Long-term (2002–2012) investigation of Saharan dust transport events at Mt. Cimone GAW global station, Italy (2165 m a.s.l.)

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Abstract

Mineral dust transport from North Africa towards the Mediterranean basin and Europe was monitored over an 11-y period (2002–2012) using the continuous observations made at Mt. Cimone WMO/GAW global station (CMN). CMN is in a strategic position for investigating the impact of mineral dust transported from northern Africa on the atmospheric composition of the Mediterranean basin and southern Europe. The identification of “dusty days” is based on coupling the measured in situ coarse aerosol particle number concentration with an analysis of modeled back trajectories tracing the origin of air masses from North Africa. More than 400 episodes of mineral dust transport were identified, accounting for 15.7% of the investigated period. Our analysis points to a clear seasonal cycle, with the highest frequency from spring to autumn, and a dust-induced variation of the coarse particle number concentration larger than 123% on a seasonal basis. In addition, FLEXTRA 10-d back trajectories showed that northwestern and central Africa are the major mineral dust source regions. Significant inter-annual variability of dust outbreak frequency and related mineral dust loading were detected and during spring the NAO index was positively correlated ($R^2 = 0.32$) with dust outbreak frequency. Lastly, the impact of transported mineral dust on the surface $O_3$ mixing ratio was quantified over the 11-y investigation period. Evidence of a non-linear and negative correlation between mineral dust and ozone concentrations was found, resulting in an average spring and summer decrease of the $O_3$ mixing ratio down to 7%.

1. Introduction

Mineral dust aerosol is ubiquitous in the atmosphere constituting most of the atmospheric particulate matter mass worldwide (Textor et al., 2007; Huneu et al., 2012), with Africa (in particular the Sahara and Sahel regions) responsible for approximately half of global emissions (Huneu et al., 2011; Ginoux et al., 2012). The resuspended aerosol can be transported over large distances by synoptic circulation over both the Atlantic Ocean (Ben-Ami et al., 2009, 2010) and the Mediterranean Basin (Isaevich et al., 2012 and references therein) with a number of direct and indirect effects on atmospheric composition, air quality and radiative budget near the dust source and downwind regions (Sokolik and Toon, 1996; Haywood et al., 2003; Highwood et al., 2003; Di Biagio et al., 2010; Heinold et al., 2008; Klüser and Holzer-Popp, 2010; Casasanta et al., 2011).

However, African mineral dust emissions are not steady: from 1980s to date a general decrease in dustiness has been observed over north Africa (Evan and Mukhopadhyay, 2010; Hsu et al., 2012; Shao et al., 2013; Chin et al., 2014) with a strong inter-annual and intra-seasonal variability (Prospero and Lamb, 2003; Moulin and Chiapello, 2004; Zender and Kwon, 2005; Evan et al., 2006). These variations therefore influence the climatic
The Mediterranean basin is considered a global hotspot in terms of air quality and climate change (Monks et al., 2012). This region is strongly affected by mineral dust outbreaks with severe implications on air quality (e.g. Pey et al., 2013; Gobbi et al., 2013) and public health (e.g. Perez et al., 2008; Zauli-Sajani et al., 2010). The Mediterranean basin also represents a hotspot area for short-term variations in the concentration of tropospheric and surface O$_3$ (Monks et al., 2012; Zanis et al., 2014), a well-known short-lived climate forcer and pollutant (UNEP and WMO, 2011). Mt Cimone (2165 m a.s.l.), in the Italian northern Apennines, is one of the first European mountain ridges affected by the northward transport of mineral dust from Africa (Figure 1). This paper presents a long-term (August 2002–November 2012) study of mineral dust transport from North Africa monitored at Mt. Cimone WMO/GAW global station (CMN). The findings provide new hints on dust outbreak seasonality, influence on atmospheric aerosol properties and impact on surface ozone mixing ratio variability. The daily average number concentration of coarse particles ($N_{1–10}$, $1 \mu m < D_p < 10 \mu m$), a specific proxy for mineral dust at CMN (Van Dingenen et al., 2005; Marenco et al., 2006), and the analysis of 3D back trajectories calculated by the FLEXTRA model and ending at CMN were used as a simple but robust tool to identify "dusty days" (DD), i.e. days when the measurement site is affected by the transport of mineral dust from Africa (e.g. Bonasoni et al., 2004; Marinoni et al., 2008). After a description of the measurement site and the methodology used to detect DD, the paper presents the seasonality of DD in terms of frequency and induced $N_{1–10}$ variations, also investigating related dust source regions and air mass transport patterns. CMN observations describe the inter-annual variability of dust outbreaks in the central Mediterranean basin disclosing new evidence of the impact of mineral dust on O$_3$ in this region.

2. Experimental

### 2.1 Measurement site and instrumental set-up

CMN is the only WMO/GAW global station in Italy and within the Mediterranean basin: it is located at the summit of Mt. Cimone (CMN, 44°12′ N, 10°42′ E, 2165 m a.s.l.), the highest peak in the northern Apennines. The atmospheric measurements carried out at CMN can be considered representative for the baseline conditions of the Mediterranean basin free troposphere (Bonasoni et al., 2000; Fischer et al., 2003). However, especially during warm months, the atmospheric composition at CMN is partially modulated by the transport of emissions from Europe and other continents (Cristofanelli et al., 2013) and by export from the regional planetary boundary layer (PBL) (Carbone et al., 2014).

The aerosol number concentration and size distribution ($0.3–10 \mu m$ in 15 bins) were continuously measured (time resolution: 1 min) by an optical particle counter (OPC 1.108 GRIMM) from August 2002 to November 2012 to determine the coarse particle number concentration ($N_{100}$). According to the manufacturer, the accuracy of the OPC is ± 2% over the entire measurement size range. As deduced by Putaud et al. (2004), a random uncertainty in particle sizing of ± 20% can be associated with a similar OPC during desert dust advection. 3D back trajectories were calculated by the FLEXTRA model (Stohl et al., 1995) based on meteorological analysis fields produced by the numerical weather prediction model of the European Centre
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for Medium Range Weather Forecasts (ECMWF), with a T106 spatial resolution and 60 vertical levels. For each day, four back trajectories were calculated at 00, 06, 12 and 18 UTC for the CMN location, with the air mass positions (geographic location and altitude) recorded every 3h backward in time. The trajectories were used to investigate the occurrence of synoptic-scale circulation favorable to the advection of air masses from northern Africa.

At CMN, tropospheric O3 mixing ratio measurements have been carried out continuously since 1996 using a UV-photometric analyzer (Dasibi 1108). The accuracy and quality of measurements (sampling time: 1 min, combined standard uncertainty less than ±2 nmol mol\(^{-1}\)) and sampling procedures are guaranteed within GAW requirements (WMO GAW, 2013). In particular, the CMN O3 analyzer was traced back to SRP#15, the Standard Reference Photometer at EMPA (Swiss Federal Laboratories for Materials Testing and Research).

2.2 Identification of dust transport events

A DD was identified when a statistically significant increase in the N\(_{1–10}\) daily average value was associated with 10-d air mass originated from northern Africa, as deduced by back trajectory calculations. To identify the N\(_{1–10}\) increase, the so-called "Kolmogorov-Zurbenko" (KZ) filter was applied: a three times repeated iteration of a 19-d running mean was applied to the time series of daily average N\(_{1–10}\) (i.e. RM1, RM2, RM3, Figure 2a): the difference between the time series and the RM3 (representing the low frequency seasonal component) is the high frequency component of the N\(_{1–10}\) time series (i.e. value N\(_{1–10}\)^{HF}) which can be related to synoptic-scale dust transport. A day was considered possibly affected by dust transport if the N\(_{1–10}\)^{HF} was significantly higher (at the 95% confidence limit) than the average N\(_{1–10}\)^{HF} value over the period 2002–2012 (i.e. all days above the dark red line in Figure 2b). This result must be corroborated by the presence of air masses that originated (or passed) over North Africa, as deduced by the FLEXTRA model (leading to the identification of DD, i.e. red diamonds in Figure 2b). In case of ambiguous identification, further information was gained from the inspection of other model outputs (i.e. NAAPS – Navy Aerosol Analysis and Prediction System, see http://www.nrlmry.navy.mil/a) or satellite data (i.e. TOMS/OMI UV Aerosol Index, MODIS AOD).

3. Results and discussions

3.1 Dust transport events statistics

Over the period August 2002–November 2012, 3022 days of aerosol size distribution observations were available at CMN, representing 80.1% of the investigated period: 474 days were affected by Saharan dust transport, corresponding to 15.7% of the days for which N\(_{1–10}\) measurements were available, roughly 43 days per year.

A total of 218 dust transport events (DTE, i.e. contiguous aggregation of DD) were recognized: 44% of DTE lasted one day, 28% two days, while 8% of DTEs lasted at least five days. The longest DTE, 13 and 14 d, were recorded in May 2003 and June 2006. The frequency of DTE time length was found to have a seasonal dependence: the average DTE time length decreased from summer (2.9 d) to winter (2.3 d) (Figure 3).

3.2 Seasonal cycle of DTEs and impact on aerosol particle number concentration

To provide information on the seasonal occurrence of DTEs at CMN, the monthly mean frequency of DD was calculated (Figure 4). To retain robust information for each year, only months with a data coverage exceeding 50% were considered. The monthly average frequency of DD at CMN showed a clear seasonal cycle characterized by a winter minimum (8%) and a broad spring–summer maximum (19.3%). On a monthly basis, the highest DD frequencies were observed in May (26.4%) and June (23%), with a secondary maximum in November (16.6%). By considering each single year, the peak months were recorded in spring for a total of
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To assess the impact of DTE on the particle concentration number at CMN, we compared the concentration of coarse particles (\(N_{1-10}\)) during DTE with that observed for non-DTE (Figure 5). Table 1 reports the statistics of aerosol particle number changes observed during DTEs at CMN. The average annual \(N_{1-10}\) cycles at CMN for non-DTE were characterized by a clear spring-summer maximum and autumn-winter minima, reflecting the enhanced vertical transport of air masses from the lower troposphere and PBL during the warm months (see Marinoni et al., 2008; Carbone et al., 2014). Clear increases in coarse aerosol particle number concentrations were observed at CMN during dust advection (Table 1 and Figure 5). On a yearly basis, \(N_{1-10}\) increased by 670% during DTE, with maxima in spring-autumn, while significant lower values were observed for winter events. On a monthly basis (Figure 5) the average \(N_{1-10}\) during DTE showed a maximum in summer with a secondary peak in autumn. Very large error bars, representing the 95th confidence level, were related to March (0.39 ± 0.75 cm\(^{-3}\)) and September (0.42 ± 0.62 cm\(^{-3}\)). An in-depth analysis of daily \(N_{1-10}\) values showed that these monthly high values were related to specific “acute” events (14–16 March 2003, with daily \(N_{1-10}\) exceeding 10.0 cm\(^{-3}\); 6–10 September 2008 and 2–3 September 2011, with daily \(N_{1-10}\) exceeding 4.0 cm\(^{-3}\)).

To investigate the occurrence of “major” dust advections, the DTEs characterized by high aerosol loading were selected (\(N_{1-10}\) daily average > 0.9 cm\(^{-3}\), representing the 75th percentile of the daily \(N_{1-10}\) during DTE). The seasonal distribution of these “major” DTEs showed the highest values in May (17.9%) and June (19.4%). Moreover, 11 “acute” DTE (\(N_{1-10}\) daily > 3.0 cm\(^{-3}\)) were recorded during the investigation period, of which 72% were recorded in autumn (especially in November: 5 events) and spring (3 events).

To quantify the impact of Saharan dust advection on \(N_{1-10}\), the average variations of \(N_{1-10}\) during DTE was calculated with respect to the typical seasonal background conditions (i.e. the dust-induced \(N_{1-10}\) variation, hereinafter referred to as \(\delta N_{1-10}\)). The seasonal background is defined by the “low” frequency spline curve obtained by applying the KZ filter. On a yearly basis, the average \(\delta N_{1-10}\) was 0.40 cm\(^{-3}\) with peak dust-induced variations during spring-autumn (0.50–0.54 cm\(^{-3}\)).

Figure 3
Time length distribution of DTEs at CMN for the different seasons: spring (MAM), summer (JJA), autumn (SON) and winter (DJF).

The reported percentages refer to the seasonal DTE number. An average DTE time length decrease from summer to winter is evident.

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Figure 4
Monthly number of DD and their average frequency at CMN over the period 2002–2012.

The DD frequency shows a clear seasonal cycle characterized by a winter minimum and a broad spring–summer maximum. The monthly average fraction of DDs characterized by \(N_{1-10}\) daily average > 0.9 cm\(^{-3}\) (left y-axis) shows two broad maxima, one in summer and one in autumn.

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3.3 Mineral dust sources and transport patterns

To investigate the source regions of the mineral dust observed at CMN, the paths and origin of the 10-d FLEXTA back trajectories were investigated (Figure 6).

A general picture of the air mass circulation characterizing the mineral dust transport and investigation of the possible contribution of dust emission regions were obtained by calculating the total number of back trajectory points n(i,j) visiting the grid cell (i,j). The spatial domain covers 20°–60° N and 10°W–35° E, with a resolution of 0.5° in latitude and longitude during the DTEs detected. A logarithmic scale was adopted to reveal the transport paths for “peripheral” regions far from the measurement site.

This elaboration clearly showed that the main transport pattern associated with DTE is related to south-westerly circulation from western North Africa, even though some variability was observed as a function of the different seasons: during winter and spring significant air masses were advected from north central Africa, crossing the central Mediterranean basin and the Italian peninsula before reaching CMN. These results are in agreement with Querol et al. (2009), who found that dust transport affects the western and central Mediterranean when low-pressure areas are present over the Atlantic Ocean/northern Africa and high pressures persist over the Mediterranean basin. While a well-marked “channel” for dust advection was evident along the western Mediterranean basin during spring and autumn, air mass back trajectories were more widespread during summer, with a fraction of transport occurring over the Iberian Peninsula. This indicated that the advection of air masses from western North Africa during summer is favored by the anticyclonic region over the Mediterranean basin. Even when associated with a low pressure trough over the western Iberian Peninsula, this region promotes favorable conditions for mineral dust from northern Africa.

Table 1. Statistical overview of DTEs at CMN

The total number of available observation days, DTE number, daily average N_{1-10}, daily average N_{1-10} when DTEs are not considered, daily average N_{1-10} during DTEs and the average dust-induced daily N_{1-10} variation (ΔN_{1-10}) are shown for all data and for each season (DJF, MAM, JJA, SON).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>All-data</th>
<th>DJF</th>
<th>MAM</th>
<th>JJA</th>
<th>SON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation days (number)</td>
<td>3022</td>
<td>659</td>
<td>764</td>
<td>877</td>
<td>723</td>
</tr>
<tr>
<td>DTEs days (number)</td>
<td>424</td>
<td>49</td>
<td>154</td>
<td>168</td>
<td>103</td>
</tr>
<tr>
<td>Average (cm$^{-3}$)</td>
<td>0.19 ± 0.01</td>
<td>0.05 ± 0.01</td>
<td>0.25 ± 0.04</td>
<td>0.27 ± 0.02</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>Average without dust (cm$^{-3}$)</td>
<td>0.10 ± 0.01</td>
<td>0.04 ± 0.01</td>
<td>0.13 ± 0.01</td>
<td>0.17 ± 0.01</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Average with dust (cm$^{-3}$)</td>
<td>0.67 ± 0.08</td>
<td>0.22 ± 0.06</td>
<td>0.70 ± 0.18</td>
<td>0.71 ± 0.11</td>
<td>0.78 ± 0.17</td>
</tr>
<tr>
<td>ΔN_{1-10}, Dust-induced variations (cm$^{-3}$)</td>
<td>0.40 ± 0.07</td>
<td>0.15 ± 0.05</td>
<td>0.40 ± 0.16</td>
<td>0.38 ± 0.09</td>
<td>0.54 ± 0.14</td>
</tr>
</tbody>
</table>

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Figure 6
Concentration of back trajectory points related to the occurrence of DTEs at CMN over the period 2002–2012.

Both horizontal field and vertical cross sections are reported for each season. The colored scale denotes the number of back trajectory points. A different scale was adopted for winter to magnify the trajectory patterns. The main transport pattern associated with DTEs is related to south-westerly circulation from western North Africa.

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Figure 7
Seasonal aggregation of the lowest (Zmin, red) and averaged (Zavg, blue) back trajectory point heights during DTEs at CMN.

For each season, the box-and-whisker plots reported the 5th, 25th, 50th, 75th and 95th percentiles as well as the mean average values (dotted lines). No significant Zmin and Zavg seasonal variability was observed.

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Overall, no robust variability of the lowest (Zmin) and average (Zavg) back trajectory point heights during DTE at CMN was observed as a function of the season (Figure 7), even if Zavg tended to be relative higher during spring-summer and Zmin lower during autumn: 75% of Zavg were below 2900 m a.s.l. on MAM-JJA and below 2300 m a.s.l. during DJF. This probably reflects the increasing role of the anticyclonic area in favoring the advection of mineral dust towards CMN during warm months. On the other hand, 75% of DTE showed Zmin values below 2000 m a.s.l. for all the seasons. As indicated by the climatology of Liu et al. (2008), this value well represents the dust aerosol layer over northern Africa.

To assess the specific contributions of the different source areas for the occurrence of dust events recorded at CMN, two "macro-regions" were selected: one encompassing Morocco, Mauritania, Algeria and Tunisia (S1) and the other Libya (S2). As shown by the satellite measurements of the UV Aerosol Index (Figure 1) provided by the OMI on board the NASA Aura satellite (Duncan et al., 2003), the S1 macro-region includes two well-known source basins of mineral dust (Israelievich et al., 2002), i.e. the Djouf (19°N, 9°W) and the...
Chotts (34°N, 9°E), while S2 includes the broad emission region of central Libya (25°–30° N; 15°–20°E). By means of the FLEXTRA back trajectories, each DD was tagged to these macro-regions, thus calculating their average 11-y monthly contribution to DD occurrence (Figure 8).

For each DD, the source region contribution was calculated from the total number of back trajectory points traveling over the S1 or S2 region. Based on the fraction of points tagged to S1 and S2, a daily percentage contribution was obtained. This analysis led to the conclusion that S1 represented the most active source region for the occurrence of DTE at CMN (accounting for 77.8% of the DD on a yearly basis). S2 accounted for 14.4% of the DD, while the remaining fraction (7.8%) was attributed to other source regions (mostly in eastern North Africa). A seasonal dependency of the source region was found out with a clear predominance of S1 during the summer season (especially during July). The contribution for the S2 region (14.4%) was maximized in winter (when region S2 accounted for 23.7% and 33.7% of DD detected in December and February), indicating the role of low pressure systems in steering the transport of mineral dust across the central Mediterranean basin during the winter, in agreement with the back trajectory plots presented in Figure 6.

We calculated the specific contribution of each single source region to dust loading at CMN, by weighting the daily $N_{1-10}$ by the number of back trajectory points belonging to each region on the same day. The result is shown as monthly averages (calculated over the period 2002–2012) in Figure 9: the predominance of the S1 region was evident during all the seasons (with the highest contribution in summer) and it applies to both fine and coarse fractions. S2 and “other” regions presented a clear seasonal cycle with a spring-summer maximum and a secondary peak in autumn (only for S2).
3.4 Inter-annual DTE variability

To investigate long-term variations in DTE occurrence at CMN, the yearly average seasonal fraction of DD, and the associated average dust $N_{1-10}$ were calculated (Figure 10). In general, no evident increasing or decreasing tendency could be observed either for the DD fraction or for $N_{1-10}$, even though some of the year were characterized by a sporadic increase in DD frequency or coarse aerosol particle number concentration. The absence of a clear tendency appeared to be in agreement with Pey et al.’s investigation (2013) into the impact of African dust outbreaks on PM10 over the Mediterranean basin: high seasonal DD frequency and coarse particle contribution were observed at CMN in winter, spring and autumn 2004.

To account for this inter-annual variability, the correlation between the North Atlantic Oscillation (NAO) and the number of DD and average dust $N_{1-10}$ (Figure 11) was analyzed. Previous studies (e.g. Cusack et al., 2012; Pey et al., 2013;) attributed part of this inter-annual variability to the NAO, an atmospheric large-scale mode influencing the intensity and location of the North Atlantic jet stream and storm track, thus affecting temperature and precipitation patterns from North America to western and central Europe (Hurrell et al., 2003). The seasonal NAO Index was calculated based on the monthly values available at the NOAA data center (http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/nao.shtml): positive and negative NAO index indicated more intense and weaker than normal pressure gradients between the Icelandic low and the subtropical high pressure center respectively. During winter, the positive NAO lead to stronger westerly

![Figure 10](image-url)

**Figure 10**
Yearly values of the seasonal percentage of DDs (%) and mean average $N_{1-10}$.

No evident tendency was observed either for the DD fraction or for $N_{1-10}$.

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![Figure 11](image-url)

**Figure 11**
Relation between the frequency of seasonal DD and dust $N_{1-10}$ versus the NAO index.

The linear regression coefficient (R) and confidence level (p) are reported for each plot. Apart from the spring significant positive correlation (i.e. at the 90% confidence interval) between the NAO index and DD frequency no other significant linear correlation was found.

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winds across northern Europe, with wet Atlantic air masses over the continent and dryer conditions across southern Europe. During negative phases, cold and dry air masses often dominate over northern Europe, and the Atlantic weather systems and storm tracks tend toward a more southerly trajectory, bringing precipitation levels higher than normal over the Mediterranean basin. The NAO is often regarded as a winter phenomenon, since the winter months are dynamically the most active and present the largest sea level pressure (SLP) amplitude anomalies. However, Barnston and Livezey (1987) showed that the NAO has a year-round influence on weather conditions in Europe, with pronounced seasonal variations in high and low pressure centers, and strong climate anomalies can also be detected outside the winter season.

As shown in Figure 11, a significant positive correlation (i.e. at the 90% confidence interval) was found between the NAO index and DD frequency in spring ($R^2$: 0.32), while a positive (but not statistically significant, $p<0.26$) correlation was found for summer ($R^2$: 0.13). Concerning the correlation between the NOA Index and dust $N_{1–10}$, a positive tendency (even if not statistically significant: $p<0.13, R^2$: 0.23) was found for autumn, while a negative correlation appeared for summer ($p<0.13; R^2$: 0.23). The positive springtime correlation between DD frequency and the NAO Index appeared to be in agreement with Salvador et al. (2014) who reported enhanced dust outbreak frequency over the western Mediterranean basin during positive NAO phases. This could be related to the expansion of the Azores anticyclone towards western Africa and the Mediterranean basin (e.g. Pausata et al., 2012) which could favor the transport of North African air masses rich in mineral dust towards northern Italy. To further assess this point, we calculated the numbers of back trajectory points during spring for negative and positive NAO phases (see Figure S3, supplementary material). Spring seasons with positive NAO indexes were characterized by a broad presence of back trajectories points over the central Mediterranean basin, thus supporting the occurrence of air mass transport from northern Africa to northern Italy, triggered by a high pressure area over north-eastern Algeria and Tunisia (Salvador et al., 2014). The negative summer tendency between the NAO index and dust $N_{1–10}$ appears to contradict Pey et al. (2013), who claimed a positive correlation between NAO phases and dust contribution over the central Mediterranean basin and Italy. By limiting the analysis to the 2007–2011 period (i.e. the time frame considered by Pey et al., 2013), a similar positive linear correlation was found ($R^2$: 0.8; $p<0.05$). This clearly indicates that the selected time frame has a major influence on the assessment of large-scale atmospheric modes on DTE occurrences, be it five years or 11 years, implying that to draw any conclusion on the relation between the NAO index and mineral dust occurrence, analyses of longer time frame is needed.

### 3.5 DTE influence on surface ozone at CMN

Since dust particles present a good surface for chemical reactions and radiative processes, several studies have investigated the direct or indirect influence of mineral aerosol on concentrations of atmospheric trace gases (e.g. Zhang et al., 1994; He and Carmichael, 1999; Bauer et al., 2004; Fairlie et al., 2010; Ramachandran, 2015). As highlighted by laboratory and model studies (Zhang et al., 1994; Dentener et al., 1996) and field observations (Dentener and Crutzen, 1993; Zhang et al., 1994; Bonasoni et al., 2004), mineral dust may strongly affect the balance of tropospheric $O_3$. Evaluation of the possible impact of DTE on $O_3$ variability is a major issue for the Mediterranean basin and southern Europe, two global hotspots known for the occurrence of high surface and tropospheric $O_3$ levels (Zanis et al., 2014; Monks et al., 2012) which are also strongly impacted by Saharan dust export and transport (Engelstaedter et al., 2006). For this reason, 11 years of concurrent measurements of $O_3$ mixing ratio and mineral dust transport occurrence in a site representative of the Mediterranean lower troposphere (see Par. 2.1) represent a unique dataset. Bonasoni et al. (2004) investigated the correlation between surface $O_3$ and mineral dust transport at CMN during June–December 2002. They observed a marked decrease of the observed $O_3$ when air masses rich in mineral aerosol were transported towards CMN from northern Africa. This was explained considering the impact of heterogeneous chemistry occurring at the dust particle surface and the ability of dust particles to modify the actinic flux (e.g. Hanisch and Crowley, 2003; Ndour et al., 2008; Fairlie et al., 2010).

To investigate a possible relationship between the presence of mineral dust particles and surface $O_3$ at CMN, the $O_3$ and $N_{1–10}$ data were de-trended to remove the seasonal variability affecting both parameters. The de-trending was achieved in agreement with Bonasoni et al. (2004):

$$X_{\text{det}} = X_i \times \left( \frac{X_{2002–2012}}{X_{\text{rm}}} \right)$$

(1)

where $X$ represents hourly $O_3$ or $N_{1–10}$ averages, $X_{\text{det}}$ is the de-trended hourly value, $X_i$ is the actual hourly value, $X_{2002–2012}$ is the mean average value over the period 2002–2012 and $X_{\text{rm}}$ is a running mean over 21 d centered around the $i$th hour. This approach completely removed the seasonal variability from the dataset but retained the day-to-day variability, which could be related to the occurrence of synoptic-scale transport (like DTE). As an example, Figure 12 reports the daily de-trended values for $O_3$ and $N_{1–10}$ for 2006 (the yearly plots for all the measurement periods are available in the supplementary material, Figure S1). Lower $O_3$ values were also noted during DTE.
Throughout the measurement period, $O_3$ during DTE was $53.8 \pm 0.2$ nmol mol$^{-1}$, while $54.4 \pm 0.1$ nmol mol$^{-1}$ was obtained for the remaining data. The $O_3$ variation ($\Delta O_3$) associated to DTEs was calculated as:

$$\Delta O_3 = \bar{O}_3_{\text{det DTE}} - \bar{O}_3_{\text{det NO DTE}}$$  \hspace{1cm} (2)

where $\bar{O}_3_{\text{det}}$ is the average (calculated for each aerosol particle size bin) of the de-trended hourly values given by (1) and DTE (NO DTE) identifies days affected (not affected) by mineral dust transport at CMN. $\Delta O_3$ was plotted as a function of increasing $N_{1-10}$ (Figure 13), both for the whole $\Delta O_3$ dataset (Figure 13 black lines) and for each distinct season (Figure 13 colored lines). Considering the whole dataset, all the dust load classes showed significant (at the 95% confidence level) negative $\Delta O_3$. As proposed by Cuevas et al. (2013), the lower $O_3$ mixing ratio during DTE could be related to the origin and passage of air masses in the $O_3$-depleted Saharan PBL, no matter the dust loading within transported air masses. To quantify this possible contribution to $O_3$ depletion at CMN, the average $\Delta O_3$ related to air masses from northern Africa without DTE was calculated. The result ($-0.1 \pm 0.1$ nmol mol$^{-1}$) indicated that at CMN the passage through the Saharan PBL does not account for the reduced $O_3$ mixing ratio observed during DTE. No relationship was evident between $N_{1-10}$ and $\Delta O_3$, at the lowest dust loads. However, by moving towards higher dust loading (i.e. higher $N_{1-10}$), $\Delta O_3$ strongly decreased. This tendency is also present on a seasonal basis, with $\Delta O_3$ decreasing and $N_{1-10}$ increasing for all the seasons. The $\Delta O_3$ decrease is particularly pronounced for summer and autumn, ranging from $1.3 \pm 0.3$ nmol mol$^{-1}$ (for dust loading with $N_{1-10} > 0.1$ cm$^{-3}$) to $-4.1 \pm 0.4$ nmol mol$^{-1}$ (for $N_{1-10} > 0.7$ cm$^{-3}$) and $-2.1 \pm 0.3$ nmol mol$^{-1}$ (for dust loading with $N_{1-10} > 0.1$ cm$^{-3}$) to $-4.1 \pm 0.6$ nmol mol$^{-1}$ (for $N_{1-10} > 2.0$ cm$^{-3}$), respectively. During winter, probably due to the rather low number of DTEs, the relationship between $\Delta O_3$ and $N_{1-10}$ is noisier. During winter and spring, the lowest dust loadings showed a positive $\Delta O_3$ (i.e. $O_3$ increase during DTEs with respect to NO DTEs). While for winter average $\Delta O_3$ was not significantly different from zero for all the dust loading classes, for spring $\Delta O_3$ was significantly negative for $N_{1-10} > 0.4$ cm$^{-3}$. 

**Figure 13**
Averaged seasonal hourly $O_3$ decrease during DTEs ($\Delta O_3$) versus $N_{1-10}$ at CMN.

Black lines refer to overall data while colored plots refer to seasonal aggregations. Vertical bars denote the 95% confidence level. The $x$-axis indicates the $N_{1-10}$ threshold values (lowest boundaries) for dust outbreak periods for which $\Delta O_3$ was calculated. Squares denote $\Delta O_3$ calculated for days with African air masses without significant dust loading. At lower $N_{1-10}$, $\Delta O_3$ appeared to be almost unaffected by the mineral dust; moving towards higher dust loading (i.e. higher $N_{1-10}$) $\Delta O_3$ strongly decreases.

**Figure 12**
De-trended ozone and coarse particles time series for the year 2006.

Gray areas denote DTE occurrences, during which $O_3$ mixing ratio and coarse particle number concentration correlate negatively. doi: 10.12952/journal.elementa.000085.f012

**Figure 13**
De-trended ozone and coarse particles time series for the year 2006.
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As shown by Cristofanelli et al. (2009), during some episodes occurring at CMN, the mineral dust might be mixed with combustion or pollution products, thus leading to photochemically produced O\textsubscript{3} within African air masses. To evaluate the possible impact of these contributions on the relationship between ΔO\textsubscript{3} and N\textsubscript{1-10} we considered carbon monoxide (CO) as a tracer of combustion processes related to biomass burning or anthropogenic pollution. At CMN, CO has been measured since 2007 using different analysis techniques: GC-RGD, GC-FID, NDIR (see Cristofanelli et al., 2013 for more details). Thus, for 2007–2012 (when CO observations are available at CMN) the periods possibly affected by enhanced CO were identified (for calculation details please refer to the supplementary material) and the seasonal ΔO\textsubscript{3} values were recalculated, resulting in a statistically significant (p<0.01) lower ΔO\textsubscript{3} when CO peaks were removed (-2.0 nmol mol\textsuperscript{-1} for spring and -2.5 nmol mol\textsuperscript{-1} for summer, for N\textsubscript{1-10}> 0.1 cm\textsuperscript{-3}, see also Figure S2 in the supplementary material). This suggests that mineral dust mixed with a polluted air mass could promote an increase in O\textsubscript{3} even in dusty air masses, especially in spring and summer.

4. Conclusion

This paper analyzed a long-term dataset of northern African mineral dust outbreaks at the Mt. Cimone GAW/WMO Global Station (Italy, 2165 m a.s.l.) (CMN). Mt. Cimone is located in the heart of the Mediterranean basin, a region characterized by elevated seasonal and episodic mineral dust outbreaks and high O\textsubscript{3} levels. Since the CMN site is well representative of the Mediterranean basin tropospheric baseline conditions, the availability of 11 years of co-located observations of mineral dust outbreaks and surface O\textsubscript{3} represents a unique dataset to characterize mineral dust outbreak variability on an experimental basis and estimate its relationship with surface O\textsubscript{3} variability in this global hotspot region.

On average, 15.7% of the measurement period was affected by dust transport events (DTE). The monthly frequency showed a marked seasonal cycle: with the expected minimum in winter and maximum during the warm season. The declining tendency of DTE frequency from summer to winter was generally interrupted by a secondary peak in autumn, especially prominent in November (16.6%) when “acute” DTE were more likely to occur. This seasonal cycle clearly showed the occurrence of African dust outbreaks in the north central Mediterranean basin, a transitional area between the western Mediterranean (more affected by African dust during summer) and the eastern Mediterranean (more impacted by African dust air masses in the autumn–spring period). These events strongly affected the variability of coarse (Dp > 1 µm) aerosol particles: the dust-induced variations of coarse particle number concentration peaked during spring-autumn (0.50–0.54 cm\textsuperscript{-3} when the seasonal average N\textsubscript{1-10} increased from 123% (on summer) to 317% (on autumn). Analyzing the 11-y dataset of 3D air mass back trajectories, the DTE observed at CMN are mostly tagged (77.8% of the DD) to a macro-region encompassing the Djouf (19°N, 9°W) and especially Chotts (34°N, 9°E) basins (north-western Africa), while 14.4% of the DD are related to transport from central Libya (25°–30° N; 15°–20°E). On average, the first macro-region is tagged to 79% (average value: 0.29 cm\textsuperscript{-3}) of the dust-induced N\textsubscript{1-10} observed at CMN, while the (secondary) contributions from other regions peak in May–July (35%) and October–November (31%).

Significant inter-annual variations in DTE frequency and dust-induced N\textsubscript{1-10} were evident at CMN. In contrast to other studies, no robust evidence of an NAO influence on that variability was found, except for spring when a significant positive correlation between the NAO index and dust outbreak frequency (R\textsuperscript{2} = 0.32) was observed. Even if caution should be exercised in commenting on the NAO impact in such a short time frame, our results suggest a scaling down of the impact of NAO variability over the central Mediterranean basin with respect to a previous study (e.g., Pey et al., 2013). Nevertheless the statistically significant results for spring would suggest that present and future variability (both natural and anthropogenic) of large scale atmospheric modes cannot be ruled out in evaluating the transport of mineral dust to the central Mediterranean basin, especially during this season.

A significant impact of DTE on surface O\textsubscript{3} variability at CMN was found. In agreement with previous investigations, the O\textsubscript{3} significantly decreased in the presence of high mineral dust loading in the atmosphere. This negative correlation was particularly evident during spring and summer when the maximum O\textsubscript{3} decrease was found to be -4.1 nmol mol\textsuperscript{-1} (-7%) for dust loading with N\textsubscript{1-10} > 1.0 cm\textsuperscript{-3} and N\textsubscript{1-10} > 2.0 cm\textsuperscript{-3}, respectively. However, as shown by a concomitant analysis of the CO mixing ratio at CMN during the period 2007–2011, mixing with polluted air masses rich in combustion emissions could limit the O\textsubscript{3} depletion observed within dusty air masses. By neglecting DTE affected by mixing with polluted air masses, the maximum O\textsubscript{3} decrease was -8% during spring (with N\textsubscript{1-10} > 0.9 cm\textsuperscript{-3}) and larger than -9% during summer (with N\textsubscript{1-10} > 0.9 cm\textsuperscript{-3}). In addition, we investigated the possibility that the lower O\textsubscript{3} values – associated with the increase in N\textsubscript{1-10} during DTE – could be solely related to the origin and passage of air masses in the O\textsubscript{3}-depleted Saharan PBL. There was no clear evidence that back trajectory height/travel time is related to ΔO\textsubscript{3}, suggesting that the O\textsubscript{3} depletion observed at CMN could be due to the mineral dust.
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References


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Contributions
- Contributed to conception and design: RD, PC, PB
- Contributed to acquisition of data: RD, PC, TCL, JA, UB, LB, MB, FC, AM, DP
- Contributed to analysis and interpretation of data: RD, PC
- Drafted and/or revised the article: RD, PC, TCL, JA, UB, LB, MB, FC, AM, DP, PB
- Approved the submitted version for publication: RD, PC, TCL, JA, UB, LB, MB, FC, AM, DP, PB

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Competing interests
The authors have no competing interests.

Supplementary material
- Figure S1. Year by year time series of the de-trended ozone mixing ratio (blue line) and the coarse particle number concentration (red line) from 2002/2003 to 2012. Gray areas denote periods affected by the transport of mineral dust from North Africa. (JPG) doi: 10.12952/journal.elementa.000085.s001
- Figure S2. Averaged seasonal relationship between hourly O₃ decrease during DTEs (ΔO₃) and N₁₋₁₀ at CMN during 2007–2012 when no CO increases were observed. Periods with CO increases were identified by applying the Kolmogrov-Zurbenko filter to the hourly CO de-trended (see Section 3.5 of the manuscript) time series, then observations with positive differences between the hourly CO observations and the smoothed Kolmogrov-Zurbenko time series were selected. Vertical bars denote the 95% confidence level. The x-axis indicates the N₁₋₁₀ threshold values (lowest boundaries) for dust outbreak periods for which ΔO₃ was calculated. (JPG) doi: 10.12952/journal.elementa.000085.s002
- Figure S3. Concentration of back trajectory points related to the occurrence of DTEs at CMN during spring for negative (upper plate) and positive (bottom plate) NAO phases. The colored scale denotes the number of back trajectory points over the grid point (0.5°×0.5°). (JPG) doi: 10.12952/journal.elementa.000085.s003

Data accessibility statement
PM₁₀ data are available on the BRACE database (http://www.brace.sinanet.apat.it/web/struttura.html). Ozone data are available at the World Data Centre for Greenhouse Gases (http://ds.data.jma.go.jp/gmd/wdkgg/) and made accessible in accordance with the policy described by GAW Data Policy-Data dissemination policy and credit for use (http://ds.data.jma.go.jp/gmd/wdkgg/gaw-data-policy.html).

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