SUMMARY OF CHANGES DONE FOLLOWING THE REFEREES' SUGGESTIONS

Dear editor,

Thanks a lot for considering our paper for the revision stage and for the editorial tasks.

As you will see we have implemented the changes and suggestions from both referees. Both reviews were extremely interesting for us, and also coincident in the fact that we miss to better describe the variation of background O_3, and the potential stratospheric contributions. You will see that we worked a lot on it and now this is clearly integrated in discussion and interpretation. You will see that we modified a lot the paper in content and format.

Because we requested the support of Dr Milllán to better understand the issue of the O_3 subsidence over the Mediterranean, and because he worked to interpret the meteorology to evidence the stratospheric contribution, as well as to prepare the new figure, we would like to introduce him as a co-author of this revised version. I hope you will accept this change also.

Once we finished with revisions we sent the manuscript to Cambridge Proofreading to correct errors in English usage.

We attach the version with track changes in order to easily detect the changes done and another one with these accepted. We also modified the S. I. We also attach a detailed description of how we took into account the referees' comments and suggestions.

We firmly believe that the review process has substantially improved the paper.

Thank you very much again and kind regards

Xavier

Barcelona, Spain, March 5, 2018

REFEREE #1

Overview: The paper deals with the phenomenology of the summer ozone episodes over the greater area of Madrid, Spain. I think that it is a very interesting study, analysing atmospheric measurements of ozone and fine particles together with many other atmospheric parameters and giving further insight to the complicated atmospheric mechanisms related with air pollution over the area. In my opinion, the document deserves publication in ACP, after the recommendations listed below are taken into account. REPLY, Thanks a lot for considering our manuscript suitable for publication after revision and also for the comments and suggestion on the stratospheric O_3 that improved a lot the article.

General comments: A weak point of the paper is that the levels of measured surface ozone are mainly related (or attributed) to the photochemical ozone production over the metropolitan area of Madrid. REPLY, Thanks a lot this comment. We also considered long range transport (named 'external' in the paper. But as you might see in the revised version we have enlarged this and also the stratospheric issue that we miss in our original submission.

On the other hand, I think that the variations of the background ozone levels within the boundary layer and the free troposphere are not discussed with sufficient detail. In relation to that comment and based on research results carried out on the other side of the Mediterranean basin, in the Eastern Mediterranean, it comes out that the regional background ozone levels in the free troposphere and the boundary layer during summer, regularly exceeding 60 ppb, contribute on the average to the greatest part of the surface ozone levels measured in large urban areas like Athens (Kalabokas et al., 2000; Kourtidis et al., 2002; Kouvarakis et al., 2002; Lelieveld et al., 2002; Kalabokas and Repapis, 2004; Gerasopoulos et al., 2005). The main origin of these high ozone background levels over the Eastern Mediterranean is tropospheric ozone subsidence, which seems to be strongly related with specific synoptic meteorological conditions, occurring very frequently during summer at the Eastern side of the Mediterranean basin (Kalabokas et al., 2013; Zanis et al., 2014; Kalabokas et al., 2015; Akritidis et al., 2016). In addition, recent research shows that during springtime ozone episodes (April – May) over the western Mediterranean similar synoptic meteorological patterns might also occur and which are linked with regional episodes mainly induced by large scale tropospheric ozone subsidence, influencing (or fumigating) the boundary layer as well as the ground surface ozone concentrations (Kalabokas et al., 2017).
REPLY, Thanks a lot for these observations. Yes you are completely right; we miss these issues in our discussions and interpretations. We have added these observations and discussions in several part of the revised paper. For example text added or changed includes:

- Abstract: We added: The results demonstrate the concatenation of venting and accumulation episodes, with relative O_3 lows (venting) and peaks (accumulation) in surface levels. Regardless of the episode type, fumigation of high altitude O_3 <u>(from different origins</u>) contributes the major proportion of surface O_3 concentrations.
- Section 1: New text added: In the Eastern Mediterranean, the regional background O3 levels in the free troposphere and the boundary layer during summer might regularly exceed 60 ppb, and fumigation of these upper air masses contribute on the average to the greatest part of the surface O3 levels measured in Greece (Kalabokas et al., 2000; Kourtidis et al., 2002; Kouvarakis et al., 2002; Lelieveld et al., 2002; Kalabokas and Repapis, 2004; Gerasopoulos et al., 2005). Furthermore, a number of studies reported contributions of stratosphere to the surface O3 concentrations during specific

meteorological scenarios in the same region (Kalabokas et al., 2013, 2015; Zanis et al., 2014; Parrish et al., 2012; Lefohn et al. , 2012; Akritidis et al., 2016, among others). In addition, recent research shows that during springtime O3 episodes (April – May) over the WMB similar synoptic meteorological patterns might also occur; and that these are linked with regional episodes mainly induced by large scale tropospheric O3 subsidence, influencing the boundary layer as well as the ground surface O3 concentrations (Kalabokas et al., 2017). However, the most intense episodes in the WMB occur in June-July according to the statistics for the 2000-2015 period by Querol et al. (2016) for Spain.

- Section 3.1. New text added: The AEMET free-sounding shows low O3 surface concentrations (<45 ppb) and high levels (>70 ppb) in the middle troposphere (3000-5000 m a.s.l.), associated with very low relative humidity and intense W to NW winds blowing at that height, which will be discussed in section 4.
- Section 4: discussion added, see below.
- New figure added (see below)
- Conclusions modified (see below)

Even if the typical meteorological conditions prevailing over the Iberian Peninsula during summer are quite different than in the Eastern Mediterranean, as it is very well described in the introduction of the manuscript, occasionally such conditions might occur. In fact, I think that this is the case of the ozone episode of 11-15 July 2016, which is the most studied period in the manuscript (when the intensive measuring campaign has taken place). As shown in Figs 3 and 12, the free tropospheric ozone levels are much higher on July 13, 2016 than the two weeks before and after and at the same time the relative humidity values in the lower troposphere are close to zero (and being in sharp contrast with the periods before and after). In fact, this feature is a very common characteristic of deep and large-scale tropospheric subsidence in summertime ozone vertical profiles over the Eastern Mediterranean, indicating an origin of air masses from the upper tropospheric or stratospheric layers (Kalabokas et al., 2013; Kalabokas et al., 2015).

Therefore, for a better assessment of the free tropospheric influence as well as the reported fumigation events over the area, I would suggest putting more emphasis on the analysis of the synoptic conditions during this most studied period, when the intensive measurement campaign has taken place (11-15 July 2016). A figure could be added including at least the daily meteorological maps of geopotential height, omega vertical velocity and specific humidity at 700hPa pressure level (representative for the free troposphere), which I think that they would be sufficient to follow satisfactorily the evolution and the geographical extent of the subsidence phenomenon (the subsiding air mass seems to originate from N-NW Atlantic). If this parameter is taken into account, then I think that the discussion concerning the origin of the fumigation events during 11-16 July 2016 would be more complete (tropospheric ozone subsidence in addition to the local ozone photochemical production associated with valley-breeze recirculation and ozone residual layers, as mentioned many times in the manuscript). So, I would suggest modifying accordingly the respective paragraphs, where sometimes the high ozone values recorded at the top of the boundary layer are not fully explained (e.g.: Page 5, lines 175-187; Page 9, lines 348 – 352, 362-365; Page 12, lines 470 – 473, 483-487; Page 14, lines 570 – 582).

REPLY. Thanks a lot for these very interesting comments. Indeed we have applied all your suggestions and modified the introduction, discussion and conclusions sections to this end. 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 my reduce the benefits of the O_3 abatement policy (since hot waves increase O_3 episodes), and this, as well as the measures and policies in N America and Asia will need to be considered into future Europe policies for O_3 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).

In addition, I think that it would be more appropriate to refer to "Western Mediterranean" ozone when analyzing ozone in Spain (instead of "Mediterranean" or "S. Europe" in general) as, according to the above mentioned papers, the phenomenology of the summertime ozone over the Eastern Mediterranean seems to be is quite different than the typical ozone phenomenology over the Western Mediterranean.
REPLY: Yes we have revised and changed following your suggestion. Thanks for this.

I would strongly recommend taking these considerations into account, which have been made in the spirit to further improve this good quality manuscript, by modifying the respective paragraphs. After responding to these remarks, I think that the paper is ready for publication.
REPLY: Yes we did implement your very good observations and we thank you a lot for your very valuable review.

Technical comments: Fig. 4: Very condensed and difficult to follow, especially on printed paper. I would suggest splitting into two parts and eventually using gridlines.
REPLY: We made it again with clearer drawings.

END OF THE REPORT

REFEREE #2

Comments from referee

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 the 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 an 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 O_3 (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 $\mu g/m^3$)

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 NOx 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 NOx 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 NOx 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).

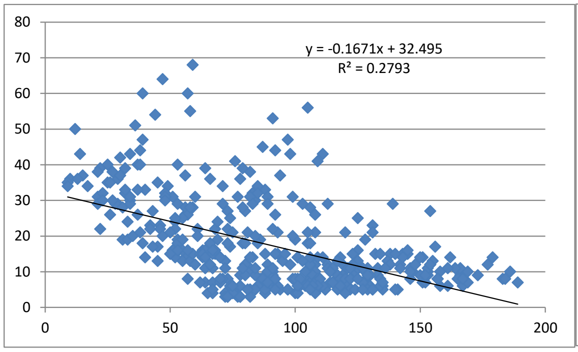
Line 142: add the period of the study. REPLY: Added.

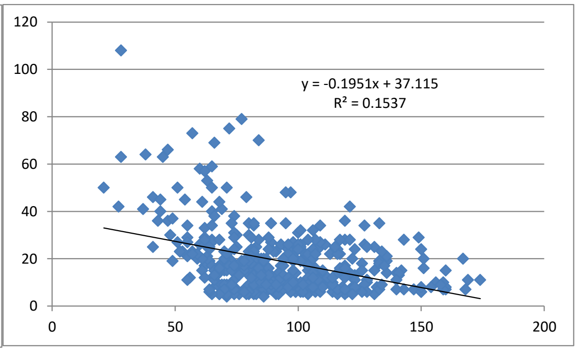
Materials & methods - The experimental protocol and methodology are consistent, well described. Even if this section is important, it can be shortened, e.g. lines 165-190: move to section "Discussion" and need to be shortened. REPLY: Done. We still believe that the right place was the first description 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/m^3)

Line 218: "very good results", please quantify (e.g. r2) this statement. REPLY: Added to text (with R^2 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 les surface UPF dilution and lower top-down contributions to O_3 to surface concentrations accounted for opposite O_3 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 NOx 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_Atm Env; Sicard et al., 2016_Env 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 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

Phenomenology of summer ozone episodes over the Madrid Metropolitan Area, C~~c~~entral Spain

Xavier Querol~~ X.~~[1], Andrés Alastuey~~ A.~~[1], Gotzon Gangoiti[2], Noemí Perez[1], Hong K. Lee[3], Heeram R. Eun[3], Yonghee Park[3], Enrique Mantilla~~ E.~~[4], Miguel Escudero[5], Gloria Titos[1], Lucio Alonso[2], Brice Temime-Roussel[6], Nicolas Marchand[6], Juan R. Moreta, M. Arantxa Revuelta[7], Pedro Salvador [8], Begoña Artíñano[8], Saúl García dos Santos[9], Mónica Anguas[10], Alberto Notario[11], Alfonso Saiz-Lopez[10], Roy M. Harrison[12]~~,~~, Millán Millán[4], Kang-Ho Ahn[3]

[1] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/Jordi Girona 18-26, Barcelona, 08034 Spain
[2] Escuela Técnica Superior Ingeniería de Bilbao, Departamento Ingeniería Química y del Medio Ambiente, Universidad del País Vasco UPV/EHU, Urkixo Zumarkalea, S/N, Bilbao, 48013 Spain
[3] Department of Mechanical Engineering, Hanyang University, Ansan 425-791, Republic of Korea
[4] Centro de Estudios Ambientales del Mediterráneo, CEAM, Unidad Asociada al CSIC, Parque Tecnológico C/ Charles R. Darwin, 14 Paterna, Valencia, 46980 Spain
[5] Centro Universitario de la Defensa de Zaragoza, Academia General Militar, Ctra. de Huesca s/n, Zaragoza, 50090 Spain
[6] Aix Marseille Univ, CNRS, LCE, Marseille, France
[7] Agencia Estatal de Meteorología, AEMET, C/ Leonardo Prieto Castro, 8, Madrid, 28071 Spain
[8] Department of Environment, CIEMAT, Joint Research Unit Atmospheric Pollution CIEMAT-CSIC, c/ Avenida Complutense 40, Madrid, 28040 Spain
[9] Centro Nacional de Sanidad Ambiental. Instituto de Salud Carlos III (ISCIII), Ctr Majadahoda a Pozuelo km 2, Majadahonda (Madrid), 28222 Spain
[10] Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, 28006 Spain
[11] University of Castilla-La Mancha, Physical Chemistry Department, Faculty of Chemical Science and Technologies, Ciudad Real, Spain.
[12] National Centre for Atmospheric Science, University of Birmingham, B15 2TT United Kingdom. [+] Also at: Department of Environmental Sciences/Centre for Excellence in Environmental Studies, King Abdulaziz University, Jeddah, Saudi Arabia

Abstract

Various studies have reported that photochemical nucleation of new ultrafine particles (UFP) in urban environments within high insolation regions occurs simultaneously with high ground ozone (O_3) levels. In this work, we evaluate the atmospheric dynamics leading to summer O_3 episodes in the Madrid Air Basin (Central Iberia) by means of measuring a 3D distribution of concentrations for both pollutants. To this end, we obtained vertical profiles (up to 1200 m~~,~~ above ground level) using tethered balloons and miniaturised instrumentation at a suburban site located to the SW of the Madrid Metropolitan Area (MMA), the Majadahonda site (MJDH) in July 2016. Simultaneously, measurements of an extensive number of air quality and meteorological parameters were carried out at 3 supersites across the MMA. Furthermore, data from O_3-soundings and daily radio-soundings were also used to interpret ~~the~~ atmospheric dynamics.

The results demonstrate the concatenation of venting and accumulation episodes, with relative ~~O_3~~ lows (venting) and peaks (accumulation) in O_3 surface levels. Regardless of the episode type, fumigation of high-~~-~~altitude O_3~~-rich layers~~ (arising from a variety of origins~~)~~) contributes ~~to~~ the major proportion of surface O_3 concentrations. Accumulation episodes are characterised by a relatively thinner planetary boundary layer (~~PBL~~< 1500 m at midday, lower

Con formato: Superíndice

Con formato: Fuente: (Predeterminado) Calibri, Color de fuente: Negro in altitude than the orographic features), ~~low~~ light synoptic winds and the development of mountain breezes along the slope of the Guadarrama Mountain Range (located W and NW of MMA, ~~and~~with a maximum elevation~~altitude~~ of >2400 m above sea level). This orographic-meteorological setting causes the vertical recirculation of air masses and ~~the~~ enrichment of O_3 in the lower tropospheric layers. When the highly polluted urban plume from Madrid is affected by these dynamics, the highest O_x (O_3+NO_2) concentrations are recorded in the MMA.

Vertical O_3 profiles during venting episodes, with ~~marked~~ strong synoptic winds and a deepening of the planetary boundary layer~~PBL~~, reaching >2000 m above sea level, were characterised by an upward gradient in O_3 levels, whereas a reverse~~d~~ situation with ~~low-altitude~~ O_3 concentration maxima at lower levels, ~~due to local/regional production~~ was~~ere~~ found during the accumulation episodes due to local/regional production. The two contributions to O_3 surface levels (fumigation from high altitude strata and local/regional production) require very different approaches for policy actions. In contrast to O_3 vertical top-down transfer, UFP are formed in the lowest levels and are transferred upwards progressively with the ~~growth~~ increase of the planetary boundary layer~~of the PBL~~.

Keywords: Ozone, ultrafine particles, photochemical pollution, air quality, vertical profiles.

1. Introduction

The EU Directive 2008/50/EC on ambient air quality, amended by Directive 2015/1480/EC, ~~on ambient air quality~~ establishes the need to comply with air quality standards to protect citizens and ecosystems. If these are not met, plans to improve air quality must be implemented by the national, regional, and local administrations. Despite the considerable improvements in air quality during the last decade, non-compliance~~s~~ with ~~the~~ European air quality standards ~~are~~ is still reported in most Europe. In particular the limit values for nitrogen dioxide (NO_2), particulate matter (PM_{10} and $PM_{2.5}$) and tropospheric ozone (O_3) target value are frequently exceeded (EEA, 2017). Therefore, in 2013, the National Plan for Air Quality and Protection of the Atmosphere (Plan AIRE) 2013-2016, was drawn up, and approved by the Spanish Council of Ministers' Agreement of 12/04/2013.

The EEA (2017) recently reported that in 2015 80% of the urban EU-28 population was exposed to $PM_{2.5}$ levels exceeding the WHO guideline, and 90% to that of O_3.

Measures to effectively reduce NO_2 and primary PM pollution are relatively easy to identify (such as abating industrial, shipping, and traffic emissions with catalytic converters for NO_X and particulate controls for PM). However, defining policies for abating O_3, other photochemical pollutants, and the secondary components of PM is much more complex.

Photochemical pollution is a subject of great environmental importance in Southern ~~(S)~~ Europe due to its climatic and geographical characteristics (Ochoa-Hueso, 2017). ~~Sub-p~~Products of this type of pollution~~contamination~~ are many, the most noteworthy being tropospheric O_3, secondary PM (nitrate, sulphate, and secondary organic compounds), and the generation of new ultra-fine particles (UFPs) by nucleation (Gomez-Moreno et al., 2011;~~,~~ Brines et al., 2015).

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

In summer, the Western Mediterranean Basin (WMB), surrounded by high mountains, falls under the influence of the semipermanent Azores anticyclone. Clear skies prevail under a generalized level of subsidence aloft, and meso-meteorological processes with marked diurnal cycles dominate. Re-circulation, strong insolation and stability in the upper layers favour the production/accumulation of O_3 (Millán et al., 1997, 2000, 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).

The abatement of tropospheric O_3 levels in this region is a difficult challenge due to its origin, which may be local, regional and/or transboundary (Millán et al., 2000; Millán 2014; Lelieveld et al., 2002; - ~~and~~ Kalabokas et al., 2008, 2013, 2015, 2017; Velchev et al., 2011; Sicard et al., 2013; Zanis et al., 2014~~Millán, 2014~~), the complexity of the meteorological scenarios leading to severe episodes (Millán et al., 1997;~~,~~ Gangoiti et al., 2001~~,~~; Dieguez et al., 2009~~, and~~ 2014; Kalabokas et al., 2017~~ and Millán, 2014~~), as well as the complexity of the non-linear chemical processes that drive its formation and sinks~~, which are not linear in many cases~~ (Monks et al., 2015~~4~~, and references therein).

This complex context has led to a lack of 'sufficient' O_3 abatement in Spain (and Europe); while for primary pollutants, such as SO_2 and CO, and the primary fractions of PM_{10} and $PM_{2.5}$ ~~the~~ improvement has been very evident (EEA, 2017~~6~~). Thus, the latest air quality assessment for Europe (EEA, 2017~~6~~) shows that: i) there has been a tendency for the peak O_3 concentration values (those exceeding the hourly information threshold of 180 µg/m^3) ~~-~~to decrease in ~~the~~ recent years, ~~but~~ although not enough to meet the WHO guidelines and EC standards; and ii) the problem of O_3 episodes is more pronounced in the South than in Northern and Central Europe. Likewise, O_3 levels are higher in rural than in urban areas, both due to i) the generation process, which requires time since the emissions of urban, industrial and biogenic precursors to the production of O_3; and ii) the consumption (NO titration) of O_3 that takes place in urban areas.

~~both due to the generation process, which requires time since the emission of urban, industrial and biogenic precursors, and the consumption (NO titration) of O~~$_3$~~ that takes place in urban areas.~~

~~Apart from this EEA report, o~~Other ~~recent~~ studies such as Sicard et al. (2013), Paoletti et al. (2014), ~~EMEP (2016),~~ Escudero et al.~~,~~ (2014),~~;~~ Garcia et al. (2014),~~ and~~ Querol et al. (2014,~~ and~~ 2016), and EMEP (2016), also evidenced that there is a general tendency for O_3 to increase in urban areas, including at traffic sites, probably due to the greater ~~relative~~ reduction of NO emissions relative~~compared~~ to NO_2, and therefore,~~ to~~ a~~the~~ lower NO titration effect. This trend in decreasing the NO/NO_2 ratio~~s~~ from diesel vehicle emissions (the main source of NO_x in urban Europe) has been widely reported (i.e. Carslaw et al., 2016). It has also~~is~~ been ~~also~~ found ~~also~~ that regional background O_3 levels have remained constant over the last 15 years, ~~but~~ while acute episodes have been drastically reduced compared to the late 1990s, although ~~and~~ these markedly increase during heat waves such as those in the summers of 2003 and 2015 (EEA, 2017~~6~~;~~,~~ Diéguez et al., 2009~~, and~~ 2014; and Querol et al., 2016).

A recent study (Saiz-Lopez et al., 2017) reported ~~that~~ an increase of 30-40% in ambient air O_3 levels, along with a decrease of 20-40% in NO_2 from 2007 to 2014 in Madrid, which may have

Con formato: Normal

Con formato: Ninguno, Fuente: (Predeterminado) Calibri, 11 pto, Inglés (Reino Unido)

Con formato: Subíndice

Con formato: Subíndice

Con formato: Superíndice

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Subíndice

Con formato: Subíndice

led to a large concentration increases of up to 70% and 90% in OH and NO_3~~ (the main tropospheric oxidants),~~ respectively, thereby changing the oxidative capacity of this urban atmosphere~~ (Saiz-Lopez et al., 2017)~~. ~~-~~We still do not know if this increase is due to a decrease in the ~~effect of ~~NO titration effect or to the fact that ~~the ~~O_3 formation is ~~by volatile organic compounds (VOCs)~~ dominated by VOCs since the urban areas are characterized by ‘VOC-limited’ conditions, and a reduction in NO_x emission might yield an increase in O_3 formation.

Intensive research on O_3 pollution has been carried out in the Mediterranean since the late 1980s~~ in the Western Mediterranean, which~~ and has been key ~~to ~~in understanding the behaviour of this pollutant in Europe. It has also been used~~, and~~ to establish ~~the ~~current ~~air quality ~~European air quality 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; ~~Doval et al., 2012; ~~Kalabokas et al., 2008, 2015, 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). The EEA (2017) reports a clear increase in exceedances of the human protection 8-h O_3 target value in Southern and Central Europe, ~~with a ~~which are higher~~ degree~~ in the Italian Po Valley and Spain, and ~~a ~~relatively lower~~ one~~ in Portugal and the Eastern Mediterranean.

Focusing on the study area, Diéguez et al. (2009,~~ and~~ 2014) describe~~d~~ in detail the temporal and spatial variation of O_3 levels in Spain. These studies highlight the low inter-annual variability in regional background stations, as well as the existence of specific areas, such as the Madrid air basin (MAB), Northern valleys influenced by the Barcelona urban plume, Puertollano basin, and~~ or~~ the interior of the Valencian region, where very high O_3 episodes are relatively frequent, and point to urban and industrial hot spots as relevant sources of precursors. Recently, Querol et al. (2016) evidenced that the highest O_3 episodes, with hourly exceedances of the information threshold for informing ~~to ~~the population (180 µg/m^3) ~~for~~ during 2000-2015 occurred mostly around these densely populated or industrialised areas.

Querol et al. (2017) report~~ed~~ that~~ the load of~~of the high-~~-~~O_3 plume transported from ~~and precursors from the plume of ~~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 O_3 episodes in July 2015. They also demonstrate~~d~~ that the associated meteorology ~~associated ~~was very complex, similar to the~~ scenarios~~ of vertical recirculation of air masses scenarios reported by Gangoiti et al. (2001), Millán (2014) and Diéguez et al. (2014) for other regions of the Western Mediterranean. Regional transport of O_3 is also very relevant, , as well as acute O_3 episodes, which exceeded the information threshold and were caused largely by regional transport (with large a contribution also from local formation recirculated during prior days, on top of which an additional smaller local ‘fresh’ contribution was added). It is also shown that the vast majority of these exceedances are recorded in July.~~and that acute O_3 episodes, exceeding the information threshold, were caused by a dominant regional transport contribution (also with high contributions from local formation recirculated during prior days) to O_3, on top of which an additional smaller local ‘fresh’ contribution was added. It was also shown that the vast majority of these exceedances are recorded in in the month of July of the respective years.~~

Con formato: Fuente: (Predeterminado) Calibri, 11 pto

Con formato: Subíndice

Con formato: Fuente: (Predeterminado) Calibri, 11 pto

Con formato: Fuente: (Predeterminado) Calibri, 11 pto

Con formato: Fuente: (Predeterminado) Calibri, 11 pto, Subíndice

Con formato: Fuente: (Predeterminado) Calibri, 11 pto

Con formato: Diseño: Claro

Con formato: Subíndice

In the Eastern Mediterranean, the regional background O_3 levels in the free troposphere and the boundary layer during summer might regularly exceed 60 ppb, and fumigation of these upper air masses contributes, on average, to the greatest part of the surface O_3 levels measured in Greece (Kalabokas et al., 2000; Kourtidis et al., 2002; Kouvarakis et al., 2002; Lelieveld et al., 2002; Kalabokas and Repapis, 2004; Gerasopoulos et al., 2005). Furthermore, a number of studies report contributions from the stratosphere to the surface O_3 concentrations during specific meteorological scenarios in the same region (Kalabokas et al., 2013, 2015; Zanis et al., 2014; Parrish et al., 2012; Lefohn et al. , 2012; Akritidis et al., 2016, among others). In addition, recent research shows that, during springtime O_3 episodes (April – May) over the WMB, similar synoptic meteorological patterns might also occur, and that these are linked with regional episodes, mainly induced by large-scale tropospheric O_3 subsidence, influencing the boundary layer as well as the ground surface O_3 concentrations (Kalabokas et al., 2017). However, the most intense episodes in the WMB occur in June-July, according to the statistics for the 2000-2015 period in Spain presented by Querol et al. (2016).

In addition to ~~the~~ primary emissions, nucleation or new particle formation (NPF) processes give rise to relevant contributions to the urban ambient air UFP concentrations, mostly during photochemical pollution episodes in spring and summer (Brines et al., 2015, and references therein). Ambient conditions favouring urban NPF are high insolation, low relative humidity, available SO_2 and VOCs, as well as low ~~pre-existing~~condensation sink potential (~~-particle surface area (low condensation sink~~i.e., a relatively clean atmosphere with low surface aerosol concentrations~~), common features that enhance new particle formation events~~) (Kulmala et al., 2000, 2004; Kulmala and Kerminen, 2008;~~,~~ Sipilä~~,~~ et al., 2010;~~,~~ Salma et al., 2016).

In this study, we evaluate the temporal and spatial variability of O_3 ~~(~~and UFP~~)~~ in the MAB~~adrid city/basin~~ (04-20/07/2016), to investigate the causes of acute summer episodes of both pollutants, and ~~to investigate~~ possible inter-relationships. In a subsequent twin article, we will focus on the phenomenology of UFP nucleation episodes linked with these photochemical events. Data on UFPs are included in this paper only where they assist in interpreting the behaviour of O_3.

2. Methodology

2.1. The study area

The ~~Madrid air basin~~MAB and the Madrid Metropolitan Area (MMA) are located in the central plain, or Meseta, of the Iberian Peninsula at around 700 m above sea level (m a.s.l.) ~~a.s.l.~~ Regarding the topographic features, the Guadarrama range, which runs in the NE-SW direction, reaches heights of up to 2400 m a.s.l. and is located 40 km north from the MMA. To the S, are the Toledo Mountains which run from E to W (Figure 1). Lower mountains,~~ are also~~ located to the NE and E,~~, which~~ are part of the Iberian range. Consequently, the Madrid plain shows a NE-SW channelling of winds, forced by the main mountain ranges, ~~and~~ following the basin of the Tagus River and its tributaries. In particular, the MMA is located to the NE of the river basin and on ~~at~~ its ~~right~~ E side.

Climatologically, the area is characterised by continental conditions with hot summers and cold winters with both seasons typically being dry. Mean annual precipitation of ~~around~~

approximately 400 mm is mainly concentrated in the autumn and spring. The MMA is one of the most densely populated regions in Spain, with more than 5 million inhabitants, including Madrid City and surrounding towns. According to Salvador et al. (2015), the main anthropogenic emissions are dominated by road traffic and residential heating (in winter), with minor contributions from industry and a large airport.

Figure 2 shows the time series of the recorded meteorology, measured at a surface station representative of the conditions in the MMA during the field campaign of July 2016 (El Retiro, in central Madrid). In order to put the field campaign into the context of the more general meteorological situation, the time series is extended backwards to the end of June and forward to the end of July 2016. Figure 2 also shows the corresponding time series ~~of~~ for O_3, NO_2, ~~2~~ and O_x concentrations in the MMA, demonstrating the occurrence of well-marked peaks alternating with relatively low O_3 and O_x concentrations periods. The intensive field campaign (11-14/07/2016, marked with a green frame) coincides with a low O_3 interval preceding a higher O_3 period in the last two days. ~~red~~ Red and blue frames in Figure 2 show days in which ~~high~~ high- resolution O_3 free soundings were performed (red and blue ~~indicate~~ indicating intervals within high and low O_3, respectively).

2.2. Monitoring sites and instrumentation

To characterise acute summer episodes of O_3 and UFP and to investigate their possible relationships, we devised an intensive field campaign in the MMA. Three measurement supersites in and around Madrid, following a WNW direction, according the previously described dynamics, were deployed in an area where the highest levels of O_3 (with hourly maxima sporadically exceeding 180 µg/m^3) are usually recorded (Reche et al., 2018,~~7~~ submitted) inside the ~~Madrid basin~~MAB (Figure 1). Table 1 shows the equipment available at the three following supersites:

- Madrid-CSIC, located at the Spanish National Research Council headquarters. This site is located in central Madrid on the sixth floor of the building of the Instituto de Ciencias Agrarias.
- CIEMAT, located at the Centro de Investigaciones Energéticas Medioambientales y Tecnológicas headquarters, ~~at~~ 4 km in a WNW direction from the CSIC site in a suburban area.
- MJDH-ISCIII, located in the Instituto de Salud Carlos III in Majadahonda, ~~at~~ 15 km in a NW direction from the CSIC site.

At MJDH-ISCIII, a PTR-ToF-MS (Proton Transfer Reaction-Time of Fly-Mass Spectrometry) was~~has been~~ deployed from 04 to 19/07/2017 and provides insights into the O_3 Formation Potential (OFP) of the VOC mixture over the MMA area. The operation procedure of the PTR-ToF-MS and OFP calculation are detailed in Table S1 and Figure S1.

Furthermore, from 11 to 14/07/2016, 28 profiles of pollutant and meteorological parameters up to 1200 m above ground level (m a.g.l.) ~~a.g.l.~~ were obtained using tethered balloons and a fast winch system (Figure S1, Tables 2). The instrumentation attached to the balloons is summarised in Table 1. The profiles were performed at the Majadahonda Rugby Course

Con formato: Sin Superíndice / Subíndice

Con formato: Superíndice

(MJDH-RC Figure 1). The balloons were equipped with a Global Position System (GPS) and ~~as~~a set of ~~the~~ instruments (Figure S3), including:

- A miniaturized CPC (Condensation Particle Counter built by~~Hy-CPC,~~ Hanyang University, Hy-CPC) was used to measure the number concentration of particles larger than 3 nm (PN_3) with a time resolution of 1 s and a flow rate of 0.125 L/min, using butanol as a working fluid (Lee et al., 2014). Previous inter-comparison studies with conventional CPCs have yielded very good results (with r^2 reaching 0.65-0.98 and slopes 0.87-1.23, Minguillón et al., 2015). In this work, we will use the terms UFP and PN3 as equivalents, but we measure concentrations between 3 and 1000 nm strictly while UFP is <100 nm. However, 80% of the total particle concentration falls in the range of UFPs.
- An ~~PO3M~~ O_3 monitor (PO3M, 2B Technologies) was used to determine O_3 concentrations. It was calibrated against an ultraviolet spectrometry reference analyser showing good agreement (n=34; $PO3MO_3=1.1058*RefO_3+4.41$, $R^2=0.93$). Concentrations (on 10 s basis) are reported in standard conditions (20 °C and 101.3 kPa) and corrected for the reference method.

In addition to the above instrumentation, we obtained the following additional meteorological and air quality data:

- Meteorological data from the CIEMAT meteorological tower (four instrumented levels between surface and 54 m a.g.l.), as well as from several AEMET (Spanish Met Office) standard meteorological stations spread out across the basin: Madrid Airport (40.46°N, 3.56°W, 609 m a.s.l), Colmenar Viejo (40.69°N, 3.76°W, 994 m a.s.l), and El Retiro (in Madrid, 40.40°N, 3.67°W, 667 m a.s.l).
- Hourly data for air pollutants (NO, NO_2, SO_2, O_3, PM_{10}, ~~–~~and $PM_{2.5}$) supplied by the air quality networks of the city of Madrid, the Regional Governments of Madrid, Castilla L~~l~~a Mancha, Castilla y León, and the ~~EMEP~~European Monitoring and Evaluation Programme (EMEP) monitoring network, all of them supplied by the National Air Quality Database of the Ministry of the Environment of Spain (MAPAMA).~~, supplied by the National Air Quality Database of the Ministry of the Environment of Spain (MAPAMA).~~
- High-~~-~~resolution O_3-sounding data performed by AEMET at midday each Wednesday at Madrid Airport.
- High-~~-~~resolution meteorological sounding data obtained each day at 00:00 and 12:00 h local time by AEMET also at Madrid Airport. They were used to estimate the height of the planetary boundary layer (PBL) at 12:00 UTC by means of the simple parcel method (Pandolfi et al., 2014).

Hourly averaged wind components were calculated and used in polar plots with hourly PM_1, $PM_{2.5}$, NO_2, O_3, O_X (O_3+NO_2), BC, and UFP concentrations, by means of the OpenAir R package (Carslaw and Ropkins, 2012).

3. Results

3.1. Meteorological context

Con formato: Sangría: Izquierda: 0 cm, Sangría francesa: 0.75 cm

Con formato: Superíndice

Con formato: Subíndice

Con formato: Subíndice

The AEMET O$_3$ ~~-~~soundings are represented in Figure 3, where it is evident that ~~together with the maps of the 500 hPa geopotential heights (gph in metres) and the MSLP (mean sea level pressure, in mb) contours at 12:00 UTC obtained from the Climate Forecast System (CFS) reanalysis (Saha et al., 2014) downloaded from http://www.wetterzentrale.de/.~~ t~~T~~he low/high O$_3$ periods coincide with the 500 hPa gph passage of, respectively, upper level troughs/ridges over the area, associated with cold/warm deep advection of air masses. Cold advections have usually an Atlantic origin.

The local meteorology during the field campaign was characterized by a progressive drop intemperature (~~-~~T) (-4°C in the maximal daily T) and an increase in the early morning relative humidity (RH) (+20%), with insolation remaining constant (maxima of 900-950 W/m^2) (Figure 4). During the nocturnal and early morning conditions of the first half of the field campaign (11-12/07/2016), relatively weak northerly winds prevailed at the main meteorological surface stations inside the basin, including CIEMAT in Figure 4, and Retiro and Colmenar in Figure ~~5~~S4. This is probably related ~~with~~ to drainage (katabatic) conditions inside the ~~Madrid basin~~MAB, with a progressive turn to a more synoptic westerly component in the central period of the day, consistent with a convective coupling with the more intense upper level wind. This coupling is also accompanied by an important increase ~~of~~ in the wind speed at midday, up to 8 m/s (venting stage), that renewed air masses in the whole basin.

During the second half of the campaign, intense and persistent north-easterly winds replaced the westerlies from the evening of 12/07/2016 on, after the evolution of the upper level trough. In contrast to the previous period, during 13-14/07/2016, night-time and early morning conditions registered more intense NE winds (up to 10 m/s) than at midday, after a decrease in intensity down to calm conditions (1 m/s) during the 12/07 morning, facilitating both fumigation from upper levels and local O$_3$ photochemical production. A weak wind veering to the south was also registered at the mentioned surface stations during the 13/07 afternoon, which lasted ~~only~~ for only 3 hours, and which is more characteristic of an O$_3$ enrichment episode, when the veering lasted longer (Plaza et al., 1997). A progressive decrease of the PBL height (-600 m difference) is observed in the AEMET daily radio-soundings , in particular,~~that showed a~~ gradual decreases of the midday PBL height~~, with~~pf 3400, 2200, 1900, and 1600 m a.s.l. from 11 to 14/07/2016~~,~~ (Figure S5~~3~~) were observed. This decrease is also observed in the 12 and 14/07/2017 UFP profiles (Figures 5 and 6 and S6-S8~~7-9, 11~~). As will be detailed later these meteorological patterns allowed O$_3$ and UFP to smoothly and progressively accumulate in the basin (Figure 4) during the campaign.

In the vertical dimension, during both the high and low O$_3$ periods analysed here, all the soundings show at midday two well-~~-~~defined layers separated by a temperature inversion marking the limit of the growing convection inside the PBL (Figure 3).

In high O$_3$ periods (6 and 27/07/2016), we found lower PBL heights (approximately 1300-1500 m a.s.l.), with weak winds from the E or NE (less than 4-5 m/s) or calm conditions. This is consistent with the scheme proposed by Plaza et al., (1997), who also describe~~d~~ a rapid evolution of the PBL height up to 2500-3000 m a.s.l. at 15:00 UTC during their field campaigns in the area under “summer anticyclonic conditions.”~~.~~ They also describe~~d~~ a morning radiative surface inversion at around 1000 m a.s.l., which was usually “destroyed 1 hour after dawn,”~~,~~ ~~and~~ containing NE winds associated with nocturnal drainage flows at lower levels (following the slope of the ~~Madrid basin~~MAB). In this context, residual layers containing pollutants processed during the previous day(s) can develop above the stably stratified surface layer during night-time conditions. These pollutants can be transported towards the S by weak north-easterly winds, or ~~either~~ remain stagnant under calm conditions, ~~and~~ which leads to fumigation and mixing with fresh pollutants emitted at the surface after the destabilization of the surface layer, as we evidenced in our profiles. These residual layers are topped by the subsidence anticyclonic inversion (1000-1500 m a.s.l.), according to Plaza et al. (1997).

Conversely, the soundings corresponding to low O_3 periods have in common more elevated PBL heights (2000-2500 m a.s.l), with more intense winds (above 6-7 m/s) that can blow from different sectors: from the NE, on ~~the~~ 13/07/2016 (with intense N-Westerlies blowing in the free troposphere), or ~~from~~ the S-SW, as observed ~~on the~~ on 29/06/2016 and 20/07/2016. The O_3 sounding on 13/07/2016, a unique day within the field campaign, presents the final stage of a low O_3 period, with winds in the free troposphere ~~with~~ having a clear NW component while channelled north-easterly winds dominate below 2000 m a.s.l. ~~The decrease of surface temperature observed in Figure 2 during the field campaign, is also consistent with the cold advection associated with the troughing in the 500 hPa heights.~~ The AEMET free-sounding shows low O_3 surface concentrations (<45 ppb) and high levels (>70 ppb) in the middle troposphere (3000-5000 m a.s.l.), associated with very low relative humidity and ~~with~~ intense W to NW winds blowing at that height, which will be discussed in Section 4. The decrease of surface temperature observed in Figure 2 during the field campaign is also consistent with the cold advection associated with the troughing in the 500 hPa heights (13/07/2016 in Figure 3).

Con formato: Subíndice

3.2. Surface O_3, O_X and UFP during the field campaign

~~Figure 4 shows the time series of meteorological parameters (CIEMAT tower), NO_2, NO, O_3, BC and UFP concentrations at Madrid-CSIC, Madrid-CIEMAT and MJDH-ISCIII, as well as at MJDH-RC, for the period 11-15/07/2016.~~ As previously stated, the field campaign was characterised by atmospheric venting conditions with the two last~~tter~~ days ~~being~~ marking ~~in the~~a transitional period to a more stable anticyclonic episode of increasing O_3. The lowering of the wind speed during diurnal periods, and other meteorological features mentioned above, favoured the gradual accumulation of pollutants, as indicated by the progressive increase of the O_3 maxima at MJDH-ISCIII, where the O_3 maximum was reached at 15:00 UTC on 13/07/2016 and at 17:00 UTC on 14/07/2016 (Figure 4). The typical accumulation O_3 cycle for the zone was found only on 13 and 14/07/2016, with a maximum at 14:00 UTC on 13/07/2016 and at 16:00 UTC on 14/07/2016. The two previous days presented a more irregular daily pattern, indicating unstable and atypical situations for July (perturbed conditions with the prevalence of the synoptic winds~~(perturbed conditions with prevalence of the synoptic winds~~). Furthermore, these meteorological conditions and the high insolation induced the concatenation of ~~nucleation~~NPF episodes in the basin (with low BC and very high UFP levels at the central hours of the day), such as the one on 13/07/2016 (Figure S9~~5~~). Morning-midday UFP bursts were caused by nucleation and growth episodes (~~. As previously stated, in a twin article~~ we will focus on the phenomenology and the vertical occurrence of these nucleation-growth events in the~~a~~ twin article).

From 11 to 12/07/2016 the highest concentrations of O_3 were recorded for W-SW and W winds, and peak UFP (PN_3) concentrations were observed with W, SW, WNW, and NE winds.~~;~~ ~~however~~ However, on 13-14/07/2016, both O_3 and UFP concentrations maximized during calm and NE winds (see polar plots from Figure S10~~6~~). $PM_{2.5}$ levels were independent of the UFP and O_3 variation, with concentrations increasing in calm situations in the first two days, and with less pronounced variations as a function of the with direction, but somewhat higher concentrations with NE winds in the last two days (Figure S10).

~~In Figure S5 the evidence for the occurrence of a NPF episode on 13/07/2016 is shown. Morning-midday UFP bursts were caused by nucleation and growth episodes. As previously stated, in a twin article we will focus on the phenomenology and the vertical occurrence of these nucleation-growth events.~~

3.3. Vertical O_3 and UFP profiles during the field campaign

~~Considering the O_3 profiles in Figure 3, high O_3 concentrations (greater than 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. However, at lower levels (inside the PBL) the higher concentrations correspond to the accumulation days (06 and 27/07/2016). As will be demonstrated in this section, O_3 concentrations within the PBL increase throughout the day under all atmospheric conditions due to fumigation from the residual layer, and new O_3 formation from fresh precursors emitted at night-time and through the day. However, larger increases of O_3 concentrations were registered on poorly ventilated days.~~

As shown in Figure S2 and Table 2, the vertical profiles for 14/07/2016 were the most complete of the campaign (wind speed was relatively low and this allowed extended measurements ~~along~~ throughout the day), and for that reason we begin with the description of~~n~~ this day.

Figure ~~7~~ 5 shows that there is a rapid growth of the PBL between 08:05 and 11:01 h UTC, as deduced from the vertical profile of UFP (PN_{3-300}) concentrations. At the beginning of the measurements the upper limit of the PBL was above 1030 m a.s.l., and in 2 h 40 min it ~~was~~ lifted 400 m (around 2.5 m/min). In this initial period, the vertical profile of O_3 was characterized by a succession of strata of different concentrations, but ~~with~~ a clear tendency to increase with ~~towards~~ height ~~higher altitudes~~ ~~elevations~~ (around 20 ppb of difference between surface level and 1950 m a.s.l. was observed). The discontinuity of the PBL ceiling reflected in the UFP, T and RH profiles did not seem to affect ~~at all~~ the O_3 profile at all. In other words, we did not notice accumulation of O_3 layers in the top of the PBL, but, instead,~~–~~ a general increasing trend ~~to increase~~ towards the highest altitudes reached with the tethered balloons.

Through the course of the day, the profile of concentrations of UFP and O_3 became homogenous in the lowest 1200 m a.g.l. (this being the maximum height reached), and a growth of O_3 concentrations at all altitudes was observed until 16:11 h UTC. This homogenisation and growth of O_3 concentrations in the PBL, caused by intense mixing by convection, resulted in ~~a~~ an uneven ~~growth~~ increase through the day with an increase of 43 ppb at surface and only 10 ppb at 1900 m a.s.l. (Figures 5 and S6~~8~~).

Comentario [C1]: Modified and moved to discussion

Figure ~~9 ~~6 shows the results from measurements taken at a fixed height (1400-1200 m a.s.l.) made to capture the effect of the growth of the PBL on O_3 and UFP levels. We started at ~~around ~~apporximately 700 m a.g.l. at 09:32 UTC, with 60 ppb of O_3 and ~~around ~~apporximately 6000 #/cm^3. At 10:25 UTC the top of the PBL reached the balloon, as deduced from the sharp increase in UFP concentrations (up to 20000 #/cm^3). Meanwhile, O_3 concentrations ~~experimented ~~experienced only a slight decrease, suggesting that O_3 fluxes are top down and not bottom up, as recorded for UFP. From 16:11 h UTC onwards, a reduction of O_3 levels at lower heights was observed (-50 ppb at surface levels from 15:55 to 17:45 h UTC, while at 1900 m a.s.l. levels remained stable, Figures 5 and ~~8~~S6).

~~The first balloon flight on 13/07/2016 was performed at 10:45 UTC because earlier the wind speed was too high (Figure 10). At that time the top of the PBL had developed beyond the maximum height reached with the tethered balloons, so in the profile above 1100 m a.g.l. a very homogeneous concentration was detected. At this time on 14/07/2016 the upper bound of the PBL was perfectly identifiable in the UFP vertical profile over 700 m a.g.l., thus the growth of the PBL was faster on 13/07/2016 than on 14/07/2016. Similarly to 14/07/2016, the 13/07/2016~~ ~~O_3~~ ~~profiles were characterised by a progressive increase of concentrations with height (more accentuated in different strata). The profiles started with concentrations close to 40 ppb~~ ~~O_3~~ ~~at the surface, and reached 83 ppb at the upper heights. As occurred on 14/07/2016, through the course of the day surface concentrations increased differentially with respect to the upper layers, to almost homogenize concentrations in the whole profile (between 68 and 80 ppb at all heights at 15:00 UTC).~~

~~In Figure 11 it can be observed that similar results to those described for UFP profiles on the 14/07/2016 were found on 12/07/2016 (upwards growth of the top of the PBL from the early morning):~~

- ~~Around 700 m a.g.l. at 07:30 UTC (5000 #/cm~~~~^{3}~~ ~~surface concentrations, 2000 #/cm~~~~^{3}~~ ~~at the top of the PBL, and 900 #/cm~~~~^{3}~~ ~~in the free troposphere).~~
- ~~Around 900 m a.g.l. at 09:00 UTC (9000, 5000 and 2000 #/cm~~~~^{3}~~ ~~for the above three levels).~~
- ~~Above 1200 m a.g.l. (this being the maximum measurement height) at 10:00 UTC (10000 #/cm~~~~^{3}~~ ~~surface concentrations and 7000 #/cm~~~~^{3}~~ ~~at 1200 m a.g.l.) and 12:55 y 13:42 h (10000 #/ cm~~~~^{3}~~ ~~surface concentrations and 20000 #/cm~~~~^{3}~~ ~~at the maximum height of 900 m a.g.l.).~~

~~In the early morning of 12/07/2016~~ ~~O_3~~ ~~strata at different heights within the PBL were detected, with concentrations reaching 30 to 55 ppb and higher levels (55 to 65 ppb) at the highest altitude reached. During the 10:00 UTC flight~~ ~~O_3~~ ~~levels reached 75 ppb at the top level decreasing gradually down to 40 ppb at surface levels. At 12:00 UTC concentrations at the top of the profile reached 87 ppb, 70-75 ppb in the 100-700 m a.g.l. transect and 60 ppb in the lowest 100 m a.g.l., where NO titration and~~ ~~O_3~~ ~~deposition was more efficient.~~

Comentario [C2]: Moved to SI

The soundings of 11 to 13/07/2016~~Thus, the 12/07/2016 profiles~~ again showed a vertical trend characterised by: i) higher O_3 concentrations at the highest sounding altitude in the early morning, ii) an increase in O_3 concentrations as the morning progressed (more pronounced at low altitudes), and iii) homogenous O_3 concentration along the entire vertical profile, except in the surface layers, where the deposition and titration markedly decreased O_3 levels reached at midday. Detailed descriptions of these soundings (Figures S7 and S8) can be found in the supplementary information.

~~These vertical trends, with concentrations exceeding 75 ppb O_3 above 100-250 m a.g.l., and a marked decrease down to 60 ppb at surface levels was also evident during the short profiles obtained on 11/07/2016 at 18:28-18:41 UTC (Figure 11).~~

4. Discussion

~~5. Plaza et al. (1997), Pujadas et al. (2000) and Artíñano et al. (2003) described the major meteorological patterns affecting the dispersion of pollutants in the basin, and their seasonality. For summer,~~ Plaza et al. (1997), ~~concluded~~show, for the summer period in ~~of~~ the study area, that the development of strong thermal convective activity, and the influence of the mountain ranges produce characteristic mesoscale re-circulations. On the other hand ~~and the development of a very deep mixing layer (~~Crespí et al. (~~,~~1995) report, also for summer and the study area, the development of a very deep mixing layer. These authors report that these re-circulations contribute markedly to the high O_3 episodes recorded in the region. ~~According to Plaza et al (1997) and Diéguez et al. (2009 and 2014) t~~The arrangement of the Guadarrama range favours the early heating of its S slopes, which ~~that~~ causes a clockwise turning of wind direction, ~~from~~with a NE component during the night, ~~towards an~~ E and S during the early morning and midday, respectively, and ~~to the~~ SW during the late afternoon, thus defining the north-western sector downwind of the city as the prone area for O_3 transport. Night-~~-~~time downslope winds inside the basin induce the observed north-easterlies at lower levels. Influenced by these contributions, the barrier effect of the Guadarrama range against the N and NW (Atlantic) winds, as well as the repeated clockwise circulation described above, cause the sloshing ~~movement~~ of the urban plume of Madrid across the basin. ~~This meteorological system allows local O_3 formation and transport.~~ Regarding the vertical scale, Plaza et al. (1997) also show~~ed~~ that fumigation from high O_3-rich layers (injected by upslope winds the previous day or days, or transported from other areas outside the MAB ~~Madrid basin~~) could also contribute to the enhancement of the surface O_3 concentrations across the basin. This ~~was~~ is attributed to the upward gradient in concentrations in the lower 1 km of the atmosphere measured in the early morning, and the subsequent mixing across the ~~planetary boundary layer (~~PBL~~)~~ at midday. ~~Similar results were found by balloon soundings at the Vic Plain (N Barcelona) by Querol et al. (2017), and by earlier studies of Millán et al. (1991, 1992, 1996a to c, 2000, 2002).~~

Con formato: Sin viñetas ni numeración

~~6.~~ On the other hand, Gómez-~~-~~Moreno et al. (2011) and Brines et al. (2015) report~~ed~~ both intensive summer and winter NPF episodes in the western border of ~~the~~ Madrid City, often ~~with the~~ simultaneously with ~~occurrence of~~ the highest O_3 episodes.

Considering the free sounding-O_3 profiles in Figure 3, high O_3 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 ~~could also have been~~ originated after a stratospheric intrusion and a subsequent deep subsidence into the middle troposphere, as is probably the case based on the ECMWF ERA-Interim reanalysis data ~~following~~. Transport of high O_3 air masses in the middle troposphere, as for 13/07/2016 in

Con formato: Cuerpo, Interlineado: Múltiple 1.15 lín.

Figure 3, was also documented by Plaza et al. (1997) over this ~~e~~ area ~~of Madrid~~ in July 1994, during the final phase of a high O_3 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 O_3 layers at high altitude ~~during the summer of the Eastern Mediterranean~~ can contribute to increased surface O_3 concentrations during the summer in the Eastern Mediterranean. This transport has been associated with large-scale subsidence within strong northerly~~N~~ ~~flows~~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 O_3 free soundings at Madrid airport for 13/07/2016~~ during the field campaign~~. The ridging at the lower troposphere over the Bay of Biscay at the rear~~ side~~ of an upper-level trough (left panels) is accompanied by intense NW winds blowing in the middle and upper troposphere and NE ~~flows~~winds ~~more~~ at ground level and up to 2000 m (see the radiosonde profile in the same figure). The O_3 intrusion is associated with 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 O_3 concentrations and low relative humidity of the ERA-Interim profiles over the airport of Madrid (green and red dotted-lines in the panel “g” of Figure S11) are in agreement with the radiosonde observations in the same panel.

-The question now is how much of this O_3 could fumigate at ground level. According ~~ttending~~ to the radiosonde data, the~~ top of the~~ mixing height top was about 2000 m a.s.l. at midday, but could increase to ~~a height of~~ 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 O_3 enriched layer originated in the tropopause folding~~ at a remote area to the N of Iberia~~. Thus, ~~it seems that~~ a certain impact seems ~~iswas probable~~likely. However, the O_3 concentrations were relatively low at all surface stations during that day, as it corresponds to a vented, low-O_3 period.~~ The highest surface concentrations of the days shown in Figure 3, with AEMET O_3 soundings, correspond to high O_3 (accumulation at lower atmospheric levels) periods occurring at the first and last week of July (06 and 27/07/2016).~~

-Thus, ~~A~~according to the O_3-soundings and radio-soundings analysed above, ~~as well as~~ previous evidence~~s~~ described by Plaza et al. (1997), and the surface air quality measurements presented here~~in this study~~, surface O_3 formation from precursor emissions within the MMA seems to develop in the core of regional processes, modulated by large-~~–~~scale meteorological conditions, distinguishing two types of episodes:

- ACCUMULATION, occurring in stable, stagnant conditions and regional accumulation of pollutants (in the sense of Millan et al., 1997, 2000; Gangoiti et al., 2001;~~,~~ Millán, 2014), with high O_3 reserve strata accumulated during the previous day(s) in~~ the~~ residual layer(s) and associated with fumigation around midday of~~in~~ the following day. The O_3 concentrations are high along the whole atmospheric column, but enriched in the lower section by additional local formation of O_3 within the PBL and transport-recirculation of the urban plume of Madrid around the area. This transport-recirculation is characterised by a net transport to the NW-N during daytime, after vertical mixing, and to the S and SW during night-time, inside the residual layer and decoupled from a more stable nocturnal surface layer. Typically, pollutants accumulate during periods of 2-6 days, resulting in ~~a~~ well-marked peak and valley concentration periods that affect background, peri-urban, and in-city stations. This is the case for the O_3-soundings of 29/06/2016 (not shown), and, particularly 27/07/2016 (Figure ~~12~~7)~~,~~ or the measurements with captive and free balloons by Plaza et al. (1997) in 1993 and 1994, with very high concentrations of O_3 in the lower atmospheric layers, usually forming a bump in the vertical profile of O_3~~,~~ below a height of 2000 m a.s.l., easily reachable after daytime convection (Figure ~~12~~7). As illustrated for 06/07/2017, OFP (Table S1 and Figure S1) may be largely dominated by the carbonyls (mostly formaldehyde and acetaldehyde), followed by aromatic compounds (benzene, ~~boluene~~toluene, and C8~~ aromatics~~, C9,~~ aromatics~~ and C10 aromatics), when considering the VOC pool during the morning traffic peaks. The influence of aromatic VOCs on OFP rapidly decreases, while the influence of biogenic VOCs (~~primary and secondary~~mostly isoprene followed by monoterpenes as primary species~~ ones~~, and methacrolein, methyl-vinyl-ketone, isoprene-derived isomers of unsaturated hydroxy hydroperoxides (ISOPOOH) and methylglyoxal, as the main secondary species) increases through the day, resulting in a similar potential influence of biogenic and aromatic VOCs on O_3 formation during accumulation periods, but with an OFP still dominated by carbonyls~~ (see supplementary information for additional supporting material)~~.

- VENTING, occurring in advective atmospheric conditions (in the sense of Millan et al., 1997, 2000; Gangoiti et al., 2001;~~,~~ Millán, 2014), with O_3-soundings characterized by (probably external) contributions from high-~~-~~altitude O_3 strata, and their fumigation on the surface (episodes 11-14/07/2016). There is no accumulation of pollutants above the stable nocturnal boundary layer~~,~~ ~~if any,~~ because more intense and steady winds ~~are charged to~~ swe~~e~~pt out the local production during the preceding day. OFP contributions of carbonyls (dominating OFP), and aromatic and biogenic VOCs did not significantly vary for 13 and 14/07/2017 from what~~ it~~ is described above for 06/07/2017.

As detailed in S~~s~~ections 3.1 and 3.2, with the weakening of general atmospheric circulation by the end of the campaign period, O_3 and UFP smoothly and progressively accumulated in the basin (Figure ~~7~~5). An observed decrease of the PBL depth (up to -1800 m at midday, according to the AEMET radio-soundings during the campaign, see Figure S~~5~~4), probably also contributed to the progressive increase ~~of~~ in pollutant concentrations through the campaign.

With respect to the vertical variability, the general pattern for UFP (N_3) clearly showed a rapid and marked growth of the PBL in the first hours of daylight (Figure ~~13~~8). In these early stages of the day, O_3 profiles were characterized by a succession of strata of different concentrations, but ~~with~~ a clear increasing trend towards the higher levels (Figure ~~13~~8). The discontinuity of the PBL ceiling, reflected in the UFP, temperature, and humidity profiles, was not identified as such in the O_3 profiles (Figures ~~7~~5, ~~9~~ 6, and ~~11~~S6 to S8). As the day progresses the UFP and O_3 concentration profiles are homogenized and a progressive diurnal growth of O_3 concentrations occurs until 16:00 or 17: 00 UTC (Figure ~~13~~8), ~~which is observed~~ most clearly observed at the surface. This vertical variability points to different aspects, such as: (i) the relevance of fumigation from high altitude O_3-rich strata; ii) surface titration by NO and deposition of O_3; (iii) surface photochemical generation of O_3 from precursors (with higher concentrations close to the surface); and (iv) ~~-~~horizontal O_3 and precursor surface transport from the urban plume of Madrid towards MJDH-RC. The upper O_3-rich strata might have an external (to the Madrid basin) origin~~,~~ or might have been injected regionally at high altitudes on the previous day(s) by the complex re-circulations of air masses already reported by Millán et al. (1997, 2000, 2002),~~;~~ EC (2002, ~~and~~ 2004),~~;~~ Gangoiti et al. (2001), Mantilla et al. (1997), Castells et al. (2008a, 2008 ~~and~~ b), and Millán (2014) for the WMB~~estern Mediterranean~~, by McKendry ~~et al.~~ and Lundgren (2000) for other parts of the world,~~;~~ and by Plaza et al (1997), and Diéguez et al. (2007, 2014 ~~and 2014~~) for the Madrid area.

According to the last referenced authors, due to the orientation of the Sierra de Guadarrama (Figure 1), the heating of its S slopes throughout the day forces the wind direction to veer, describing an arc that sweeps the zones to the N of Madrid clockwise, from the W to the NE. Dieguéz et al. (2014) show~~ed~~ that the O_3 maxima are recorded at an intermediate point on this route (El Pardo, Colmenar V., see location in Figures ~~14~~9 and ~~S6~~S12), which is determined by the wind speed,~~ the~~ initial composition of the urban plume, and ~~the~~ results of photochemical processes on its route from the metropolitan area to tens of kilometres away. In addition, our results and those of Plaza et al. (1997) show that O_3 fumigation from high atmospheric layers decisively contributes to the increases in the surface levels, since surface concentrations during our measurements never exceeded those recorded at the highest altitude reached, and at midday homogeneous O_3 levels are measured across the lower 1.2 km of the PBL.

During the whole month of July 2016, there was a clear veering of the urban plume from Madrid, with night plume transport towards the SW (MJDH-San Martin de V., Figures 9 and S12), and towards the 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 the SW. ~~-~~This veering seems to be causally associated with the high O_3 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 O_3 information threshold~~During the whole month of July 2016 the described veering of the urban plume, towards W (MJDH-San Martin de V., see location in Figures 14 and S6) in the early hours, and towards NW, N-NE, and, in some cases E and SE, followed by the decoupling and onset of the nocturnal flow towards SW, seems to be causally associated with the O_3 information threshold exceedances, since the maps of exceedances recorded by the official air quality network follow this spatial and temporal evolution (Figure S6)~~. These plume impacts occur in periods when the O_3 concentration is already high because of accumulation from one day to the next in the (same) air mass~~ from one day to the next~~, which is not completely renewed due to general circulation conditions. The relevance of the latter has been recently demonstrated by Otero et al. (2016), who report ~~ed~~ the maximum temperature as the parameter more directly related with high O_3 concentrations in ~~central~~ Central Europe, whereas, in the WMB region, the O_3 concentrations were more related to the concentrations recorded the day before. ~~The relevance of the latter has been recently demonstrated by Otero et al. (2016), who reported the maximum temperature as the parameter more directly related with high O_3 concentrations in central Europe, whereas in the WMB Mediterranean regions it was a high O_3 concentrations were recorded with a lag of -24 h.~~

On the other hand,~~T~~ the differential afternoon-evening decrease of O_3 surface concentrations, compared with those found at the top of the soundings~~ flights~~ ~~can be attributed to (i) the~~

Con formato: Color de fuente: Texto 1

Con formato: Fuente: 11 pto

Con formato: Fuente: 11 pto, Color de fuente: Texto 1

Con formato: Color de fuente: Texto 1

~~lower intensity or weakening of the fumigation processes; (ii) a greater O_3 titration and deposition in the lower PBL; and (iii) the lower photochemical O_3 production after the midday insolation maxima. Thus, this process ~~again demonstrates the relevance of high~~-~~altitude layers and their fumigation to the surface~~,~~ in the hours of maximum convection.

Regarding the concentrations of UFP, they were very homogeneous throughout the PBL during the vertical profiles, especially in the hours of maximum convection, showing a marked increase from 11 to 14/07/2016 ~~in~~for the whole depth for all profiles (Figure ~~13~~8). Thus, on the 12/07/2016, the upper limit of the PBL (marked by a sharp reduction in~~of~~ UFP levels) reached 900 and~~-~~ 1200 m a.g.l., ~~-~~respectively, in the soundings~~ flights~~ conducted at 08:05 and 10:12 UTC (Figure ~~1~~8~~3~~). In turn, on ~~the ~~14/07/2016, the top of the PBL ~~at midday ~~exceeded 1200 m a.g.l. only in the afternoon, being constrained to 300 to 700 m a.g.l. from 08:05 and 10:45 h UTC (also shown in the progressive loss of -1800 m in the midday PBL height from 11 to 14/07/2016, revealed by AEMET radio-soundings).

The enhanced convection on ~~the ~~12/07/2016 probably favoured the dilution of UFP concentrations and reinforced the fumigation of O_3 from the upper levels. Conversely, the lower development of the PBL on 14/07/2016, ~~hindered the fumigation of upper O_3 layers~~causing less surface UPF dilution and lower top-down contributions to O_3~~ to~~, surface concentrations~~,~~ accounted for the ~~resulting in an ~~opposite ~~temporal trend for ~~O_3 and UFP ~~along th~~the profiles. Thus, a weaker development of the PBL might result in the increase of UFP concentrations, even if UFP emission/formation rates did not vary significantly. However, we cannot discard the possibility that this UFP increase on the last day was the result of a higher intensity and duration of the nucleation episodes.

Con formato: Subíndice

Consideration of the evolution of surface O_3 concentrations on ~~the ~~11 and 12/07/2016 (as shown in Figure ~~14~~9~~, on the 11 and 12/07/2016~~), depicts a double wave: the first peak around midday (11:00-14:00 UTC on the first day, and 12:00-13:00 on the second), and the second ~~one~~ peak in the afternoon-evening (19-22:00 and 16:00-20:00 UTC, respectively), showing relative peaks (~~not always, ~~sometimes just a plateau). We interpret that the morning increase of O_3 concentrations is dominated by both local production~~,~~ and~~ still dominated by~~ anthropogenic VOCs (Figure S1), and fumigation of upper levels, with an early maximum when layers above are rich in O_3, which progressively decreases with dilution with surface concentrations. The secondary evening concentration peak corresponds to the advection of a locally enriched O_3 air mass (titration always causes O_3 depletion towards nocturnal values). When both processes (morning fumigation and evening advection) are not so strong, O_3 local production results in a more "typical" diurnal time evolution, with a single maximum at 15:00-16:00 UTC, as seen on 13-14/07/2016 (Figure ~~14~~9).

The relative importance of the local contribution of the MMA to the O_x concentrations registered in the monitoring stations has also been ~~elucidated ~~evaluated by comparing the observations at upwind and downwind locations relative to the city. In~~At~~ this respect, Atazar and Alcobendas (Figure ~~14~~9) are located downwind for 11 and 12/07/2016, and MJDH and Fuenlabrada are upwind, while the opposite occurs for 13 and 14/07/2016. As the urban air mass is transported towards the E and NE during the first two days, a local O_x contribution is superimposed ~~to ~~on the background at Atazar and Alcobendas where recorded O_x was the highest in the basin (Figure ~~14~~9). The contrary holds during the next two days, when these sites show lower concentrations than the rest. MJDH and Fuenlabrada show a reversed behaviour, with lower concentrations during the first two days and higher for the last days.

In addition of the local O_3, the background contribution~~s~~ can also be very relevant. At high elevation, changes in the background tropospheric O_3 can be attributed to: (i) hemispheric background concentrations, (ii) ~~the~~ exchange between the free troposphere and boundary layer, and iii) ~~the~~ stratospheric inputs (Chevalier et al., 2007; Kulkarni et al., 2011; Parrish et al., 2012; Lefohn et al., 2012; Kalabokas et al., 2013, 2015, 2017; Zanis et al., 2014; Akritidis et al., 2016; Sicard et al., 2017).

Con formato: Subíndice

Con formato: Subíndice

5. Conclusions

The phenomenology of O_3 episodes in the Madrid Metropolitan Area (MMA, Central Iberia) has been characterised. We found that O_3 episodes linked with precursors emitted in the Madrid conurbation are modulated by the complex regional atmospheric dynamics.

Vertical profiles (up to 1200 m a.g.l.), obtained using tethered balloons and miniaturised instrumentation at~~in~~ Majadahonda (MJDH), a sub-urban site located on the southwestern flank of the Madrid Metropolitan Area (MMA) during 11-14/07/2016, showed how complex i O_3~~ritical~~ evolution~~ve processes developed~~ with altitude and time. Simultaneously, measurements of ~~a number of~~ air quality and meteorological parameters were carried out at 3 supersites within the MMA, where spatial differences highlight the influence of atmospheric dynamics ~~at~~ on different scales.

Con formato: Subíndice

The results presented here confirm prior findings regarding the concatenation of relatively low (venting) and high (accumulation) O_3 episodes in summer. In the Madrid Air Basin (MAB), during both types of episodes, fumigation of high altitude O_3-rich layers (from ~~an external~~ a remote or regional origin) contributes ~~with~~ a relevant ~~proportion~~ fraction to surface O_3 concentrations. Moreover, we propose here a conceptual model (~~-~~shown in Figure 10)~~5~~. To be specific:

- A~~Particularly, a~~ccumulation episodes are activated by a relatively thinner PBL (< 1500 m a.g.l. at midday), ~~low~~ light synoptic winds, and the development of anabatic winds along the slope of the Sierra de Guadarrama (W and NW of MAB, with >2400 m a.g.l. peaks). This PBL height, lower than the mountain range, and the development of the mountain breezes cause the vertical recirculation of air masses, ~~and the~~ enrichment of O_3 in the lower troposphere, as well as the formation of ~~reserve strata~~reservoir layers that fumigate to the surface as the diurnal convective circulation develops. This~~ese atmospheric~~ dynamics accounts for the occurrence of the high ~~O_x~~ O_X (O_3+NO_2) surface concentrations.

Con formato: Subíndice

- During venting episodes, with~~ a~~ more intense synoptic winds, and the top of the PBL usually reaching >2000 m a.g.l., vertical O_3 profiles were characterised by an upward increase ~~of~~ in concentrations (~~,~~ whereas lower-~~-~~altitude O_3 maxima were observed in the accumulation periods). Interestingly, vertical profiles demonstrated that, during the study period, O_3 fumigation (top-down~~ flow~~) from upper layers prevailed as a contribution to surface O_3 concentrations, whereas the increase of UFP takes place bottom-up, progressing with the development of the PBL and the occurrence of nucleation and growth episodes occurring within the PBL. Thus, ~~when~~ crossing the boundary of the PBL from the free troposphere increases of UFP concentrations by an order of magnitude, and ~~a~~ slight decrease in~~of~~ O_3 levels were registered. This O_3 and UFP vertical distribution through the day is consistent with the existence of an efficient venting mechanism, which is able to sweep out the local production of the day. Thus, there is no accumulation of pollutants above the observed stable nocturnal boundary layer from one day to the next, and new UFP production is added from below the following day. The presence of O_3-~~-~~enriched layers well above the stable nocturnal boundary layer, –transported by –sustained intense westerly winds, suggests a remote origin of this pollutant, after~~-in~~ photochemical ~~processes~~ reactions and uplift processes developed at least the day before away from the ~~Madrid basin~~MAB, or stratospheric~~-~~ intrusions, such as~~-like~~ the one documented~~-~~ on ~~the~~ 13/07/2016, during the field campaign. However, s~~S~~urface ~~ozone~~O_3 concentrations ~~in~~at all stations of the MAB were ~~kept~~ low during this day;~~,~~ consequently, even when fumigation from this intrusion was ~~certainly~~ very likely, its air quality affection was irrelevant for the same days, but the effect in the forthcoming days of subsided O_3 cannot be evaluated with our tools.~~–~~ The high-~~-~~O_3 period in the area initiated the day after, ~~on July 14th~~ 14/07/2016, and attained ~~the~~its highest concentration on the 16/07/2016.~~th~~.

The results obtained in this intensive field campaign can be summarized in the following conclusions~~,~~ and recommendations concerning O_3 abatement policies:

- The O_3 source apportionment is very complex, with contributions from local/regional ~~a~~and remote sources, including the stratosphere. The relative contributions of these might vary in time and space (v.g. ~~see~~ Lefhon et al., 2014)~~-as an example)~~.
- Climate change might~~y~~ reduce the benefits of the O_3 abatement policies~~y~~ (since heat waves increase O_3 episodes). ~~, and t~~This, as well as the measures and policies in N America and Asia, will need to be considered in future Europe policies for O_3 mitigation (Lefohn and Cooper, 2015; Sicard et al., 2017).
- The phenomenology of O_3 episodes in ~~S Europe~~the WMB~~estern Mediterranean~~ is extremely complex, mainly due to the close coupling~~relation~~ between photochemistry processes and mesoscale atmospheric dynamics. This ~~,~~ requires~~ing~~, consequently, abatement policies very different ~~to~~ from the ones useful for Central Northern Europe, as intensive research has demonstrated in the last decades.
- In the MAB, d~~D~~uring the highest O_3 (accumulation) episodes, ~~to~~ in addition to the ~~apart from~~ the contribution (to surface concentrations) ~~of remote sources, after~~by fumigation of upper O_3 ~~-enriched layers~~ ~~-fumigation~~(from regional transport, hemispheric free troposphere O_3, and intruded stratospheric O_3) ~~,contribution (~~ X in Figure 10)~~5) to surface O$_3$ concentrations~~, there is an added fraction ~~of O$_3$~~ produced locally and~~or~~ transported-recirculated ~~horizontally~~within the MAB, which accumulates from one day to the next (Y in Figure 10~~5~~). If sensitivity analyses demonstrate that abatement of specific precursors would have an effect on reducing O_3 peaks, then the reduction strategies (geographic extension, timing, and so on~~...~~) ~~to~~ for ~~decrease~~ decreasing the ~~Y~~ X and ~~X~~ Y components are very different, and, in most cases, the X component will dominate the relative contributions. Thus, probably, structural measures over wider regions would be more effective than local episodic measures~~,~~

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

Con formato: Superíndice

Con formato: Sin Superíndice / Subíndice

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

Con formato: Subíndice

(~~that ~~which might have a larger effect on the Y component). In terms of precursors, the OFP analysis carried out at the~~...) to decrease the Y and X components are very different, and, in most cases, the X component will dominate in the relative contributions. Thus, Thus, pprobably, structural measures over wider regions would be more effective than local episodic tactics measures, (that might have a larger effect on the Y component). In terms of precursors, the OFP analysis carried out at~~ ISCIII site shows that, even if anthropogenic emissions may ~~still ~~dominate the O_3 formation through the potential impact of alkenes and alkanes (not measured~~ here~~)~~,~~ and the high contribution of carbonyls (formaldehyde and acetaldehyde), biogenic emissions must be considered. Biogenic VOC (primary and secondary) and aromatic compounds (C6 to C10) contribute to the same extent to the OFP, according our calculations (Table S1 and Figure S1).

- The meteorological scenarios causing the summer accumulation episodes in the MAB (high temperatures, low synoptic winds and relatively thinner PBL) should be forecast in order~~,~~ to drive an effective alert system~~ on their possible occurrence of pollution episodes~~.

- ~~It is necessary to achieve a~~A more detailed characterisation of O_3 precursors (VOC and ~~biogenic VOCs, ~~BVOCs) in the MAB is necessary, especially in the source areas, to effectively predict the photochemical evolution of the plumes, ~~and ~~the main impact areas where O_3 from high-altitude reservoir layers formed the previous day(s) ~~before from other precursors ~~fumigates to the surface levels enriched in O_3 and other precursors.

- Modelling techniques and s~~S~~ensitivity analyses ~~using modelling techniques ~~will allow ~~permit ~~the ~~o~~ ~~simulation ~~simulation~~e~~ of ~~of the ~~real conditions ~~situation ~~concerning ~~the~~ O_3 abatement potential~~, but~~ only if the following is achieved in advance: i) ~~reproduce~~ the recirculation cells and other local/regional ~~complex ~~meteorological processes,~~atterns such~~ as the fumigation timing~~ processes~~ and regional ~~the ~~plume transport, are reproduced; ii) ~~include ~~a geographically resolved and accurate emission inventory of O_3 precursors in the source areas and their temporal modulation is included; and iii) T~~reproduce t~~he origin of the high-altitude O_3 strata from external origins is reproduced.

- ~~Thus a~~A good combination of regional/local scale modelling, able to reproduce horizontal/vertical recirculations of air masses and the behaviour of ~~with~~ urban/industrial plumes in complex topography/meteorology, with modelling ~~that being ~~able to calculate contributions from long-range transport, free troposphere, and stratospheric O_3, will be needed to efficiently support policy (see, for example,~~v.g. ~~ the ACP special issue on the Atmospheric Chemistry and Climate Model Intercomparison 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)).

The conceptual model described ~~here ~~in this study for O_3 episodes in the MMA confirms~~ing~~ the relevance of the vertical re-circulations (on top of the high atmospheric multi-source O_3 background) that Millan et al (1997, 2000), Gangoiti et al. (2001), and Millán (2014)

Con formato: Subíndice

highlighted, ~~and~~ controlled in this case by specific synoptic conditions and ~~-~~the PBL depth, may also be ~~also~~ applicable to most of the ~~S Europe~~Western Mediterranean Basin (WMB). Thus, Otero et al. (2016) demonstrate~~d~~ that in C~~c~~entral Europe, the highest temperature is the most statistically related parameter for O_3 episodes, whereas~~ile~~ in ~~S Europe~~the WMB~~Western Mediterranean~~ it is the O_3 level~~s~~ recorded the day before (reflecting re-circulation).

Con formato: Normal, Sangría: Izquierda: 0 cm, Primera línea: 0 cm

Acknowledgements

The present work was supported by the Spanish Ministry of Agriculture, Fishing, Food and Environment, Madrid City Council and Madrid Regional Government, and by the Ministry of Economy, Industry and Competitiveness and FEDER funds under the project HOUSE (CGL2016-78594-R), and by the Generalitat de Catalunya (AGAUR ~~2015~~ 2017 ~~SGR33~~SGR41). Part of this research was supported by the Korea Ministry of Environment through "The Eco-Innovation project". The support of the CUD of Zaragoza (project CUD 2016-05), UPV/EHU (UFI 11/47, GIU 16/03), the project PROACLIM CGL2014-52877-R, the City Council of Majadahonda for logistic support and AEMET for providing surface meteorological data, and data from radiosoundings and ozone free-soundings is also acknowledged. We thank Alava Ingenieros, TSI, Solma Environmental Solutions, and Airmodus for their support, and ~~-~~María Díez for her computer support in the treatment of radiosonde data.

6. References

~~Artíñano B., Salvador P., Alonso D.G., Querol X., Alastuey A., 2003. Anthropogenic and natural influence on the PM10 and PM2.5 aerosol in Madrid (Spain). Analysis of high concentration episodes. Environmental Pollution 125, 453-465.~~

Akritidis D., Pozzer A., Zanis P., Tyrlis E., Škerlak B., Sprenger M., Lelieveld J., 2016. On the role of tropopause folds in summertime tropospheric ozone over the eastern Mediterranean and the Middle East. Atmos. Chem. Phys. 16, 14025–14039.

Brines M., Dall'Osto M., Beddows D.C.S., Harrison R.M., Gómez-Moreno F., Núñez L., Artíñano B., Costabile F., Gobbi G.P., Salimi F., Morawska L., Sioutas C., Querol X., 2015. Traffic and nucleation events as main sources of ultrafine particles in high-insolation developed world cities. Atmos. Chem. Phys. 15, 5929-5945.

Carslaw, D. C.~~ and K. ~~, Ropkins K., ~~(~~2012.~~)~~ O~~o~~penair --- an R package for air quality data analysis. Environ.~~mental~~ Modelling & Software ~~. Volume~~ 27-28, 52-61.

Carslaw D.C., Murrells T.P., Andersson J., Keenan M., 2016. Have vehicle emissions of primary NO_2 peaked? Faraday Discuss. 189, 439-454.

Castell N., Mantilla E., ~~and~~ Millán M.M., 2008a. Analysis of tropospheric ozone concentration on a Western Mediterranean site: Castellon (Spain). Environ.~~mental~~ Monit.~~oring and~~ Assess.~~ment,~~ 136, 3-11.

Con formato: Ninguno, Fuente: (Predeterminado) Calibri, 11 pto, Color de fuente: Negro

Con formato: Cuerpo, Justificado, Espacio Después: 6 pto

Con formato: Interlineado: Múltiple 1.15 lín.

Castell N., Stein A.F., Salvador R., Mantilla E., ~~and~~ Millán M.M., 2008b.The impact of biogenic VOC emissions on photochemical ozone formation during a high ozone pollution episode in the Iberian Peninsula in the 2003 summer season. Advances in Sci.~~ence and~~ Res.~~earch,~~ 2, 9-15.

Castell N., Tellez L., and Mantilla E., 2012. Daily, seasonal and monthly variations in ozone levels recorded at the Turia river basin in Valencia (Eastern Spain). Environmental Science and Poll.~~ution~~ Res.~~earch,~~ 19, 3461-3480.

~~Commission EU Directive (EU) 2015/1480 of 28 August 2015 amending several annexes to Directives 2004/107/EC and 2008 /50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality~~

Chevalier A., Gheusi F., Delmas R., Ordóñez C., Sarrat C., 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.

Crespí S.N., Artíñano B., Cabal H., 1995. Synoptic classification of the mixed-layer height evolution. J.~~ournal of~~ App.~~lied~~ Meteorol.~~ogy,~~ 34, 1668-1677.

Dieguez J.J., Calatayud V., Mantilla E., 2014. CEAM Report for the Ministry of Agriculture, Food and Environment, Fundación Biodiversidad. Informe Final. Memoria Técnica Proyecto CONOZE. CONtaminación por OZono en España. 137 pp http://www.magrama.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/Informe_t%C3%A9cnico_CONOZE%5B1%5D_tcm7-330956.pdf

Dieguez J.J., Millán M., Padilla L., Palau J.L., 2009. Estudio y evaluación de la contaminación atmosférica por ozono troposférico en España. CEAM Report for the Ministry of Agriculture, Food and Environment, INF FIN/O3/2009. 372 pp. http://www.magrama.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/8_A_Informe_final_ozono-ceam_Julio_2009_tcm7-152609.pdf

Directive 2008/50/EC of the European Parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe.

Directive 2015/1480 of 28 August 2015 amending several annexes to Directives 2004/107/EC and 2008 /50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality.

Doval M., Castell N., Téllez L., and Mantilla E., 2012. The use of experimental data and their uncertainty for assessing ozone photochemistry in the Eastern Iberian Peninsula. Chemosphere 89, 796-804.

EC, 2002. Ozone dynamics in the Mediterranean Basin: A collection of scientific papers resulting from the MECAPIP, RECAPMA and SECAP Projects. Air Pollution Report 78. DG RTD I.2, LX 46 2/82, B-1049 Brussels.

EC, 2004. European Commission Decision of 19 March 2004 "Concerning guidance for implementation of Directive 2002/3/EC of the European Parliament and the Council relating to ozone in ambient air (2004/279/EC). Official Journal of the European Union L87/50 of 25.3.2004.

EEA, 2017~~6~~. Air quality in Europe-2017~~6~~ report. EEA Report, No 13~~28~~/2017~~6~~. ISBN 978-92-9213-920-9~~978-92-9213-824-0~~, Luxembourg: Publications Office of the European Union, ~~88~~ 74 pp. https://www.eea.europa.eu/publications/air-quality-in-europe-2017

Con formato: Cuerpo

Con formato: Español (alfab. internacional)

Con formato: Fuente: (Predeterminado) Calibri, 11 pto

EMEP, 2016. Air pollution trends in the EMEP region between 1990 and 2012. EMEP/CCC-Report 1/2016, ISBN : 978-82-425-2834-6, 107 pp.

Escudero M., Lozano A., Hierro J., del Valle J., Mantilla E., 2014. Urban influence on increasing ozone concentrations in a characteristic Mediterranean agglomeration. ~~Atmospheric Environment~~Atmos. Environ. 99, 322–332.

Gangoiti G., Millán M.M., Salvador R., and Mantilla E., 2001.Long-range transport and re-circulation of pollutants in the western Mediterranean during the project Regional Cycles of Air Pollution in the West-Central Mediterranean Area. ~~Atmospheric Environment~~Atmos. Environ. 35, 6267-6276.

Garcia Dos Santos S., Benarroch Benarroch R., Fernández Patier R., Sintes Puertas M.A., Cantón Gálvez J.M., Alonso Herreros J. y Guevara Hernández S. 2014. Atmospheric Pollution in North Africa. Facts and lessons in the Spanish City of Ceuta. 9TH International Conference on Air Quality Science and Application. Garmish (Germany) March 24 – 28.

Gerasopoulos E., Kouvarakis G., Vrekoussis M., Kanakidou M., Mihalopoulos N., 2005. Ozone variability in the marine boundary layer of the Eastern Mediterranean based on 7-year observations. J. Geophys. Res., 110, D15309, doi:10.1029/2005JD005991.

Giannakopoulos C., Le Sager P., Bindi M., Moriondo M., Kostopoulou E., Goodess, C.M., 2009. Climatic changes and associated impacts in the Mediterranean resulting from a 2 oC global warming. Global and Planetary Change 68, 209-224.

Gómez-Moreno F.J., Pujadas M., Plaza J., Rodríguez-Maroto J.J., Martínez-Lozano P., Artíñano B., 2011. Influence of seasonal factors on the atmospheric particle number concentration and size distribution in Madrid, ~~Atmos. Environ.~~Atmos. Environ. 45, 3199-3180.

Kalabokas P.D., Viras, L.G., Bartzis, J.G., Repapis, C.C., 2000. Mediterranean rural ozone characteristics around the urban area of Athens. Atmos. Environ. 34, 5199–5208.

Kalabokas P.D., Repapis C.C., 2004. A climatological study of rural surface ozone in central Greece. Atmos. Chem. Phys., 4, 1139–1147.

Kalabokas P.D., Mihalopoulos N., Ellul R., Kleanthous S., Repapis C.C., 2008. An investigation of the meteorological and photochemical factors influencing the background rural and marine surface ozone levels in the Central and Eastern. Mediterranean. Atmos. Environ. 42, 7894-7906.

Kalabokas, P.D., Cammas, J.P., Thouret, V., Volz-Thomas, A., Boulanger, D., Repapis, C.C., 2013. Examination of the atmospheric conditions associated with high and low summer ozone levels in the lower troposphere over the eastern Mediterranean. Atmos. Chem. Phys. 13, 10339–10352.

Kalabokas, P.D., Thouret, V., Cammas, J.P., Volz-Thomas, A., Boulanger, D., and Repapis, C.C., 2015. The geographical distribution of meteorological parameters associated with high and low summer ozone levels in the lower troposphere and the boundary layer over the Eastern Mediterranean (Cairo case). Tellus B, 67, 27853.

Kalabokas P.D., Hjorth J., Foret G., Dufour G., Eremenko M., Siour G., Cuesta J., Beekmann M., 2017. An investigation on the origin of regional springtime ozone episodes in the western Mediterranean. Atmos. Chem. Phys. 17, 3905–3928.

Kourtidis K., Zerefos C., Rapsomanikis S., Simeonov V., Balis D., Perros P. E., Thomson A. M., Witte J., Calpini B., Sharobiem W. M., Papayiannis A., Mihalopoulos N., Drakou R., 2002. Regional levels of ozone in the troposphere over eastern Mediterranean. J. Geophys. Res., 107, 8140, doi:10.1029/2000JD000140.

Kouvarakis G., Vrekoussis M., Mihalopoulos N., Kourtidis K., Rappenglueck B., Gerasopoulos E., Zerefos C., 2002. Spatial and temporal variability of tropospheric ozone in the boundary layer above the Aegean Sea (eastern Mediterranean). J. Geophys. Res., 107, 8137, doi:10.1029/2000JD000081.

Kulkarni P.S., Bortoli D., Salgado R., Anton M., Costa M.J., et al., 2011. Tropospheric ozone variability over the Iberian Peninsula. Atmos. Environ. 45, 174-182.

Kulmala M., Pirjola L., Mäkelä J.M., 2000. Stable Sulphate Clusters as a Source of New Atmospheric Particles.~~,~~ Nature ~~2000,~~ 404, 66-69.

Kulmala M., Vehkamehk H., Pet P.T., Dal Maso M., Lauri A., Kerminen V.-M., Birmili W., McMurry P., 2004. Formation and growth rates of ultrafine atmospheric particles: a review of observations. J. Aerosol Sci.~~,~~ 35, 143-176.

Kulmala M., ~~and~~ Kerminen V.M, 2008. On the formation and growth of atmospheric nanoparticles, Atmos.~~,~~ Res.~~earch~~ 90, 132-150.

Lee, H.-K., Hwang, I.-K., Ahn, K.-H., 2014. Development and Evaluation of Hy-CPC. Particle and Aerosol Research 10, 93-97.

Lefohn A.S., Wernli H., Shadwick D., Oltmans S.J., Shapiro M., 2012. Quantifying the frequency of stratospheric-tropospheric transport affecting enhanced surface ozone concentrations at high- and low-elevation monitoring sites in the United States. Atmos. Environ. 62, 646-656.

Lefohn A. S., Emery C., Shadwick D., Wernli H., Jung J., Oltmans S. J., 2014. Estimates of background surface ozone concentrations in the United States based on model-derived source apportionment. Atmos. Environ. 84, 275–288.

Lefohn A.S., Cooper O.R, 2015. Introduction to the Special Issue on Observations and Source Attribution of Ozone in Rural Regions of the Western United States. Atmos. Environ. 109, 279-281.

Lelieveld J., Berresheim H., Borrmann S., Crutzen P.J., Dentener F.J., Fischer H., Feichter J., et al., 2002. Global air pollution crossroads over the Mediterranean. Science 298, 794-799.

MACC (2018). Monitoring Atmospheric Composition & Climate. http://www.gmes-atmosphere.eu/services/raq/raq_nrt/

Mantilla E., Millán M.M., Sanz M.J., Salvador R., and Carratalá A., 1997. Influence of mesometeorological processes on the evolution of ozone levels registered in the Valencian Community. In: I Technical workshop on ozone pollution in southern Europe. Valencia.

McKendry I.G., Lundgren J., 2000. Tropospheric layering of ozone in regions of urbanized complex and/or coastal terrain: a review. Progress in Physical Geography 24, 3.

~~Millán M.M., 2002. Ozone dynamics in the Mediterranean basin. A collection of scientific papers resulting from the MECAPIP, RECAPMA and SECAP Projects. Air Pollution Research Report 78.Fundación Centro de Estudios Ambientales del Mediterráneo – CEAM. Valencia, España. 287 pp.~~

~~Millán, M.M. 2014. Extreme hydrometeorological events and climate change predictions in Europe. J. Hydrol. 518B, 206-224.~~

Millán M.M., Artiñano B., Alonso L., Navazo M., Castro M., 1991. The effect of meso-scale flows on regional and long-range atmospheric transport in the Western Mediterranean area. ~~Atmospheric Environment~~ Atmos. Environ. 25A, 5/6, 949-963.

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

~~Millán, M.; Artíñano B. 1992. Mesometeorological Cycles of Air Pollution in the Iberian Peninsula; Air Pollution Research Report 44, EUR14834; Commission of the European Communities.~~

Millán M.M., Salvador R., Mantilla E., Artiñano B., 1996a. Meteorology and photochemical air pollution in southern Europe: experimental results from EC research projects. ~~Atmospheric Environment~~ Atmos. Environ. ~~,~~ 30, 1909-1924.

Millán M.M., Mantilla E., Salvador R., Kallos G., 1996b. Regional and long-range transport scenarios for photo-oxidants on the Mediterranean basin in summer. Ninth joint conference on applications of air pollution meteorology. 438-441. Am.~~erican~~ Meteorol~~ogical~~ Soc.~~iety~~, Boston.

Millán M.M., Salvador R., Mantilla E., 1996c. Mesoscale processes and photo-oxidants cycles on the Spanish Mediterranean coast. Ninth joint conference on applications of air pollution meteorology.434-437. Am.~~erican~~ Meteorolo.~~gical S~~ Soc.~~ociety~~, Boston.

Millán M.M., Salvador R., Mantilla E., and Kallos G., 1997. Photooxidant dynamics in the Mediterranean basin in summer: Results from European research projects. J~~ournal of~~. Geophys.~~ical~~ Res.~~earch~~ 102, 8811-8823.

Millán M.M. , ~~and~~ Sanz M. J., 1999. Ozone in Mountainous regions and in Southern Europe. In: Ad hoc Working group on Ozone Directive and Reduction Strategy Development, (eds.). Ozone Position Paper ~~.~~145-150. European Commission, Brussels.

Millán M.M., Mantilla E., Salvador R., Carratalá A., Sanz M.J., Alonso L., Gangoiti G., ~~and~~ Navazo M., 2000. Ozone Cycles in the Western Mediterranean Basin: Interpretation of Monitoring Data in Complex Coastal Terrain. J~~ournal of~~. App~~lied~~. Meteorol~~ogy~~.~~,~~ 39,~~:~~ 487-508.

Millán M.M., Sanz M.J., Salvador R., ~~and~~ Mantilla E., 2002. Atmospheric dynamics and ozone cycles related to nitrogen deposition in the western Mediterranean. Environ~~menta~~.~~l~~ Poll.~~ution,~~ 118, 167-186.

Millán M.M., 2002. Ozone dynamics in the Mediterranean basin. A collection of scientific papers resulting from the MECAPIP, RECAPMA and SECAP Projects. Air Pollution Research Report 78.Fundación Centro de Estudios Ambientales del Mediterráneo - CEAM. Valencia, España. 287 pp.

Millán M.M. 2014. Extreme hydrometeorological events and climate change predictions in Europe. J. Hydrol. 518B, 206-224.

Minguillón M.C., Brines M., Pérez N., Reche C., Pandolfi M., Fonseca A.S., Amato F., Alastuey A., Lyasota A., Codina B., Lee H.-K., Eun H.-R., Ahn K.-H., Querol X., 2015. New particle formation at ground level and in the vertical column over the Barcelona area. Atmos.~~pheric~~ Res.~~earch~~ 164–165, 118–130.

Monks P.S., Archibald A.T., Colette A., Cooper O., Coyle M., Derwent R., Fowler D., Granier C., Law K.S., Mills G.E., Stevenson D.S., Tarasova O., Thouret V., von Schneidemesser E., Sommariva R., Wild O., Williams M.L., 2015. Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer. Atmos. Chem. Phys., 15, 8889-8973.

Ochoa-Hueso R., Munzi S., Alonso R., Arróniz-Crespo M., Avila A., Bermejo V., Bobbink R., Branquinho C., Concostrina-Zubiri L., Cruz C., Cruz de Carvalho R., De Marco A., et al., 2017. Ecological impacts of atmospheric pollution and interactions with climate change in terrestrial

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

ecosystems of the Mediterranean Basin: Current research and future directions. Environ. Poll., 227, 194-206.

Otero N., Sillmann J., Schnell J.L., Rust H., Butler T., 2016. Synoptic and meteorological drivers of extreme ozone concentrations over Europe. Environ. Res. Lett. 11, 024005.

Pandolfi M., Tobías A., Alastuey A., Sunyer J., Schwartz J., Lorente J., Pey J., Querol X., 2014. Effect of atmospheric mixing layer depth variations on urban air quality and daily mortality during Saharan dust outbreaks. Sci. Total Environ.~~,~~ 494-495, 283-289.

Paoletti E., De Marco A., Beddows D.C.S., Harrison R.M., Manning W.J., 2014. Ozone levels in European and USA cities are increasing more than at rural sites, while peak values are decreasing. Environ. Poll. 192, 295-299.

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

Plaza J., Pujadas M., Artíñano B., 1997. Formation and Transport of the Madrid Ozone Plume. J. Air & Waste ~~Manage~~Management~~.~~ Association~~.~~ 47, 766-774.

~~Pujadas M., Plaza J., Terés J., Artíñano B., Millán M. Passive remote sensing of nitrogen dioxide as a tool for tracking air pollution in urban areas: the Madrid urban plume, a case of study. Atmospheric Environment, 34, 3041-3056.~~

Querol X., Alastuey A., Pandolfi M., Reche C., Pérez N., Minguillón M.C., Moreno T., Viana M., Escudero M., Orio A., Pallarés M. and Reina F., 2014, '2001–2012 trends on air quality in Spain', Science ~~of the~~ Total Environment 490, 957–969.

Querol X., Alastuey A., Orio A., Pallares M., Reina F., Dieguez JJ., Mantilla E., Escudero M., Alonso L., Gangoiti G., Millán M., 2016. On the origin of the highest ozone episodes in Spain. . Sci. Total Environ.~~Science of the Total Environment, ~~ 572, 379-389.

Querol X., Gangoiti G., Mantilla E., Alastuey A., Minguillón M. C., Amato F., Reche C., Viana M., Moreno T., Karanasiou A., Rivas I., Pérez N., Ripoll A., Brines M., Ealo M., Pandolfi M., Lee H.-K., Eun H.-R., Park Y.-H., Escudero M., Beddows D., Harrison R.M., Bertrand A., Marchand N., Lyasota A., Codina B., Olid M., Udina M., Jiménez-Esteve B., Soler M.R., Alonso L., Millán M., Ahn, K.-H., 2017. Phenomenology of high-ozone episodes in NE Spain. Atmos. Chem. Phys. 17, 2817-2838

Reche ~~et al.,~~C., Moreno T., Amato F., Pandolfi M., Pérez J., de la Paz D., Díaz E., Gómez-Moreno F.J., Pujadas M., Artíñano B., Reina F., Orio A., Pallarés M., Escudero M., Tapia O., Crespo E., Vargas R., Alastuey A., Querol X., 2018~~7~~. On the complexity of Spatial and time dependence of high ozone events in central Spain. Atmos.~~pheric~~ Res.~~earch~~, submitted.

Saha, S.; S. Moorthi, X. Wu, J. Wang, S. Nadiga, P. Tripp, D. Behringer, Y. T. Hou, H. Y. Chuang, M. Iredell, M. Ek, J. Meng, R. Yang, M. Peña Mendez, , H. van den Dool, Q. Zhang, W. Wang, M. Chen, and E. Becker, 2014.~~:~~ The NCEP Climate Forecast System Version 2. Journal of Climate, 27, 2185–2208.

Saiz-Lopez, A., Borge, R., Notario, A., Adame, J.A., De la Paz, D., Querol, X., Artíñano, B., Gomez-Moreno, F.J., Cuevas, C.A., 2017.~~:~~ Unexpected increase in the oxidation capacity of the urban atmosphere of Madrid, Spain, Sci.~~.~~ Rep,~~.,~~ 7, 45956, doi:10.1038/srep45956~~, 2017~~.

Salma I, Németh Z, Kerminen V-M, Aalto P, Nieminen T, Weidinger T, Molnár Á, Imre K, Kulmala M., 2016. Regional effect on urban atmospheric nucleation, ~~Atmospheric Chemistry and Physics~~ Atmos. Chem. Phys. 16, 8715-8728.

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Salvador R., Millán M.M., Mantilla E., ~~and~~ Baldasano J.M., 1997. Mesoscale modelling of atmospheric processes over the western Mediterranean area during summer. International Journal of Environ.~~ment and~~ Poll.~~ution,~~ 8, 513-528.

Salvador R., Millán M.M., Calbo J., 1999. Horizontal Grid Size Selection and its influence on Mesoscale Model Simulations. J~~ournal~~. ~~of~~ App.~~lied~~ Meteorol.~~ogy,~~ 38, 1311-1329.

Salvador P., Artíñano B., Viana M., Alastuey A., Querol X., 2015. Multicriteria approach to interpret the variability of the levels of particulate matter and gaseous pollutants in the Madrid metropolitan area, during the 1999-2012 period. ~~Atmospheric Environment~~Atmos. Environ. 109, 205-216.

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.

Sicard P., Anav A., De Marco A., Paoletti E., 2017. Projected global tropospheric ozone impacts on vegetation under different emission and climate scenarios. Atmos. Chem. Phys. 17, 12177–12196.

Sipilä M., Berndt T., Petäjä T., Brus D., Vanhanen J., Stratmann F., et al. 2010. The role of sulfuric acid in atmospheric nucleation. Science~~,~~ 327, 5970, 1243-1246.

~~Skrabalova L., Zikova N., Zdimal V., 2015. Shrinkage of newly formed particles in an urban environment. Aerosol Air Qual. Res. 15, 1313-1324.Stanier C.O., Khlystov A.Y., Pandis S.N., 2004. Nucleation events during the Pittsburgh air quality study: description and relation to key meteorological, gas phase, and aerosol parameters. Aerosol Sci. Tech. 38, 253-264.~~

Stein A.F., Mantilla E., ~~and~~ Millán M.M., 2004. Ozone formation downwind an industrial complex in the western Mediterranean. In: 13th World Clean Air and Environmental Protection,~~.~~ August 22-27. London, U.K.

Stein A.F., Mantilla E., and Millán M.M., 2005. Using measured and modelled indicators to assess ozone-NOx-VOC sensitivity in a western Mediterranean coastal environment. ~~Atmospheric Environment~~ Atmos. Environ.~~,~~ 39~~:~~, 7167-7180.

Thunis P., Pisonia E., Degraeuwe B., Kranenburg R., Schaap M., Clappier S., 2015. Dynamic evaluation of air quality models over European regions. Atmos. Environ. 111, 185-194.

Velchev K., Cavalli F., Hjorth J., Marmer E., Vignati E., Dentener F., Raes F., 2011. Ozone over the Western Mediterranean Sea e results from two years of shipborne measurements. Atmos. Chem. Phys. 11, 675-688.

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.

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Español (alfab. internacional)

Con formato: Fuente: (Predeterminado) Calibri, 11 pto, Color de fuente: Negro

Con formato: Fuente: (Predeterminado) Calibri, 11 pto, Color de fuente: Negro