values at CMN and at other baseline sites in the Alpine and Mediterranean basin (Mt. Krvavec- KVC; Sonnblick – SON; Jungfraujoch – JUN; Malta/Giordan Lighthouse – GLH). The vertical line denotes the expanded uncertainty of the mean ($p < 0.05$ and $k = 2$). In the legend, for each station, we reported the periods over which average values were calculated.

With the aim of better understanding the surface O_3 at CMN in the Mediterranean basin, we compared the mean annual cycle with those observed at other WMO/GAW baseline measurement sites (Fig. 1): Sonnblick – Austrian Alps (SON: 47°03′N; 12°57′E, 3106 m a.s.l.), Jungfraujoch – Swiss Alps (JUN: 7°59′N; 46°32′E; 3580 m a.s.l.), Mt. Krvavec –Slovenia (KVC; 46°18′N, 14°32′E, 1720 m a.s.l.) and Giordan Lighthouse – Malta (GLH; 36°04′N; 14°13′E, 167 m a.s.l.). Experimental details and environment classification for these stations can be found in the Supplementary data (Table S2). Data from these stations have been obtained from the World Data Centre for Greenhouse Gases (WDCGG, http://gaw.kishou.go.jp/wdcgg) as hourly mean values for 1991–2011 (for SON and JUN), 1997–2011 for GLH and 2000–2011 for KVC. While CMN, JUN, SON and KVC are mountain stations, GLH is a marine station located at a significant lower latitude than CMN and more than 900 km southwards: this should be clearly keep in mind when comparing O_3 at GLH with CMN. JUN and SON are located at a higher elevation than CMN and more than 300 km northwards, while KVC is lower than CMN, with a possible larger influence of PBL air-masses, and more than 400 km north-eastwards (see Fig. S1 in the Supplementary Data for a map showing all station locations). Thus it is possible to expect differences in the O_3 mole fraction at these stations arising from local and regional scale dynamical as well as chemical processes.

The shape of the mean annual variation of O_3 at CMN is well comparable with the one observed at the other baseline sites in the Alps as well as at KVC and GLH, which are also characterised by a broad spring-summer maximum (with monthly mole fraction from 56 to 58 nmol/mol) and a winter minimum (39–40 nmol/mol). With the aim of pointing out specific features of the surface O_3 variability at CMN compared to the other baseline stations, we computed the differences of monthly O_3 values between CMN and the other stations. Mean yearly bias ranged from 1.5 ± 4.3 nmol/mol ($\pm 1\sigma$) and 3.2 ± 4.5 nmol/mol against JUN and SON to 5.0 ± 4.0 nmol/mol and 5.0 ± 6.9 nmol/mol against KVC and GLH. These biases did not change significantly considering only the data from the year 2000, i.e. when surface O_3 data were simultaneously available for all the measurement sites. These station biases were fairly conserved without substantial discrepancies also from year to year. In general, the differences maximized during summer months (see Fig. 1), indicating a systematic occurrence of higher O_3 mole fraction at CMN. As will be discussed later, this is likely to be related with the occurrence of elevated O_3 associated with uplift of polluted air masses at regional and continental scales (Cristofanelli et al., 2006, 2013; Tositti et al., 2012). The differences are particularly evident in comparison with the marine station GLH, with an average excess of 11.7 nmol/mol in August. It should be noted that, being representative of maritime conditions (see also Tarasova et al., 2007), GLH is characterised by the lowest average summer O_3 among the considered stations. However, it is noteworthy that CMN O_3 is higher also in respect with measurement stations located at higher altitudes (i.e. JUN and SON), which should be characterised by higher mole fraction given the vertical gradient in tropospheric O_3 (e.g., Logan, 1999; Chevalier et al., 2007; Parrish et al., 2012). On a seasonal basis, for JUN and SON, these biases are highest during summer (4.3 ± 3.4 nmol/mol and 6.7 ± 3.8 nmol/mol, respectively) and lowest in winter (−1.0 ± 3.3 nmol/mol and 0.1 ± 2.9 nmol/mol, respectively). This confirms that during the cold months, when the atmosphere is more stable and photochemistry is less efficient, O_3 mole fraction at CMN is consistent with those observed at the other baseline sites and thus reflects the regional baseline of the lower free troposphere of southern Europe.

3.2. Long-term O_3 variability

Long-term O_3 time series at CMN (1991–2011) is illustrated in Fig. 2a as monthly mean values calculated based on the 1-h average values with a 75% data coverage criterion. The overall O_3 mean value is 53.4 ± 9.0 nmol/mol. CMN data series from 1991 to 1993 has not been presented before. As stated before, we are conscious that the change of the sampling site between the two time series might affect data homogeneity and that the presence of data gap extending from more than 2 years can potentially cause artefacts in the environmental trends. Therefore on account of the lack of similar measurements in remote regions of the Mediterranean basin in the same period, we decided to take the risk and to include the 1991–1993 data set in this analysis.

3.2.1. Comparison with other baseline measurement sites

Monthly mean O_3 anomalies relative to 1997–2003 were calculated to compare long-term O_3 variations at CMN with those at other baseline sites in the Alpine region/Mediterranean basin (Fig. 2b). We decided to use this reference period to calculate the monthly anomalies so as to compare them with the results provided by Logan et al. (2012) who analysed long-term changes in O_3 over Europe from 1990 to 2010.

In agreement with the measurements at CMN, low monthly O_3 mole fractions were also observed at other high mountain stations in the Alps before 1994 (see also Table 1), suggesting that this is a broad-scale O_3 feature that affected the Alps and the north Apennine regions during these years. In good agreement with Logan et al. (2012), for CMN and the other measurement sites, a low O_3 variability was observed from 1998 to 2004 (except for April 2011 when negative O_3 anomalies of −7.8 nmol/mol affected CMN), while mostly negative anomalies were observed from mid-2008 until 2011 at CMN (average values: −1.8 nmol/mol).

Table 1
Monthly mean average O_3 with expanded uncertainties ($p < 0.05$) of the means at CMN, Jungfraujoch (Switzerland: 46.54°N, 7.98°E; 3580 m a.s.l.) and Sonnblick (Austria: 47.05°N, 12.95°E, 3106 m a.s.l.) WMO/GAW stations during 1991–1993 and 1996–2011.

Measurement site	1991–1993	1996–2011
CMN	48.0 ± 3.4	54.1 ± 1.2
JUN	46.5 ± 2.1	50.7 ± 0.9
SON	47.2 ± 2.3	52.6 ± 0.9

Differently from other stations, an almost uninterrupted period of positive O_3 anomalies was recorded at CMN from February 2004 to May 2008, when O_3 was considerably higher (average excess: +6 nmol/mol) (Fig. 2b): 76% of these monthly anomalies presented statistically significant higher values in respect to the average anomalies observed at the other stations. An exceptional high positive anomaly was observed at CMN on July 2006 (monthly O_3 mean: 82.3 nmol/mol). As shown in the Section 3.2.2, these high O_3 values were related to a strong HW which affected western, central and southern Europe (EEA, 2007). The HW signal on O_3 was also well discernible at KVC (O_3 anomaly: 8.0 nmol/mol), JUN (8.7 nmol/mol) and SON (9.3 nmol/mol), thus pointing out the broad spatial extension of this event.

3.2.2. Influence of summer heat-waves to the O_3 variability

The application of the selection methodology presented in Section 2.3, led to the identification of 13 HWs during the period 1991–2011 (Table 2). It is interesting to notice that all the identified events were recorded in the time window 1996–2011. Totally, during the period 1991–2011, 115 days were found to be affected by

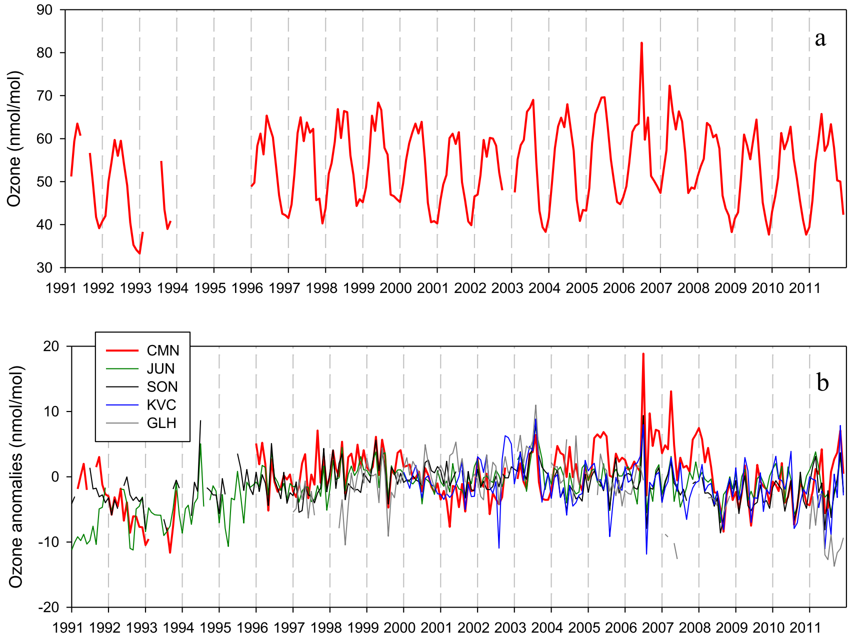

Fig. 2. (a) Time series of monthly mean O_3 mole fractions at CMN (only months with a data coverage of at least 75% are reported). (b) Time series of monthly mean O_3 anomalies relative to period 1997–2003 for CMN (red line) and other baseline stations in the Mediterranean basin.

Table 2
List of HWs identified in northern Italy from 1991 to 2011. For each year (column 1), we report the detected events in terms of start day (column 2), end day (column 3), time length (column 4). Moreover, we report the average O_3 value recorded during each HW (mean ± 1σ, column 5) and, for reference, the corresponding mean seasonal O_3 value (mean ± 1σ, column 6).

Year	Start day	End day	Time length (days)	Average O_3 (nmol/mol)	Mean seasonal O_3 (nmol/mol)
1996	08/06/1996	13/06/1996	5	78.6 ± 16.9	61.7 ± 8.8
2002	16/06/2002	24/06/2002	8	66.0 ± 10.1	58.8 ± 6.0
2003	05/05/2003	09/05/2003	4	58.4 ± 6.5	57.6 ± 7.8
	07/06/2003	26/06/2003	19	67.2 ± 14.2	66.7 ± 10.5
	08/08/2003	14/08/2003	6	79.8 ± 7.3	66.7 ± 10.5
2005	22/06/2005	28/06/2005	6	73.6 ± 8.7	66.7 ± 9.7
2006	17/06/2006	28/06/2006	11	62.2 ± 14.9	65.2 ± 11.9
	20/07/2006	28/07/2006	8	95.6 ± 15.8	65.2 ± 11.9
2007	10/04/2007	18/04/2007	8	73.1 ± 6.3	64.4 ± 11.5
2008	22/06/2008	27/06/2008	6	62.9 ± 6.8	59.4 ± 8.3
2009	18/05/2009	26/05/2009	8	54.3 ± 10.3	56.8 ± 8.1
2011	19/08/2011	26/08/2011	8	68.0 ± 7.3	58.9 ± 8.0
	10/09/2011	17/09/2011	8	58.0 ± 7.1	52.2 ± 7.7

this type of events with frequency peaks in June representing the month for which HWs are the most frequent.

Most of the identified HWs (10/13) were characterised by significant O_3 increase at CMN in comparison with the average seasonal levels (Table 2), suggesting that these events are conducive for the occurrence of high O_3. As shown in previous works (Cristofanelli et al., 2007 and Cristofanelli et al., 2009) these high O_3 values can be explained by considering photochemical O_3 production directly related to anthropic activities or to positive feedbacks between heatwave weather conditions and O_3 production efficiency (e.g., increased biogenic emissions, increased forest fires, decreased O_3 uptake by vegetation). During HWs, the large vertical extension of the PBL could enhance the transport of these PBL air masses to altitudes that would usually be in the free troposphere. Major HWs affected northern Italy and CMN on June 2005–2006, July 2006, April 2007 and May 2008, when very high monthly O_3 anomalies were observed at CMN and significant higher O_3 was observed compared to the other baseline stations (Fig. 2b).

3.2.3. Influence of the North Atlantic Oscillation (NAO) to O_3 variability

As reported by Lin et al. (2014), tropospheric O_3 is affected by climatic variability signatures acting from the interannual to the decadal scale. The North Atlantic Oscillation (NAO), i.e. a north-south shift (or vice versa) in the track of storms and depressions across the North Atlantic Ocean and into Europe, has been shown to influence winter and summer climate over the Mediterranean basin (Wang et al., 2011). Due to the effect on circulation patterns and meteorological conditions in the Mediterranean basin, a potential influence on tropospheric O_3 is expected too (see e.g. Pausata et al., 2012; Cuevas et al., 2013). With the aim of pointing out a possible relationship between NAO variability and tropospheric O_3 at CMN, we investigated the correlation between the seasonal NAO Index (Hurrell et al., 2001) and the anomalies of seasonal O_3 for the period 1996–2011 (Fig. 3). We found a positive correlation between NAO Index and winter O_3 (r: 0.49 ± 0.18; a: 1.29 ± 0.70, $p = 0.05$), while a positive but not statistically significant correlation was found for summer (r: 0.44 ± 0.13; a: 1.29 ± 0.70, $p = 0.09$). No clear tendencies were observed both for spring (r: 0.08 ± 0.01; a: 0.21 ± 0.74, $p = 0.77$) and fall (r: 0.02 ± 0.01; a: 0.05 ± 0.85, $p = 0.95$). It is noteworthy that the large positive O_3 anomalies observed during winter 2007 and 2008 were both associated to strongly positive NAO index values. These winter values were also characterised by the highest average air-temperature (+5.0 °C and +3.7 °C, respectively) observed at CMN during the period 1996–2011 (average value: 0.85 ± 0.65 °C), suggesting the occurrence of anomalous meteorological regimes at the measurement site. This can be related to the expansion of the Azores anticyclone towards the Mediterranean basin and CMN location (e.g. Pausata et al., 2012), possibly triggering anomalous favourable conditions for photochemical O_3 production and vertical transport even during winter period.

3.2.4. Influence of thermal transport to the O_3 variability

Diurnal thermal transport of air-masses from the regional PBL can significantly influence O_3 values at CMN, especially during warm months (see Supplementary Data) as previously assessed for both CO_2 (Colombo et al., 2000) and airborne particulate matter (Marinoni et al., 2008) at this station. To investigate the occurrence of periods characterised by significant contributions from these processes to the O_3 interannual variability, we analysed long-term variations of the seasonal O_3 diurnal cycle: Fig. 4 reports the average seasonal diurnal O_3 anomalies from 1996 to 2011 computed relatively to the reference period January 1997–December 2003 (see Section 3.2). The large monthly anomalies observed at CMN in spring 2005 and summer-spring-autumn 2006 (Fig. 2b), were related to the presence of statistically significant (at the 95% confidence level) anomalies (up to 8 nmol/mol on an hourly basis) during the afternoon-evening time frame (roughly from 15:00 to 22:00); this suggests that for these periods a significant amount of photochemically-produced O_3 was vented to CMN by thermal transport processes.

3.2.5. Influence of stratospheric air-mass intrusions to O_3 variability

Based on the screening approach presented in Section 2.4, a total of 372 days were found to be potentially affected by SI over the period 1996–2011 (6% of the whole period). Fig. 5a reports the frequency of occurrence of SI-influenced days at CMN: on average the highest frequency of SI-influenced days was observed in winter (10%) with a minimum in summer (3%), in good agreement with the earlier work by Cristofanelli et al. (2006). Except that during the summer season, the SI affected days showed significant higher O_3 values than the remaining days (Table 3). Long-term variability of SI-influenced days showed a maximum occurrence during winter–spring 2002 (21.1% and 20.6%) and autumn 2006 (14.2%), when high O_3 monthly anomalies were observed at CMN (Fig. 2). A period characterised by a relatively low number of SI-influenced days was observed from 2009 to 2011, when a prevalence (83%) of negative SI-occurrence seasonal anomalies was detected (10/12). Fig. 5b reports the normalized seasonal anomalies (with respect to the 1996–2011 period) of O_3 recorded during detected SI (O_3^{SI}) together with their 12-month running means (O_3^{SI}- RM) as well as the running mean of the normalized seasonal anomalies of all O_3 data (O_3-RM). No evident correlations existed between O_3^{SI} and O_3 over

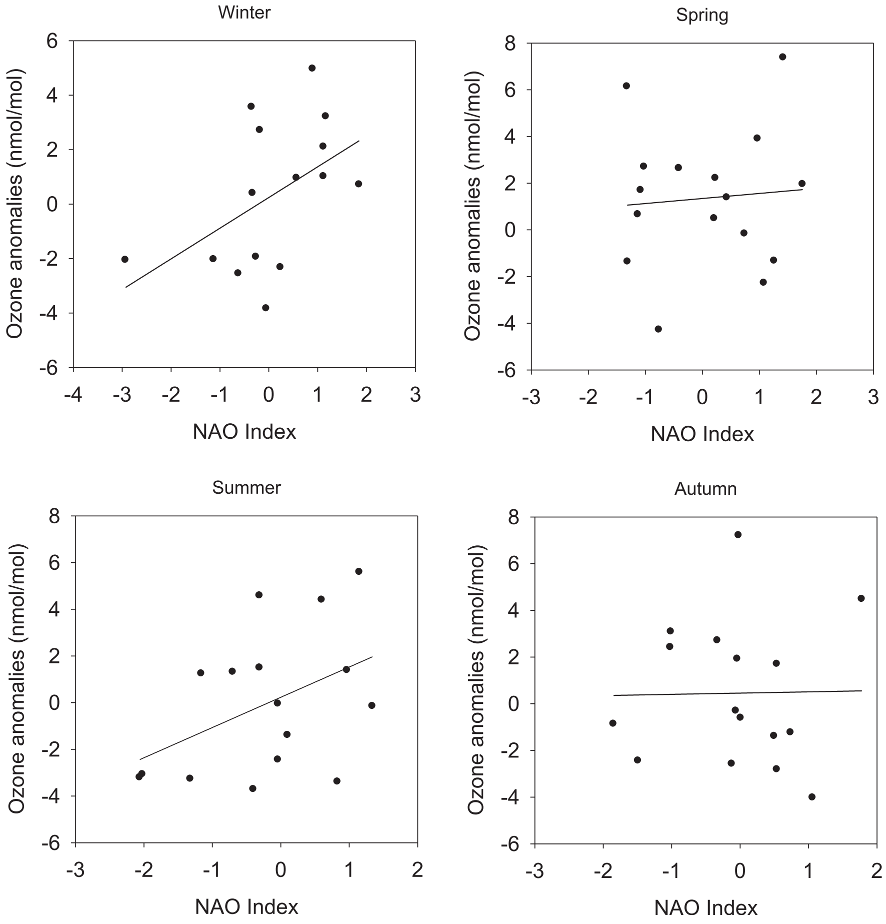

Fig. 3. Correlation analysis between seasonal ozone anomalies and seasonal NAO Index for the period 1996–2011 (Hurrell et al., 2001).

the period 1996–2011 (r: 0.01 ± 2.18; a: −0.05 ± 0.24). Despite a rather stable frequency of SI occurrence at CMN (see Fig. 5a), an upward tendency of O_3^{SI} was observed from 2002 to 2010. This lead to a significant positive correlation with overall O_3 (r: 0.48 ± 0.28; a: 0.52 ± 0.25, $P < 0.05$) over the period 2001–2006. This correlation is lost when considering the most recent years 2007–2011, when a negative (not statistically significant) correlation appeared between O_3^{SI} and O_3 (r: −0.10 ± 0.21; a: −0.31 ± 0.44).

3.3. *Long-term trend evaluation at CMN*

Since the Mediterranean basin represents a very important region in terms of climate and air composition changes, in this work we provided a first assessment on the possible existence of long-term O_3 trends at CMN.

Since as previously explained, we cannot completely rule out the non-homogeneity in the O_3 data from the earlier and from the ongoing long-term series at CMN station and with the aim of taking into account the existence of a long data gap from 1994 to 1995, we analysed trends of surface O_3 in a "segmented" way: linear regressions of monthly mean anomalies were calculated over two reference periods:

(a) over the whole measurement period, also encompassing the earlier measurements (1991–1993) performed at the Air Force Observatory, i.e. 1991–2011 assuming overall data homogeneity;

(b) over the period for which measurements were continuously carried out in a rigorously homogeneous way i.e. at the ICO-OV, i.e. 1996–2011.

The monthly mean anomalies have been calculated using the original time resolution (i.e. 1-hour mean values). With the aim of evaluating the statistical significance of the calculated trend, 95% confidence level of the growth rates has been calculated as $\pm 2\sigma$. The statistical significance of a trend is also determined based on two-sided t-test as recently done by Gilge et al. (2010). In the following, we adopt the terminology "trend" only for statistically significant growth rates, otherwise the notation "tendency" is used.

As previously described before, surface O_3 at CMN can be significantly influenced by vertical air-mass mixing related with diurnal thermal processes (especially during the warm season). With the aim of specifically investigating possible long-term changes of O_3 as a function of the different diurnal phases of this vertical mixing, we performed trend analysis for different sub-sets: "all data", "night-time" data (from 23:00 to 4:00 UTC + 1), "day-time" data (from 11:00 to 16:00 UTC + 1) and "evening" data (from 17:00 to 22:00 UTC + 1). In particular, the last time-window has been selected to take into account for the occurrence of the maximum O_3 values usually observed at CMN during episode of polluted air-mass transport by thermal circulation (see Section 3.2.3 and Cristofanelli et al., 2013).

As reported in Fig. 6 and Table 4, positive trends characterised monthly O_3 mole fraction at CMN during the entire period, with averages slopes (0.21 ± 0.10 nmol/mol yr^{-1}) which were not

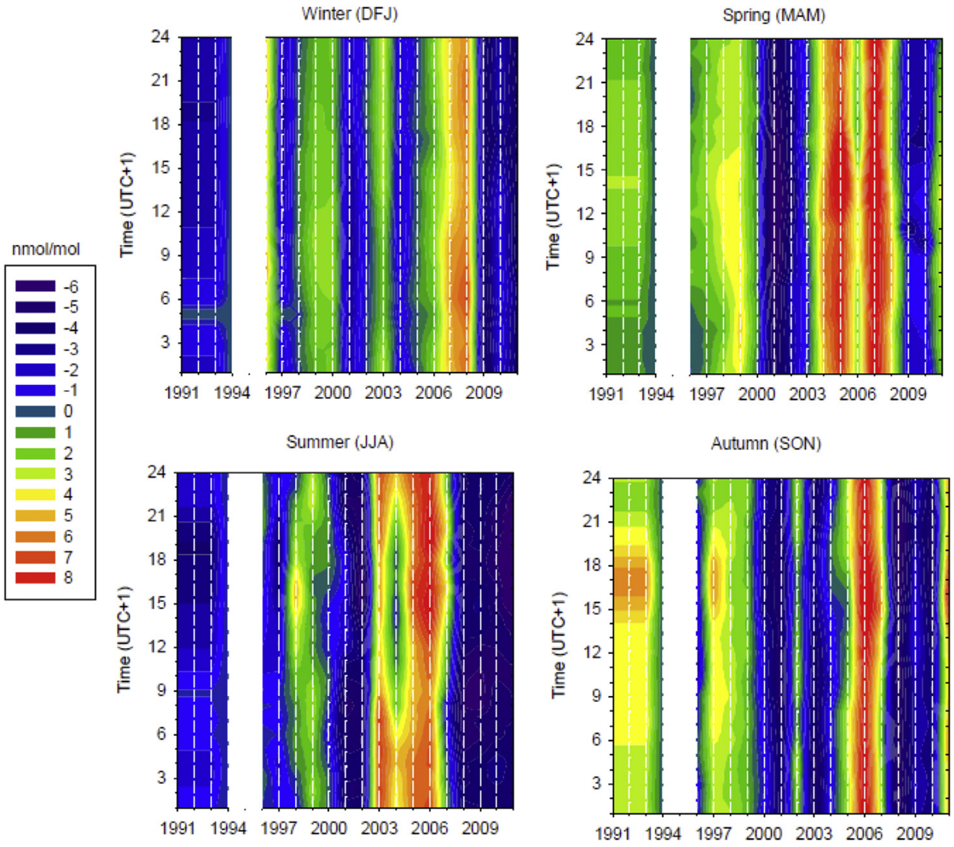

Fig. 4. CMN: Average seasonal diurnal O_3 anomalies over the reference period 1997–2003. The coloured scale reports the O_3 anomalies expressed as nmol/mol.

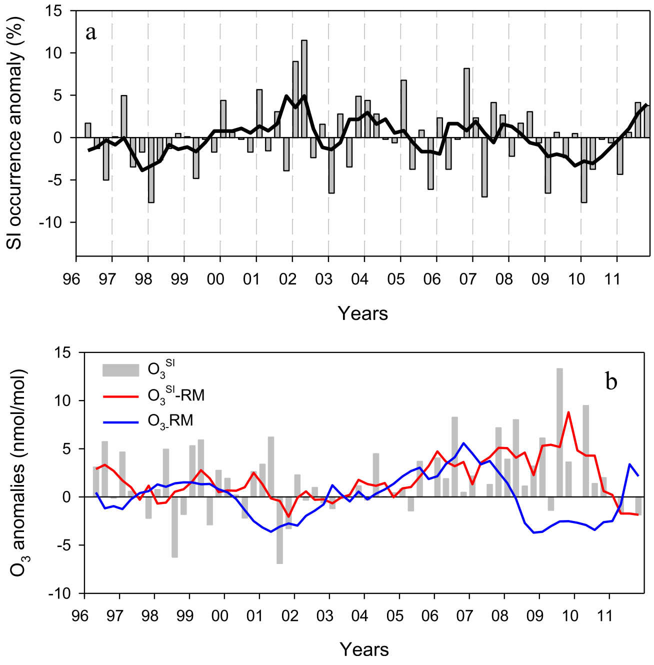

Fig. 5. (a) Normalized seasonal anomalies with respect to the 1996–2011 mean annual cycle of the stratospheric intrusion (SI) frequency (grey bars) together with their 12-month running means (black line). (b) Normalized seasonal anomalies of O_3 during SI (O_3^{SI}) with their 12-month running mean (O_3^{SI-RM}) and 12-month running means of overall O_3.

statistically different for the various daily time windows. These values appear to be in relatively good agreement with those observed at SON (0.22 ± 0.17 ppb yr^{-1}) from 1989 to 2007 (Gilge et al., 2010) but in contrast with those reported by Logan et al. (2012) for a “mean” composite alpine time series that did not show statistically significant annual trends for the period 1990–2009. As clearly shown by the time series of O_3 monthly anomalies (Fig. 6), the positive trends of 1991–2011 were strongly influenced by the presence of negative values occurring during the years 1991–1993. No significant differences have been observed as a function of the different monthly percentiles (Table 4).

When the period 1996–2011 was considered, very small tendencies (not much different from zero) have been calculated both for the different time windows as well as for the different percentiles (Table 4). Also this finding appears to be in agreement with

Table 3
Average variations of O_3 in respect to the seasonal values for SI-influenced days (SI days) and remaining days (other days). For each seasons we also reported the expanded uncertainty of the mean (with $k = 2$) and the number of analysed days (N).

Season	SI days	Other days
All	3.2 ± 0.9 nmol/mol *N*: 372	−0.25 ± 0.8 nmol/mol *N*: 5188
Winter	2.8 ± 1.3 nmol/mol *N*: 134	−1.5 ± 0.5 nmol/mol *N*: 1180
Spring	3.9 ± 1.6 nmol/mol *N*: 103	−0.7 ± 0.5 nmol/mol *N*: 1305
Summer	−0.5 ± 2.6 nmol/mol *N*: 51	0.2 ± 0.6 nmol/mol *N*: 1399
Autumn	5.6 ± 2.5 nmol/mol *N*: 84	0.5 ± 0.6 nmol/mol *N*: 1304

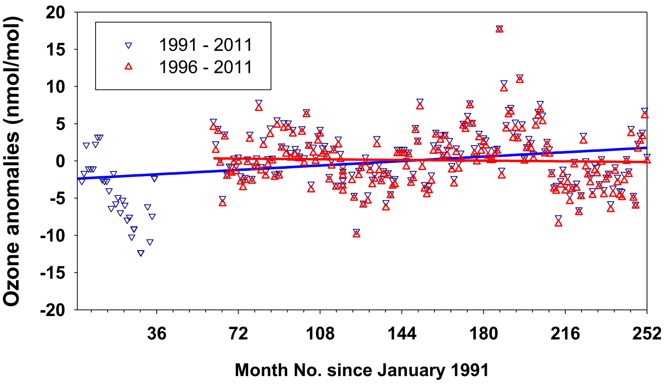

Fig. 6. Monthly O_3 anomalies and linear trend fitting (continuous lines) for the period 1991–2011 (blue) and 1996–2011 (red), based on the "all data" selection. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the results for the high-mountain alpine stations presented by Gilge et al. (2010) and Logan et al. (2012), which showed non-significant O_3 trends over the period 1995–2007 and 1995–2008, respectively. Not significant long-term O_3 trends were also detected by Saliba et al. (2008) at GLH (1997–2006).

O_3 trends have been also calculated on a seasonal basis (December–February: DJF; March–May: MAM; June–August: JJA; September–November: SON). For the period 1991–2011 a significant positive trend (0.34 ± 0.32 nmol/mol yr^{-1}) has been detected for spring, while only tendencies can be observed for other seasons (Table 5). This feature partially agrees with Logan et al. (2012), who show significant increase in O_3 for spring and winter for the "mean" alpine station time series between 1990 and 2009. On the other side Gilge et al. (2010) found positive tendencies at the Alpine high-mountain stations for spring and winter (statistically significant only for JUN) for the period 1995–2007.

It is interesting to notice that over the period 1996–2011 a negative tendency (even if not statistically significant) was recorded for all the data selections in summer. This result appears to be (at least qualitatively) in agreement with the decreasing O_3 trends observed at JUN (Logan et al., 2012) for summer 1998–2008 and with the decreasing tendencies observed at the Alpine stations reported by Gilge et al. (2010) over the summer 1995–2007.

With the aim of investigating the changes of the O_3 growth rate, following Parrish et al. (2012), we analysed the seasonal long-term variability by interpolating the annual mean O_3 averages with a polynomial quadratic fit for the period 1991–2011 (Fig. 7 top) and 1996–2011 (Fig. 7 bottom). In this case we decided to use average O_3 mole fraction instead of anomalies and considering the entire data-set of O_3 observations. This approach was chosen to fit the CMN analysis into the "global" picture provided by Parrish et al. (2012). As far as the quadratic regression is concerned, for the period 1991–2011, the results appeared to be broadly consistent with those reported by Parrish et al. (2012) for ZUG and JUN stations. Statistically significant negative values of the second order parameter ($d[O_3]/dt^2$) are found at CMN in all seasons except autumn, indicating a slowing of O_3 increase rate and maxima in the quadratic regression fits occurring in the early 2000s. In particular, by considering the confidence intervals, the CMN acceleration parameter overlaps with those at ZUG (0.054 ± 0.037 nmol/mol yr^{-2}) and JUN (0.062 ± 0.064 nmol/mol yr^{-2}) in spring, as well

Table 4
Analysis of O_3 trends at CMN. For different data selections (Column 1, see Section 2.1 for definition), and reference periods (1991–2011, 1996–2011), the statistical parameters describing the linear regression (slope ± 2σ expressed as nmol/mol yr^{-1}) are reported. Statistically significant trends are reported in bold.

Time period	1991–2011			1996–2011		
Data selection	25th	Mean value	75th	25th	Mean value	75th
All data	**0.22 ± 0.10** **r^2: 0.081**	**0.21 ± 0.10** **r^2: 0.061**	**0.22 ± 0.12** **r^2: 0.055**	−0.03 ± 0.12 r^2: 0.002	−0.02 ± 0.12 r^2: 0.002	−0.03 ± 0.14 r^2: 0.001
Day-time	**0.22 ± 0.09** **r^2: 0.079**	**0.22 ± 0.11** **r^2: 0.071**	**0.20 ± 0.11** **r^2: 0.050**	−0.03 ± 0.11 r^2: 0.001	−0.03 ± 0.12 r^2: 0.001	−0.04 ± 0.13 r^2: 0.002
Evening	**0.17 ± 0.10** **r^2: 0.051**	**0.17 ± 0.12** **r^2: 0.037**	**0.18 ± 0.16** **r^2: 0.022**	−0.04 ± 0.12 r^2: 0.002	−0.06 ± 0.14 r^2: 0.004	−0.04 ± 0.19 r^2: 0.001
Night-time	**0.22 ± 0.10** **r^2: 0.085**	**0.21 ± 0.10** **r^2: 0.067**	**0.22 ± 0.12** **r^2: 0.054**	−0.01 ± 0.12 r^2: 0.001	−0.02 ± 0.12 r^2: 0.005	−0.01 ± 0.14 r^2: 0.001

Table 5
Seasonal O_3 trends (slope ± 2 sigma) at CMN in nmol/mol yr^{-1}. Statistically significant trends are reported in bold. For different data selections (column 1, see Section 2.1 for definition), and reference periods (column 2), the statistical parameters describing the linear regression are reported for winter (DJF), spring (MAM), summer (JJA) and autumn (SON).

Data selection	Reference period	DJF	MAM	JJA	SON
All data	1991–2011	0.12 ± 0.34 r^2: 0.031	**0.34 ± 0.32** **r^2: 0.219**	0.11 ± 0.32 r^2: 0.033	0.17 ± 0.30 r^2: 0.001
	1996–2011	−0.14 ± 0.32 r^2: 0.050	0.07 ± 0.38 r^2: 0.013	−0.15 ± 0.38 r^2: 0.055	0.00 ± 0.34 r^2: 0.001
Night-time	1991–2011	0.20 ± 0.32 r^2: 0.088	0.17 ± 0.24 r^2: 0.103	0.09 ± 0.28 r^2: 0.025	0.15 ± 0.28 r^2: 0.060
	1996–2010	−0.08 ± 0.30 r^2: 0.020	0.09 ± 0.30 r^2: 0.023	−0.10 ± 0.32 r^2: 0.023	−0.09 ± 0.34 r^2: 0.020
Evening	1991–2011	0.30 ± 0.34 r^2: 0.163	0.12 ± 0.28 r^2: 0.040	−0.19 ± 0.39 r^2: 0.061	0.14 ± 0.36 r^2: 0.038
	1996–2010	0.01 ± 0.34 r^2: 0.001	0.03 ± 0.38 r^2: 0.002	−0.10 ± 0.42 r^2: 0.015	−0.11 ± 0.40 r^2: 0.022
Day-time	1991–2011	0.28 ± 0.38 r^2: 0.116	0.21 ± 0.26 r^2: 0.117	0.17 ± 0.34 r^2: 0.056	0.20 ± 0.32 r^2: 0.089
	1996–2010	−0.09 ± 0.32 r^2: 0.021	0.09 ± 0.36 r^2: 0.061	−0.14 ± 0.32 r^2: 0.045	−0.07 ± 0.39 r^2: 0.009

as that at JUN in summer (0.086 ± 0.077 nmol/mol yr^{-2}) and autumn (0.097 ± 0.048 nmol/mol yr^{-2}), as calculated by Parrish et al. (2012).

Considering the years 1996–2011, a statistically significant (negative) acceleration is found only for the summer. As pointed out by Parrish et al. (2013), the seasonal differences in long-term O_3 changes at northern mid-latitudes could lead to a change of O_3 seasonal cycle over the time. Actually, this can be also observed at CMN concerning the season on which the maximum mean average O_3 values are usually observed: while until year 2005 a robust summer maximum characterised the CMN yearly cycle, more recently spring maximum or nearly equivalent spring–summer seasonal maximum have been observed.

4. Discussion and conclusions

Surface O_3 observations carried out at Mt. Cimone WMO/GAW global station (CMN, 44°12′ N, 10°42′ E, 2165 m a.s.l., Italy) from 1991 to 2011 were studied. Given a 2-year data gap (1994–1995), a sum of 19 full years of O_3 measurements were available for statistical analysis. During warm months, CMN appears to be characterised by average positive biases with respect to the other baseline stations considered in this study. This can be partially explained by the particular location of CMN, directly facing to the Po basin, one of the world's hot-spots in terms of anthropogenic O_3 pollution which during the warm months can be efficiently transported towards higher altitude by thermal transport (Cristofanelli et al., 2009, 2013). As reported by the European Environmental Agency (EEA, 2012), emission sources, chemical composition of the air, and climatic conditions along the north-south and east-west gradients in Europe result in considerable regional differences in O_3 mole fraction with the highest number of high O_3 levels occurring more and more frequently in the Mediterranean region than in northern Europe. In fact, the occurrence of major HWs over northern Italy, favoured the systematic occurrence of high O_3 conditions at CMN, due to the efficient vertical transport of air-masses rich on photochemically produced O_3.

In agreement with other baseline measurements in Europe (see also Gilge et al., 2010; Logan et al., 2012), the first part of the measurement period (1991–1993) at CMN was characterised by significantly lower O_3 values (48.0 ± 8.9 nmol/mol) compared to the subsequent part of the time series (54.1 ± 8.8 nmol/mol), though some uncertainty on data homogeneity might in principle affect this subset of O_3 data. It can be assumed that the increasing O_3 values observed at CMN, from the earlier to the more recent measurements, could represent the last phase of a period of positive O_3 trends occurring over Europe in agreement with different baseline stations from 1970s to early 1990s (Gilge et al., 2010; Jenkin, 2008; Oltmans et al., 2013; Logan et al., 2012; Parrish et al., 2012). With respect to the other measurement sites, comparable constant O_3 mole fractions were generally observed at CMN from 1998 to mid-2004. On the contrary, at CMN larger positive O_3 anomalies were observed for the years 2005–2008 with respect to other baseline measurement sites in the Alps and in the Mediterranean basin. These high O_3 values can be, at least partially, explained considering the synergic occurrence of the atmospheric processes we analysed in this work (HW, SI and NAO variability). In particular, major HWs were detected during summer months (June 2005–2006, July 2006, April 2007 and May 2008) and strongly positive NAO index values characterised winter 2007 and 2008 when large positive O_3 anomalies were observed at CMN. Finally, SI could have played a not negligible role on autumn 2006 when a maximum of occurrence has been detected (14.2%) and a statistically significant correlation characterised O_3^{SI} and overall O_3 over the period 2001–2006. It is thus conceivable that different factors/processes could play together in explaining the large O_3 anomalies observed at CMN during the period 2005–2008.

For the overall time interval 1991–2011, significant (95% confidence level) positive linear trends have been calculated for monthly average values as well as for the 25th and 75th percentiles. Caution should be deserved in commenting long-term trend for this time interval, also considering the rather long data gap (1994–1995) affecting the O_3 time series at CMN. On a seasonal basis, only for spring a positive trend has been observed at CMN for 1991–2011. For the shorter period 1996–2011 no significant O_3 trends were detected at CMN, in fairly good agreement with observations at other high mountain stations in Europe (e.g. Gilge et al., 2010; Logan et al., 2012; Parrish et al., 2012) and in the Mediterranean

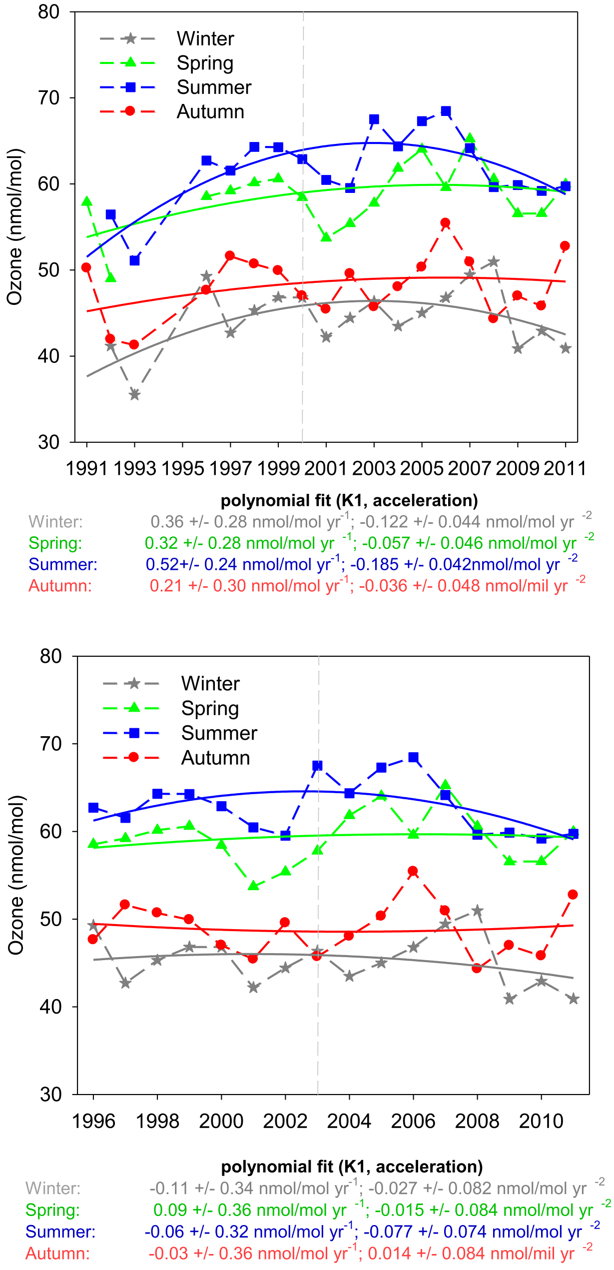

Fig. 7. Seasonal O_3 averages measured at CMN for 1991–2011 (upper plate) and 1996–2011 (bottom plate). The solid lines indicate quadratic regressions for the entire data sets. The annotations in each figure give the derived parameters of those regressions, along with their confidence limits (±2σ).

Islands of Cyprus (Kleanthous et al., 2014) and Malta (Saliba et al., 2008). Ordoñez et al. (2007) suggested a strong relationship between stratosphere-to-troposphere exchange and O_3 changes at Alpine stations during 1990s: however no evident correlations existed between O_3 at CMN and long-term SI frequency variability or O_3^{SI} over the period 1996–2011. Only for the period 2001–2006 a positive correlation appeared with O_3^{SI}. By considering the 1991–2011 period, we detected a slowing down of the O_3 growth-rates in all seasons at CMN and a lower mean O_3 mole fraction observed during recent years (i.e. from 2009 to 2011: 51.9 ± 8.3 nmol/mol), in agreement with other Alpine and Mediterranean baseline sites. For summer, a significant negative "acceleration" is detectable also for the period 1996–2011. This could be related with the decrease of O_3 precursor emissions within Europe (Sicard et al., 2013) which led to reductions in peak summertime O_3 at surface continental sites (Royal Society, 2008). This would also affect CMN observations since, especially during summer, the northern Apennines can be exposed to polluted air-masses from the regional and continental PBL (see Cristofanelli et al., 2007; Cristofanelli et al. 2013). Moreover, it can be noted that the most recent years were characterised by a prevalence of negative NAO regimes (Section 3.2.4): thus a possible role of changes in the large-scale circulation cannot be ruled out. However, due to the strong year-to-year variability which affects surface O_3, further years of measurements are necessary to assess the "persistency" of this signal in the subsequent years. This is in agreement with earlier statistical considerations by Weatherhead et al. (1998) who pointed out that up to five decades of observations are required to detect statically significant trends in surface O_3 data. Moreover, as shown by Lin et al. (2014) for the Mauna Loa Observatory in Hawaii, changes in the tropospheric O_3 can be influenced by decadal shifts in atmospheric circulation patterns related with climate variability. Our work provided a first analysis of the possible impact of atmospheric processes (i.e. NAO variability and SI) capable to affect O_3 at CMN, even if further studies need to be carried out to better assess this point.

Finally, it was recently shown (Parrish et al., 2014) that chemistry-climate models do show substantial and consistent quantitative disagreement with measured surface O_3 patterns. Thus, the present thoroughly quality-controlled and evaluated 19-year dataset of surface O_3 from CMN can be also suitable for further assessments of such models.

Acknowledgements

This work was supported by MIUR and CNR thanks to the Project of National Interest NEXTDATA. The authors would like to thank "Magera team" (Cesarino Magera, Pio Giambi and Nicola Gherardini) and the Italian Air Force (CAMM Monte Cimone) for the valuable co-operation at the CMN station. Air temperature data in northern Italy have been provided by the Italian Air Force Meteorological Service by ECA&D data-base (http://eca.knmi.nl/). Air mass trajectories were calculated using the Flextra model developed by Andreas Stohl (NILU) in cooperation with Gerhard Wotawa and Petra Seibert (Institute of Meteorology and Geophysics, Vienna) and using meteorological data provided from ECMWF (European Centre for Medium Range Weather Forecast). The authors gratefully acknowledge the Environmental Agency of the Republic of Slovenia for providing O_3 data for Krvavec. The authors are grateful to the two anonymous referees for their valuable revisions.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.11.012.

References

Bonasoni, P., Stohl, A., Cristofanelli, P., Calzolari, F., Colombo, T., Evangelisti, F., 2000. Background ozone variations at Mt. Cimone station. Atmos. Environ. 34, 5183–5189.
Brunetti, M., Maugeri, M., Monti, F., Nanni, T., 2006. Temperature and precipitation variability in Italy in the last two centuries from homogenised instrumental time series. Int. J. Clim. 26, 345–381.
Chevalier, A., Gheusi, F., Delmas, R., Ordóñez, C., Sarrat, C., Zbinden, R., et al., 2007. Influence of altitude on ozone levels and variability in the lower troposphere: a ground-based study for western Europe over the period 2001–2004. Atmos. Chem. Phys. 7, 4311–4326.
Colombo, T., Santaguida, R., Capasso, A., Calzolari, F., Evangelisti, F., Bonasoni, P., 2000. Biospheric influence on carbon dioxide measurements in Italy. Atmos. Environ. 34 (29–30), 4963–4969.
Cristofanelli, P., Bonasoni, P., Tositti, L., Bonafè, U., Calzolari, F., Evangelisti, F., et al., 2006. A 6-year analysis of stratospheric intrusions and their influence on ozone at Mt. Cimone (2165 m above sea level). J. Geophys. Res. 111 (D03), 306.
Cristofanelli, P., Bonasoni, P., Carboni, G., Calzolari, F., Casarola, L., Zauli Sajani, S., et al., 2007. Anomalous high ozone concentrations recorded at a high mountain station in Italy in summer 2003. Atmos. Environ. 41, 1383–1394.
Cristofanelli, P., Marinoni, A., Arduini, J., Bonafè, U., Calzolari, F., Colombo, T., et al., 2009. 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. Atmos. Chem. Phys. 9, 4603–4619.
Cristofanelli, P., Fierli, F., Marinoni, A., Calzolari, F., Duchi, R., Burkhart, J., Stohl, A., Maione, M., Arduini, J., Bonasoni, P., 2013. Influence of biomass burning and anthropogenic emissions on ozone, carbon monoxide and black carbon at the Mt. Cimone GAW-WMO global station (Italy, 2165 m a.s.l.). Atmos. Chem. Phys. 13, 15–30.
Cuevas, E., González, Y., Rodríguez, S., Guerra, J.C., Gómez-Peláez, A.J., Alonso-Pérez, S., Bustos, J., Milford, C., 2013. Assessment of atmospheric processes driving ozone variations in the subtropical North Atlantic free troposphere. Atmos. Chem. Phys. 13, 1973–1998. http://dx.doi.org/10.5194/acp-13-1973-2013.
Cui, J., Sprenger, M., Staehelin, J., Siegrist, A., Kunz, M., Henne, S., Steinbacher, M., 2009. Impact of stratospheric intrusions and intercontinental transport on ozone at Jungfraujoch in 2005: comparison and validation of two Lagrangian approaches. Atmos. Chem. Phys. 9, 3371–3383. http://dx.doi.org/10.5194/acp-9-3371-2009.
European Environmental Agency, 2007. Air Pollution by Ozone in Europe in Summer 2006. EEA, Copenhagen.
European Environmental Agency, 2012. Air Pollution by Ozone in Europe in Summer 2011. EEA, Copenhagen.
Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., et al., 2007. Changes in atmospheric constituents and in radiative forcing. In: Climate Change 2007: the Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge and New York.
Gilge, S., Plass-Duelmer, C., Fricke, W., Kaiser, A., Ries, L., Buchmann, B., et al., 2010. Ozone, carbon monoxide and nitrogen oxides time series at four alpine GAW mountain stations in central Europe. Atmos. Chem. Phys. 10, 12295–12316.
Henne, S., Brunner, D., Folini, D., Solberg, S., Klausen, J., Buchmann, B., 2010. Assessment of parameters describing representativeness of air quality in-situ measurement sites. Atmos. Chem. Phys. 10, 3561–3581.
Hurrell, J.W., Kushnir, Y., Visbeck, M., 2001. The North Atlantic oscillation. Science 291, 603–605.
Jenkin, M.E., 2008. Trends in ozone concentration distribution in the UK since 1990: local, regional and global influences. Atmos. Environ. 42, 5434–5445.
Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermitzaki, E., Unal, A., Kocak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A.F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C., Burrows, J.P., 2011. Megacities as hot spots of air pollution in the East Mediterranean. Atmos. Environ. 45 (6), 1223–1235. http://dx.doi.org/10.1016/j.atmosenv.2010.11.048.
Kleanthous, S., Vrekoussis, M., Mihalopoulos, N., Kalabokas, P., Lelieveld, J., 2014. On the temporal and spatial variation of ozone in Cyprus. Sci. Tot. Environ. 476–477, 677–687.
Klein Tank, A.M.G., Wijngaard, J.B., Können, G.P., et al., 2002. Daily dataset of 20th-century surface air temperature and precipitation series for the European Climate Assessment. Int. J. Clim. 22, 1441–1453.
Lelieveld, J., et al., 2002. Global air pollution crossroads over the mediterranean. Science 298, 794–799.
Lin, M., Horowitz, L.W., Oltmans, S.J., Fiore, A., Fan, S., 2014. Tropospheric ozone trends at Mauna Loa Observatory tied to decadal climate variability. NGEO 7, 1–8.
Logan, J.A., Staehelin, J., Megretskaia, I.A., Cammas, J.P., Thouret, V., Claude, H., 2012. Changes in ozone over Europe: analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites. J. Geophys. Res. 117 (D09), 301.
Marinoni, A., Cristofanelli, P., Calzolari, F., Roccato, F., Bonafè, U., et al., 2008. Continuous measurements of aerosol physical parameters at the Mt. Cimone GAW Station (2165 m asl, Italy). Sci. Tot. Environ. 391, 241–251.
Monks, P.S., 2000. A review of the observations and origins of the spring ozone maximum. Atmos. Environ. 34, 3545–3561.

Monks, P.S., et al., 2009. Atmospheric composition change – global and regional air quality. Atmos. Environ. 43 (33), 5268–5350.

Oltmans, S.J., Lefohn, A.S., Shadwick, D., Harris, J.M., Scheel, H.E., Galbally, I., et al., 2013. Recent tropospheric ozone changes - a pattern dominated by slow or no growth. Atmos. Environ. 67, 331–351.

Ordòñez, C., Brunner, D., Staehelin, J., Hadjinicolaou, P., Pyle, J.A., Jonas, M., Wernli, H., Prévôt, A.S.H., 2007. Strong influence of lowermost stratospheric ozone on lower tropospheric background ozone changes over Europe. Geophys. Res. Lett. 34 (L07), 805.

Parrish, D.D., Law, K.S., Staehelin, J., Derwent, R., Cooper, O.R., Tanimoto, H., et al., 2012. Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes. Atmos. Chem. Phys. 12, 11485–11504.

Parrish, D.D., Law, K.S., Staehelin, J., Derwent, R., Cooper, O.R., Tanimoto, H., Volz-Thomas, A., Gilge, S., Scheel, H.-E., Steinbacher, M., Chan, E., 2013. Lower tropospheric ozone at northern midlatitudes: changing seasonal cycle. Geophys. Res. Lett. 40, 1631–1636.

Parrish, D.D., Lamarque, J.-F., Naik, V., Horowitz, L., Shindell, D.T., Staehelin, J., Derwent, R., Cooper, O.R., Tanimoto, H., Volz-Thomas, A., Gilge, S., Scheel, H.-E., Steinbacher, M., Fröhlich, M., 2014. Long-term changes in lower tropospheric baseline ozone concentrations: comparing chemistry-climate models and observations at northern mid-latitudes. J. Geophys. Res. 119, 5719–5736.

Pausata, F.S.R., Pozzoli, L., Vignati, E., Dentener, F.J., 2012. North Atlantic Oscillation and tropospheric ozone variability in Europe: model analysis and measurements intercomparison. Atmos. Chem. Phys. 12, 6357–6376. http://dx.doi.org/10.5194/acp-12-6357-2012.

Saliba, M., Ellul, R., Camilleri, L., Güsten, H., 2008. A 10-year study of background surface ozone concentrations on the island of Gozo in the Central Mediterranean. J. Atmos. Chem. 60, 117–135.

Sicard, P., De Marco, A., Troussier, F., Renou, C., Vas, N., Paoletti, E., 2013. Decrease in surface ozone concentrations at Mediterranean remote sites and increase in the cities. Atmos. Environ. 79, 705–715.

Tarasova, O.A., Brenninkmeijer, C.A.M., Jöckel, P., Zvyagintsev, A.M., Kuznetsov, G.I., 2007. A climatology of surface ozone in the extra tropics: cluster analysis of observations and model results. Atmos. Chem. Phys. 7, 6099–6117. http://dx.doi.org/10.5194/acp-7-6099-2007.

The Royal Society, 2008. Ground-level Ozone in the 21th Century: Future Trends, Impacts and Policy Implications. The Royal Society, London.

Tositti, L., Riccio, A., Sandrini, S., Brattich, E., Baldacci, D., Parmeggiani, S., Cristofanelli, P., Bonasoni, P., 2012. Short-term climatology of PM10 at a high altitude background station in southern Europe. Atmos. Env. 65, 142–152.

Trickl, T., Feldmann, H., Kanter, H.-J., Scheel, H.-E., Sprenger, M., Stohl, A., Wernli, H., 2010. Forecasted deep stratospheric intrusions over Central Europe: case studies and climatologies. Atmos. Chem. Phys. 10, 499–524. http://dx.doi.org/10.5194/acp-10-499-2010.

UNEP and WMO, 2011. Integrated Assessment of Black Carbon and Tropospheric Ozone. UNEP, Nairobi.

Vautard, R., Honoré, C., Beekmann, M., Rouil, L., 2005. Simulation of ozone during the August 2003 heat wave and emission control scenarios. Atmos. Environ. 39, 2957–2967.

Wang, G., Dolman, A.J., Alessandri, A., 2011. A summer climate regime over Europe modulated by the North Atlantic Oscillation. Hydrol. Earth Syst. Sci. 15, 57–64. http://dx.doi.org/10.5194/hess-15-57-2011.

Weatherhead, E.C., Reinsel, G.C., Tiao, G.C., Meng, X.L., Choi, D.S., Cheang, W.K., Keller, T., DeLuisi, J., Wuebbles, D.J., Kerr, J.B., Miller, A.J., Oltmans, S.J., Frederick, J.E., 1998. Factors affecting the detection of trends: statistical considerations and applications to environmental data. J. Geophys. Res. 103, 17149–17161.

Wild, O., 2007. Modelling the global tropospheric ozone budget: exploring the variability in current models. Atmos. Chem. Phys. 7, 2643–2660.

Zanis, P., Ganser, A., Zellweger, C., Henne, S., Steinbacher, M., Staehelin, J., 2007. Seasonal variability of measured ozone production efficiencies in the lower free troposphere of Central Europe. Atmos. Chem. Phys. 7, 223–236.

Zanis, P., Hadjinicolaou, P., Pozzer, A., Tyrlis, E., Dafka, S., Mihalopoulos, N., Lelieveld, J., 2014. Summertime free-tropospheric ozone pool over the eastern Mediterranean/Middle East. Atmos. Chem. Phys. 14, 115–132. http://dx.doi.org/10.5194/acp-14-115-2014.

Zellweger, C., Steinbacher, M., Buchmann, B., 2012. System and Performance Audit of Surface Ozone, Methane, Carbon Dioxide, Nitrous Oxide and Carbon Monoxide at the Global GAW Station Mt. Cimone, Italy, September 2012. WCC-Empa Report 12/3.