

Dear anonymous referee #2,

Thanks a lot for considering our manuscript suitable for publication after revision and also for the comments and suggestion that you gave us, which improved a lot the article. As you will see in the revised version we took into account all your valuable comments and suggestions. We also attach below a report on changes addressed and reply to your specific queries.

Following your suggestions we also evaluated in detail the stratospheric contributions. To this end we requested the support of Prof. M. Millán, who accepted and contributed a lot; so we have included him as a co-author in this revised version.

Thanks a lot for your constructive review.

Xavier Querol on behalf of all co-authors

Report on changes addressed and reply to specific queries

The study aimed to explore if changes in nucleation of ultrafine particles and high Surface ozone levels in urban areas could be related to the atmospheric dynamics changes over the European region at highest ozone risk. The content and the methodology are consistent and this study reports valuable conclusions based on experimental investigation by means of simultaneous vertical profiles of concentrations for both pollutants and meteorological parameters using balloons.

However, the conclusions can be improved (other than ozone levels are low with thick PBL and high wind speed) and some parts are really heavy going and need to be reformulated. In general, the English language can be improved and some parts need to be reformulated in a simpler way. The entire paper needs to be (deeply) reorganized (i.e. section Results & Discussions & Materials and Methods) and shortened.

REPLY, Thanks a lot for considering our manuscript suitable for publication after revision and also for the detailed revision done that improved a lot the presentation of our results. We have also revised again English usage.

The term "altitude" must be correctly used, i.e. use "altitude" for a.g.l. (for vertical profiles) and "elevation" for a.s.l. Please, revise all figures and manuscript. REPLY: Corrected in all text, figures and tables.

Abstract - Line 34: "high O3 level" or "ground-level O3". REPLY: Done.

Introduction - The state-of-the-art is consistent, however for a non-European scientist; the references are limited to Spain instead of Western Mediterranean region. The state-of-the-art must be documented e.g. including an overview of ozone impacts (Ochoa-Hueso et al., 2017, EnPo) and I found different studies (Lelieveld et al., 2002_Science; Kalabokas et al., 2008_ Atm Env; Giannakopoulos et al., 2009_Global&Planetary Change; Velchev et al., 2011_ACP; Sicard et al., 2013_Atm Env).

REPLY: Thanks for the constructive comment. Yes indeed we went directly to focus referencing of Millan's team in Spain, because they were pioneering the ozone research in this region in the 1980s-1990s, and in our opinion they built the basis of knowledge for atmospheric dynamics governing O3 levels in The Western Mediterranean, clearly different from those prevailing in the Eastern side of the basin. We recognize now that we missed first reviewing the whole Mediterranean issue. We have added now this view and included references you supplied us with and commented them in the introduction and discussion sections.

Particulate matter and tropospheric ozone are the most threatening air pollutants in cities (EEA, 2015). More than 75% of the urban population is exposed to levels exceeding WHO guidelines for PM2.5, PM10 and surface O3 (EEA, 2015). REPLY, we understand that you require us to add this into our text, and we did it using updated EEA (2017). Thanks

Line 66: "implemented" by? REPLY: Added: by the national, regional and local administrations

Line 70: add a reference. REPLY Added: EEA, 2017

Line 73: add an example for "easy to identify". REPLY: Added: (such as abating industrial, shipping and traffic emission with catalytic converters for NO_x and particulate controls for PM).

Lines 76-77, add a reference, what are the climatic and geographical characteristics leading to high ozone levels? In summer, the western part of the Mediterranean basin is dominated by anti-cyclonic subsidence (Hadley circulation +Azores), high pressure, low winds and strong insolation and thus atmospheric stability favouring photochemical production of O₃ (Kalabokas et al., 2008; Giannakopoulos et al., 2009; Velchev et al., 2011; Sicard et al., 2013) and emissions of biogenic VOCs (Giannakopoulos et al., 2009). **REPLY: Added: In summer, the Western Mediterranean Basin (WMB), surrounded by high mountains, falls under the influence of the semi-permanent Azores anticyclone. Clear skies prevail under a generalized level of subsidence aloft, and meso-meteorological processes with marked diurnal cycles dominate. Re-circulations, strong insolation and stability of upper layers favour the production/accumulation of O₃ (Millán et al., 1997, 2000 and 2002; Kalabokas et al., 2008; Giannakopoulos et al., 2009; Velchev et al., 2011; Sicard et al., 2013), and the emissions of biogenic volatile organic compounds (BVOCs) (Giannakopoulos et al., 2009).**

Line 90: add a value and a reference for "peaks O₃ concentrations". **REPLY: We added (those exceeding the hourly information threshold of 180 µg/m³)**

The ozone control measures are effective at rural sites while ozone levels are rising in cities (Paoletti et al., 2014_EnPo; Sicard et al., 2013_Atm Env). **REPLY: Thank you, yes we added these references to the others that find this trend in Europe. We missed them and these are very important.**

Line 99: NO titration, add a reference. What is the situation in Spain as compared to other European countries such as France and Italy? **REPLY: Yes we added reference; This NO/NO₂ is widely accepted in Europe. We added: This trend to decrease the NO/NO₂ rate from diesel vehicle emissions (the main source of NO_x in urban Europe) has been widely reported (i.e. Carslaw et al., 2016)**

Line 107: the urban areas are characterized by "VOC-limited" conditions, and a reduction in NO_x emission increases the O₃ formation. **REPLY, Yes we also gave this possibility in the original paper, but to make it more clear we added: We still do not know if this increase is due to a decrease in the NO titration effect or to the fact that the O₃ formation is by VOCs dominated, since the urban areas are characterized by 'VOC-limited' conditions, and a reduction in NO_x emission might yield to an increase of the O₃ formation.**

Lines 112-116: too many references and autocitation, the state-of-the-art need to be enlarged (e.g. Italy, France, Portugal) and add a comparison + quantification of the spatio-temporal changes for surface ozone levels. **REPLY. OK we changed this focus on the whole Mediterranean and we added the references (but no auto-citation, no one paper of the main author of this paper is cited here). Now we stated: Intensive research on O₃ pollution has been carried out in the Mediterranean since the late 1980s, which has been key to understand the behaviour of this pollutant in Europe, and to establish the current air quality European standards (Millán et al., 1991, 1996a, 1996b, 1996c, 2000, 2002; Millán, 2002; Lelieveld 2002; EC, 2002, 2004; Millán and Sanz, 1999; Mantilla et al., 1997; Salvador et al., 1997, 1999; Gangoiti et al., 2001; Stein et al., 2004, 2005; Chevalier et al. , 2007; Kalabokas et al., 2008, 2015 and 2017; Castell et al., 2008a,**

2008b, 2012; Kulkarni et al., 2011; Velchev et al., 2011; Doval et al., 2012; Sicard et al., 2013; Millán et al., 2014; Escudero et al., 2014; Zanis et al., 2014; Sicard et al., 2017; among others). EEA (2017) reports a clear gradient to increase the exceedances of the human protection 8-h O₃ target value in Southern and Central Europe, higher in the Italian Po Valley and Spain, and relatively lower in Portugal and the Eastern Mediterranean.

Lines 124-127: to be reformulated. **REPLY:** Done: Querol et al. (2017) reported that the high-O₃ plume transported from the metropolitan area of Barcelona contributed decisively to cause the frequent exceedances of the information threshold in the northern areas of Barcelona during the acute O₃ episodes in July 2015.

Line 128: what are the scenarios? **REPLY:** We modified the text: They also demonstrated that the meteorology associated was very complex, similar to the scenarios of vertical recirculation of air masses reported by.....

Line 139: "lowpre-existing: ::", please explain. **REPLY:** Modified to: low condensation sink potential (i.e. relatively clean atmospheres with low surface aerosol concentrations).

Line 142: add the period of the study. **REPLY:** Added.

Materials & methods - The experimental protocol and methodology are consistent, well described. Even if this section is important, it can be shortened, e.g. lines 165-190: move to section "Discussion" and need to be shortened. **REPLY:** Done. We still believe that the right place was the first description of the study area, but following requirements of the referee we moved to 'discussion' and shortened.

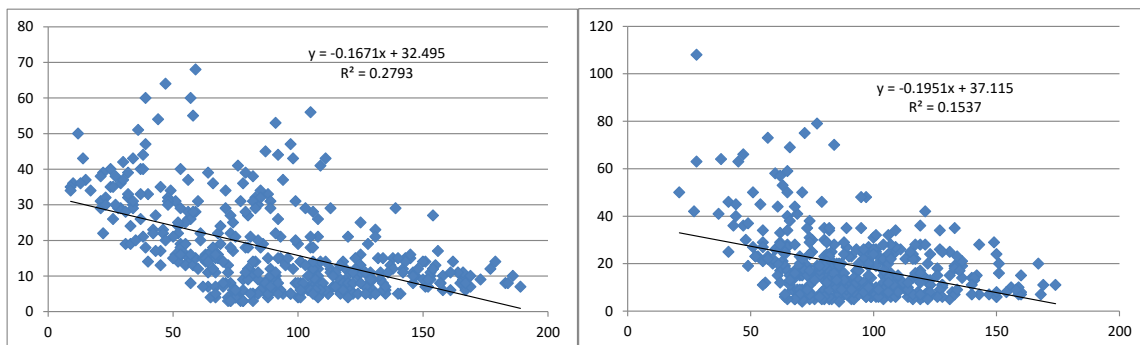
Line 195: "highest levels of O₃", how much? **REPLY:** Added (with hourly maxima sporadically exceeding 180 µg/m³)

Line 218: "very good results", please quantify (e.g. r²) this statement. **REPLY:** Added to text (with R² reaching 0.65-0.98 and slopes 0.87-1.23, Minguillón et al., 2015).

Results – Please avoid describing Figures (e.g. 260-262, 318-320), this is really heavy. **REPLY:** Deleted in both cases.

Lines 249-253: move to section "Materials & Methods". **Reply:** Done

Line 254: what is the correlation coefficient between NO₂ and ozone? **REPLY,** below you have it for 2 of the sites having the highest O₃ (NO₂ is in Y, and O₃ in X),



Lines 271-272: move to section "Discussion". **REPLY:** We do not understand here what you mean, moving 2 lines breaks the explanation of this paragraph. We decided to keep them in.

Lines 260-264: move to section "Materials & Methods". **REPLY:** In a prior observation you suggested deleting this description and we did it. Now is only 2 lines well inserted in this section.

Line 344: "high hourly O3 concentrations: ::" **REPLY:** Corrected and added, thanks

Lines 345-348: move to section "Discussion". **REPLY:** Moved

Lines 353-414: long section, boring, need to be shortened. **REPLY** We reduced it by 60% by moving descriptions of the first 3 days of soundings to SI and synthesising the results in the main text.

Line 441: "biogenic VOCs", please specify the source (e.g. isoprene). **REPLY:** Added: The influence of aromatic VOCs on OFP rapidly decreases while the influence of biogenic VOCs (mostly isoprene followed by monoterpenes, as primary ones, and methacrolein, methyl-vinyl-ketone, isoprene-derived isomers of unsaturated hydroxy hydroperoxides (ISOPOOH) and methylglyoxal, as the main secondary species)...

Lines 459-464: move to section "Results". **REPLY.** This is one of the only two cases that we decided to keep the original text here because, this discussion is summarising the evolution of the UFP and O3 profiles across the day, If we move these 5 lines, we start description from midday here and we lose the early to midday scenarios.

Line 468: titration by NO. **REPLY:** Added, thanks

Lines 487-495: to be reformulated, unclear. **REPLY:** Re-written: During the whole month of July 2016 there was a clear veering of the urban plume from Madrid, with night plume transport towards SW (MJDH-San Martin de V., Figures 9 and S12), and towards NW, N-NE, and, in some cases, E-SE during the morning and midday, followed by the decoupling and onset of the evening and nocturnal flow towards SW. This veering seems to be causally associated with the high O3 levels recorded in the W to E areas surrounding northern Madrid, since the peak concentrations recorded by the official air quality network follow this spatial and temporal evolution (Figure S12) for the exceedances of the O3 information threshold.

Lines 500-505: typical diurnal ozone concentrations, well documented in the literature, not innovative for ACP. **REPLY:** Done, we delete it.

Lines 506-5014: move to section "Results". **REPLY.** This is one of the two cases that we decided to keep the original text here because, this discussion is summarising the evolution of the UFP and O3 profiles across the day.

Lines 518-519: confusing compared to line 560, need to be reformulated. **REPLY, thanks a lot, changed to:** Conversely, the lower development of the PBL on 14/07/2016 causing less surface UFP dilution and lower top-down contributions to O₃ to surface concentrations accounted for opposite O₃ and UFP the profiles.

Lines 538-541: move to section "Results". At high elevation, changes in the background tropospheric ozone can be attributed to to i) hemispheric background concentrations, in part due

to the reduction in NO_x emissions; ii) the exchange between the free troposphere and the boundary layer and iii) the stratospheric inputs (Chevalier et al., 2007_ACP, Kulkarni et al., 2011; Lefohn et al., 2012_Atmospheric Environment; Sicard et al., 2016_Environmental Research). The “stratospheric inputs” need to be discussed in this section, as well as exchanged between the lower stratosphere and free troposphere.

REPLY: Yes this was a weakness, thanks a lot. We added: In addition of the local O₃, the background contribution can be also very relevant. At high elevation, changes in the background tropospheric O₃ can be attributed to (i) hemispheric background concentrations; (ii) exchange between the free troposphere and the boundary layer; and iii) stratospheric inputs (Chevalier et al., 2007; Kulkarni et al., 2011; Parrish et al., 2012, Lefohn et al., 2012; Kalabokas et al., 2013, 2015 and 2017; Zanis et al., 2014; Akritidis et al., 2016; Sicard et al., 2017).

We also modified several parts to discuss these free-troposphere and stratospheric contributions. Examples are:

- Section 4. We added the following discussion: Considering the free sounding O₃ profiles in Figure 3, high O₃ concentrations (>70 ppb) can be observed above the PBL, between 3000 and 5000 m a.s.l., which may be related to larger scale transport of pollutants, previously uplifted to the mid-troposphere or originated after a stratospheric intrusion and a subsequent deep subsidence into the middle troposphere, as it is probably the case based on the ECMWF ERA-Interim reanalysis data. Transport of high O₃ air masses in the middle troposphere, as for the 13/07/2016 in Figure 3, was also documented by Plaza et al. (1997) over this area in July 1994, during the final phase of a high O₃ period. More recently, Kalabokas et al. (2013, 2015, 2017), Zanis et al. (2014) and Akritidis et al (2016), among others, have shown that similar transport processes of enriched O₃ layers at high altitude, can contribute to increase surface O₃ concentrations during the summer in the Eastern Mediterranean. This transport has been associated with large scale subsidence within strong northerly winds in the Eastern Mediterranean (Etesian winds), and the affected layers are dryer than average and show negative temperature anomalies. Figure S11 shows the ECMWF ERA-Interim reanalysis together with the AEMET O₃ free soundings at Madrid airport for the 13/07/2016. The ridging at the lower troposphere over the Bay of Biscay at the rear of an upper-level trough (left panels) is accompanied by intense NW winds blowing at the middle and upper troposphere and NE winds at ground level and up to 2000 m (see the radiosonde profile in the same figure). The O₃ intrusion is associated to the upper-level trough (Sections A-A and B-B in the figure), and a large area of deep subsidence and extremely low relative humidity observed within the NW flows over Madrid and to the north of the Iberian Peninsula and the Bay of Biscay. High O₃ concentrations values and low relative humidity of the ERA-Interim profiles over the airport of Madrid (green and red dotted-lines in the panel “g” of the Figure S11) are in agreement with the radiosonde observations in the same panel.

The question now is how much of this O₃ could fumigate at ground level. According to the radiosonde data, the mixing height top was about 2000 m a.s.l. at midday, but could increase to about 3100 m a.s.l. after the projection of the surface temperature increase observed during the afternoon at near-by stations. This height reaches the lower part of the O₃ enriched layer originated in the tropopause folding. Thus, a certain impact seems likely. However, the O₃ concentrations were relatively low at all surface stations during that day, as it corresponds to a vented low O₃ period.

- A new figure S11 has been added and discussed to show the stratospheric intrusion following your suggestion.
- We added these two paragraphs in the conclusions:

- The O₃ source apportionment is very complex, having contributions from local/regional and remote sources, including the stratosphere. The relative contributions of these might vary in time and space (e.g. Lefohn et al., 2014).
- Climate change might reduce the benefits of the O₃ abatement policies (since hot waves increase O₃ episodes). This, as well as the measures and policies in Northern America and Asia, will need to be considered into future Europe policies for O₃ mitigation (Lefohn and Cooper, 2015; Sicard et al., 2017)
- And we modified the fourth as follows: In the MAB, during the highest O₃ (accumulation) episodes, in addition of the contribution (to surface concentrations) by fumigation of upper O₃ (from regional transport, hemispheric free troposphere O₃, and intruded stratospheric O₃, X in Figure 10), there is an added fraction produced locally and transported-recirculated within the MAB, which accumulates from one day to the next (Y in Figure 10).

Conclusions – Line 587-588: climate change might reduce the benefits of the ozone control strategies. This can be discussed e.g. climate change and the measures and policies in North America or Asia will need to be considered into future ozone policies in Europe for ozone mitigation (Lefohn and Cooper, 2015_Atmo Env; Sicard et al., 2017_ACP). REPLY. Yes, thanks for this key suggestion for this section on air quality policy. We added 2 bullets:

- The O₃ source apportionment is very complex, having contributions from local/regional and remote sources, including the stratosphere. The relative contributions of these might vary in time and space (e.g. Lefohn et al., 2014).
- Climate change might reduce the benefits of the O₃ abatement policies (since hot waves increase O₃ episodes). This, as well as the measures and policies in Northern America and Asia, will need to be considered into future Europe policies for O₃ mitigation (Lefohn and Cooper, 2015; Sicard et al., 2017)

Line 612: a statement of ACP Special Issues (Lamarque et al., 2013_ACP and Young et al. 2013_ACP) with respect to the ACCMIP models can be done, or the validation of ACCMIP ozone simulations using sonde throughout the free troposphere and lower stratosphere for both seasonal and year-to-year variations of ozone (Kazuyuki Miyazaki and Kevin Bowman, 2017_ACP). REPLY. Yes we recognise we may add a bit on these inter-comparison exercises, but the number of tem is large, and come from different scientific-policy forums. The we decided to insert this text: A good combination of regional/local scale modelling, able to reproduce horizontal/vertical re-circulations of air masses, and the behaviour of urban/industrial plumes in complex topography/meteorology; with modelling able to calculate contributions from long range transport, free troposphere, and stratospheric O₃, will be needed to efficiently support policy (see v.g. the ACP special issue on the Atmospheric Chemistry and Climate Model Inter-comparison Project, ACCMIP https://www.atmos-chem-phys.net/special_issue296.html; the FAIRMODE initiative, Thunis et al., 2015; and the Monitoring Atmospheric Composition & Climate (MACC)).

Grammatical suggestions and typos

Lines 69, 88: PM 10 and 2.5 in subscript. REPLY. Done, thanks

Line 86: Monks et al., 2015 rather than 2014. REPLY. Done, thanks

Line 133: to be reformulated as “recorded in July” (a simpler way). REPLY. Done, thanks

Line 142: why did you put (and UFP) with brackets? REPLY. Brackets deleted

Line 188: Gómez-Moreno (hyphen) REPLY. Added, thanks
Some acronyms need to be defined e.g. lines 206, 215, 236 REPLY. Defined there and some additional ones, thanks
Line 206: 19 or 20 July, to be checked. REPLY: It is 19/July, this finished one day before other instruments. Then we leaved it
Line 442: "through the" (space). REPLY: Corrected, thanks
Line 444: remove all the text given in parentheses (really heavy). REPLY: Deleted, thanks
Line 475: McKendry and Lundgren (instead of "et al."): REPLY: Corrected, thanks
Line 601: add a reference REPLY: Added: according our calculations (Table S1 and Figure S1).

Tables & Figures

There are too many figures, it would be necessary to select the most informative figures (5-6 maximum) and move the other to SI. REPLY, as you will see we moved a number of them to SI. Please, change "altitude" as "elevation" in Figures and Tables when necessary. REPLY: Done, thanks for observations and corrections
Figures 7-10-11 can be joined. Too many Figures seem similar and not useful. REPLY, We removed Figure 10 and 11 and inserted in the SI.
Figure 1: put units (m) on X- and Y-axis and "elevation (a.s.l)". REPLY, corrected, many thanks
Figure 3: how is possible to read variations of values, I don't see the units for each parameter (e.g. T, RH), please add a second Y-axis with units. REPLY: We added a nex X axis for T as requested
Figure 4: blurred. REPLY: We made it again with higher resolution.
Figure 13: units on Y-axis. REPLY, done, thanks for the correction
Table 1: add the station "El Retiro" and define the acronyms in caption (RH, Temp., UFP: : :) REPLY, done, thanks for the correction
Table 2: m (a.g.l). :) REPLY, done, thanks for the correction

References

Kulmala et al., 2000 (Line 702), Millán & Artíñano, 1992 (Line 725) & Skrabalova et al., 2015 are missing. REPLY, thanks a lot and sorry for these errors. We added cite in the first case and we deleted the 2 last ones.
Line 766: Pujadas et al., the year is missing (2000). REPLY. This reference was deleted due to the shortening of text, thank you
Line 781: "et al.," please supply the full author list. Please, read the advices in the guidelines for authors for the "list of references" (e.g. publication year, lines 787, 702) and consider a chronological order for the same author e.g. Millán. REPLY, Thanks a lot for detecting these errors. Revised all references.

END OF THE REPORT