Dear Dr Dentener,

Thank you very much again for taking the editorial task on our paper.

We applied all the suggestions of the two referees in the revised and submitted manuscripts.

We are attaching below the following material:

1. The replies to the requests of the 2 referee separately, describing how we did take into account their suggestions in this new revised manuscript.
2. The document with highlighted changes marked in red to show the modifications.

Thanks again and very kind regards

Xavier Querol

Barcelona, Spain 16/01/2017-

Reply to referees: Phenomenology of the highest ozone episodes in NE Spain"
by Querol X. et al.

Anonymous Referee #1, Received and published: 9 December 2016

We appreciate very much the critical and constructive review made by the referee. As you might see in the revised version we applied all suggestions made by the referee

REFEREE #1: The manuscript submitted by Querol et al. presents a detailed analysis of the generation of ozone episodes in the Catalunia region (North-Eastern Spain), elucidating key mechanisms yielding to acute ozone episodes in the area. The analysis is carried out exploiting a comprehensive dataset of measurements at ground level and on the vertical profile by means of balloons. The authors were able to identify two types of synoptic patterns associated to high ozone episodes and convincingly describe the underlying processes. For the type associated with highest ozone levels, the authors also suggest that emission reduction in the Barcelona metropolitan area during the days preceding the event might reduce the risk of having the most severe ozone peaks in the valley to the north of the city. Although specific of the area, the analysis may be taken as a useful example also for other similar areas.

This is a well-conceived study reported in a well written manuscript. Publication on ACP after addressing the minor points listed below is recommended. These are mostly typos and request of clarification at a few points not clear to this reviewer.

REPLY: Thanks a lot for your comments and review that greatly helped us to improve the presentation of our results in the paper. As you will see have applied all your suggestions in the revised version. Thanks a lot for your critical and positive review.

REFEREE #1.1. Abstract, l. 24: "vertical measurements". It would be useful to state immediately here that vertical measurements were performed using tethered and non-tethered balloons. **REPLY:** Done. Thank you very much.

REFEREE #1.2. Abstract, l. 39-40: "At the highest altitudes reached in this study (900-1000 m a.g.l.) ..." this is somewhat in contradiction with the height interval specified above (1500-3000 m a.g.l., see line 29). Please rephrase.

REPLY: Done, we clarified in text that in the first case we refer to tethered balloon measurements, and at the higher altitudes was modelling and non-tethered balloon measurements. Thank you very much.

REFEREE #1.3. Abstract, l. 45: "free sounding data". Not immediately clear what does it mean. I suggest to write "non-tethered balloons" in place of "free".

REPLY: Done.

REFEREE #1.4. abstract, l. 46-48: unclear paragraph. UFP are said to be low in the lower 100-200 m a.g.l., but nucleation events were detected in the PBL: does it mean that the PBL itself is stratified and nucleation only occurred above 100-200 m? Moreover, the paragraph does not seem to contain strictly necessary information for an abstract, I would consider removing it at all. Please clarify.

REPLY: Done. We reduced the sentence to: "Relatively low concentrations of ultrafine particles (UFP) during the study, and nucleation episodes were only detected into the boundary layer."

REFEREE #1.5. Abstract, l. 54-57: This paragraph may be removed. It does not add significant and crucial information, as it is written now. Otherwise, please clarify the importance of the statement.

REPLY: Done.

REFEREE #1.6. l. 78: "(where no exceedances are recommended)": misleading statement. Perhaps rephrase as "(where no specific number of exceedances is recommended)".

REPLY: You are right!!! Done.

REFEREE #1.7. l. 86: "... to yield secondary aerosols". I would also add "organic nitrates", which may sequester a significant fraction of NOx.

REPLY: Done.

REFEREE #1.8. l. 108: "In days," replace with "There,".

REPLY: Done.

REFEREE #1.9. l. 266: "are bivariate polar plots concentrations are ...", add "where" between "plots" and "concentrations".

REPLY: Done.

REFEREE #1.10. p. 7, subsection "Modelling system for O3": from the description apparently a continuous run for all the period analysed is carried out (it is mentioned a 24-h spinup period). In that case, probably grid nudging of WRF was used. Please clarify and eventually specify the variables used in nudging, the nudging coefficients, and if nudging were applied also in the PBL.

REPLY: Nudging was only applied for the coarse domain D1 that uses the initial and boundary conditions from the ECMWF meteorological model, but nudging is deactivated for the inner domains D2, D3 and D4 in order to allow the development of the small-scale features. Nudging in the 27-km domain is done for the horizontal wind components (coefficient=0.0001 s-1), potential temperature (coefficient=0.0001 s-1) and water vapor mixing ratio (coefficient=0.00001 s-1). Within the PBL, nudging is only applied for the horizontal wind components u and v. The text is modified indicating that we use the nudging option in the first domain, but we do not specify additional information (the variables, coefficients and application of nudging within the PBL). If you consider it necessary, please let us know and we will include that information. The new text is as follows: "……. For the coarser domain, initial and boundary conditions for the meteorological model were taken for the European Centre for Medium-Range Weather Forecast global model (ECMWF) with a 0.5º x 0.5º resolution using nudging and the boundary conditions are forced every 6 h, …….

REFEREE #1.11. l. 291: "pressures" should be "pressure".

REPLY: Done.

REFEREE #1.12. l. 292-293: "... changing the direction at nighttime". Misleading statement. Apparenlty, the meaning is that air masses circulate clockwise during the day and counterclockwise at night. Please clarify.

REPLY: Yes we agree with the misleading of the statement. We re-phrased the paragraph to: "Type A episode: Under "usual summer conditions", with the Azores High located west of Iberia, and a ridge of high pressures extending into southern France, air masses in the Western Mediterranean basin rotate clockwise (anticyclonic) during the day, following the combined sea breezes and upslope flows at eastern Iberia and a simultaneous generalized compensatory sinking is observed in the basin. During nighttime, drainage flows into the sea develop at the coastal strip, subsidence over the basin weakens and the wind over the sea is observed moving southward, transporting the coastal emissions almost parallel to the shoreline (Gangoiti et al., 2001). At the same time, Atlantic

gap winds (through the Ebro and Carcassonne valleys), weaken during daytime due to inland sea breezes and become strengthened during nighttime (Millán et al. 1997; Gangoiti et al., 2001, Gangoiti et al., 2006 and Millán 2014)."

REFEREE #1.13. l. 385: "nitrate ... concentrations increased during the evening". This is not true. In Figure S6 nitrate decrease in the evening, while shows a peak in the morning period. Moreover, the effect is attributed to changed "gas/particle partitioning": is this an effect of temperature? Please correct and clarify.".

REPLY: Thanks a lot, we corrected and clarified sentence: whereas nitrate (and in a minor proportion ammonium) concentrations increased during the 00:00-08:00 UTC periods as a result of gas/particle partitioning (Figure S6) due to de thermal instability of ammonium nitrate under typical high daytime temperatures (Harrison and Kito, 1990) reached in July 2015 in the study.

Harrison R.M., Kito A.M.N., 1990. Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants. Atmospheric Environment, 24, 2633–2640.

REFEREE #1.14. l. 420-421: "O_3 variations at the coastal BEG are opposed to those at the inland MSC". Not clear what the authors mean with "opposed". The two signals are actually qualitatively correlated. Please clarify.

REPLY: We clarified in text that the anti-correlation takes place in 01-03, 10-12 and 26/07/2015 and several periods from 14-20/07/2015. You are right that ion several periods these are correlated.

REFEREE #1.15. l. 472-477: Here, a quantitative estimate of the non-local contribution to the O_3 peak in the Vic Plain is attempted. However, it is not really clear how the authors estimated it. Please clarify, explaining in depth the calculation.

REPLY: We clarified the way it was calculated. Now we stated: "For these exceedances, an hourly contribution of up to 150 µg/m^3 of O_X (mostly O_3) both from fumigation of recirculated return layers (injected at an altitude of 1500-3000 m a.g.l. in the prior day(s)), and from transport and photochemical generation of O_3 of the BMA plume, might be estimated based on the differences of the O_X early afternoon maxima recorded at the coastal BMA sites (CTL, PLR) and the ones in the Vic Plain (TON, MON, VIC). Thus, as shown in Figure 5, on 14-18/07/2016 midday maxima recorded at CTL (into BMA) range between 38-62 ppb O_X, on an hourly basis; whereas at TON (in the Vic Plain), these reach 102-115 ppb. Accordingly, differences of 50-73 ppb O_X (close to 100-150 µg/m^3 O_X) between CTL and TON can be estimated for these days."

REFEREE #1.16. l. 488: "... more than 50% of the O_3 hourly ...". Again, the authors attempt quantification of different contribution to O_3 levels, but do not explain in details the calculations. Please clarify.

REPLY: We have now already clarified the procedure in the prior paragraph, nonetheless we also clarified this issue here: "As described above, this variation points to the process of O_3 and O_X formation with a mean O_X difference between the urban-coastal sites and the Vic Plain hourly maxima of up to 73 ppb O_X (around 150 µg/m^3) for the TON site when subtracted O_X hourly maxima from CTL (Figure 5), with a maximum average O_3 hourly levels of around 200 µg/m^3. These O_X differences are mostly due to O_3 differences (Figure 6). Accordingly, during these intense O_3 pollution episodes, more than 50% of the O_X and O_3 hourly maxima concentrations are attributable to....."

REFEREE #1.17. l. 529: "150 ug/m^3". Probably the authors mean "100 ug/m^3". Please check.

REPLY: Thanks we checked and modify it!! Now we stated: "On 14/07/2015 07:06-08:21 UTC a well stratified atmosphere (Figure 9) with both thermal and O_3 layers is observed, with a general upward increasing trend for O_3 from 40 µg/m^3 at ground level to much higher levels in different strata, such as one reaching 150 µg/m^3 in strata at 500 and others with 140, 100 or 40 µg/m^3, such as the ones at 300, 800-1000 or 400 m a.g.l., respectively, reflecting, in addition to stratification of O_3 concentrations in altitude, the effect of surface depletion by NO titration and by deposition during the night (see in Figure 9 the progressive O_3 depletion from 150 µg/m^3 at 500 m a.g.l. to 40 µg/m^3 at surface levels)".

REFEREE #1.18. l. 586: " ... more marked in the episode." Probably a "A" is missing at the end of the sentence.

REPLY: Thanks, Yes there was an A missing. We checked and modify it!!

REFEREE #1.19. l. 586-589: Here the authors refer to previous quantitative estimate of contributions to O_3 levels from specific mechanism. This reinforced the need for clarification, as mentioned above.

REPLY: Thanks, we already explained above in two sections how we calculated.

REFEREE #1.20. l. 701-703: Here the authors qualitatively suggest that NOx reduction in BMA should reduce ozone peaks in Vic Plain during type A episodes. They are thus implicitly assuming a NOx-limited ozone regime. Please state this point explicitly, and possibly support the claim referencing previous studies, if any available.

REPLY: Sorry for this, we would like to mean 'the reduction of NOx and/or VOCs'. We changed the sentence: "From the perspective of possible precursor abatement strategies, direct mitigation measures at the BMA would have had a minor effect on O_3 concentrations at the Vic Plain area during the type B episode. However, during the type A episode, a reduction of NO_x and/or VOCs emissions in the BMA, some days before and during the episode, might have an effect on O_3 concentrations recorded in the Vic Plain." But in any case we also explicitly mentioned in the first version that "Nonetheless, due to the non-linearity of the O_3 generation processes, sensitivity analysis with high resolution modelling is necessary to evaluate the possible effects in terms of absolute concentrations."

REFEREE #1.21. One concluding natural question is: are type A and B the only two situations expected to yield high ozone events in the area? May the authors rule out other types of situation from the analysis of this period only? Please add a comment on that point.

REPLY: Thanks we have added it: "We are aware that we only analysed the most intense O_3 episodes occurring in July 2015, and that there might be other scenarios, different to type A and B, yielding high O_3 events, such as the transport of aged air masses from other regions of Europe or the transport of the BMA emissions in meteorological scenarios different to those described here. However in a recent study (Querol et al., 2016) we demonstrated with the analysis of the 2000-2015 O_3 data series, that the Vic Plain, 40-50 km north of Barcelona) is the area of Spain recording the highest number of annual exceedances of the O_3 information threshold, orders of magnitude higher that the surrounding areas of the axis BMA-Vic Plain-Pre-Pyrenean ranges, thus it is clear that the BMA emissions and the vertical re-circulations caused by the local complex orography have an important role in the occurrence and development of intensive O_3 episodes in the region."

We added in addition a missing reference:

Gangoiti, G., L. Alonso, M. Navazo, J. A. García, and M. M. Millán (2006), North African soil dust and European pollution transport to America during the warm season: Hidden links shown by a passive tracer simulation, J. Geophys. Res., 111, D10109, doi: 10.1029/2005JD005941

Reply to referees: Phenomenology of the highest ozone episodes in NE Spain"
by Querol X. et al.

Anonymous Referee #2, Received and published: 11 December 2016

We appreciate very much the critical and constructive review made by the referee. As you might see in the revised version we applied all suggestions made by the referee

REFEREE #2: This study, that is based on a comprehensive set of both ground level and balloon borne measurements of air pollutants as well as model simulations, gives a detailed description of the characteristics of two high ozone episodes observed during the month of July 2015 in the North Eastern part of Spain, where the highest ozone concentrations in the country typically are found. The authors show that the episode with the highest ozone concentrations is characterized by what they call 'closed circulation' with a high degree of recirculation of air masses due to the sea and land breezes, while during the other episode no major recirculation takes place and horizontal advection over a larger scale plays a more important role. The manuscript builds on a long series of previous studies, mainly carried out by the group of Millan Millan, that have highlighted the influence of the particular orographic and meteorological conditions on air pollution at the Iberian Mediterranean coast and in the western part of the Mediterranean Basin in general.

The manuscript presents an interesting set of observations and what seems to be a scientifically sound analysis of these; it is well written and generally clear, apart from a few points mentioned in the following. I think that the manuscript would only need minor corrections and recommend that it be published after the authors have addressed the comments and suggestions given below.

REPLY: Thanks a lot for your comments and review that greatly helped us to improve the presentation of our results in the paper. As you will see have applied all your suggestions in the revised version. Thanks a lot for your critical and positive review.

REFEREE #2.1: As a general comment, I find that while the qualitative description of the contribution of different processes to the episodes is clear, in the cases where a more quantitative evaluation of these contributions to the ozone or Ox-levels is given a more explicit description of the calculations that were performed is needed, as mentioned below.

REPLY: Thanks for this comment (that also REFEREE #1 made). See below how we replied to your suggestions of clarifying the way calculations were done.

REFEREE #2.2: There seems to be a discrepancy between what is written about the altitude up to which ozone rich layers may influence surface ozone concentrations in different parts of the paper. In the abstract it is stated that surface fumigation takes place "from high O_3 reservoir layers located at 1500-3000 m a.g.l: ", in accordance with what is written in lines 477-478 and 556-560 but in apparent disagreement with the text in lines 119-120, where the ozone rich layers descending to the surface are said to be located at 1000-1500 m.a.s.l. I realize that there is a difference between 'a.g.l.' and' a.s.l.' but as the layers are descending over the sea it seems that this cannot explain the difference.

REPLY: Sorry for this, there was an error in lines 119-120 and it is 1000-3500 m a.s.l, and not 1000-1500 m.a.s.l. We corrected accordingly in the text.

REFEREE #2.3: Line 106, 'Seco et al., 2011': The paper by Seco et al. from 2011 is not in the list of references. There is another paper by Seco et al. from 2013, but probably not the one that the authors have in mind because it deals with emissions during wintertime.

REPLY: Yes, sorry for the mistake. The reference as you noticed should be Seco et al 2011. We replaced Seco et al., 2013 by: Seco R., Peñuelas J., Filella I., Llusià J., Molowny-Horas R., Schallhart S., Metzger A., Müller M., Hansel A., 2011. Contrasting winter and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: the effect of local biogenic emissions. Atmospheric Chemistry and Physics 11, 13161-13179.

REFEREE #2.4: Line 135-136, 'which combined with BVOCs emissions, very often cause severe O_3 episodes': Is there any study showing that BVOC emissions are dominating VOC reactivity in the Barcelona area? I understand from the paper by Valverde et al. (2016) that VOC emissions from traffic and from the harbour are relatively large in this area**.**

REPLY: Sorry again. Yes, we agree with you that high NOx but also VOCs anthropogenic emissions occur in the BMA. Seco et al., 2011 showed also prevalence of BVOCs in the rural area where high O_3 episodes are recorded. In any case we modified the sentence**: "**High anthropogenic NO_X and VOCs emissions arise both from road (and shipping) traffic and power generation, which combined with BVOCs emissions, very often cause severe O_3 episodes in the northern plains and valleys (Toll and Baldasano, 2000; Barros et al., 2003; Gonçalves et al., 2009; Seco et al., 2011; Valverde et al., 2016; Querol et al., 2016)."

REFEREE #2.5: Lines 245-246, 'SPECIFY SIZE RANGES: 'This seems to be a comment left from the internal reviewing process among the authors. I agree with the comment!

REPLY: Yes, it was a mistake, Thanks a lot. We deleted this message and added the size ranges.

REFEREE #2.6: Line 336: 'Figure S5' should probably be 'Figure S7'.

REPLY: Yes, thank you. Changed

REFEREE #2.7: Line 414, 'This is due to': It is possible that the higher ozone levels at the coastal sites may be related to a higher proportion of primary NO2 (due to ship traffic, I suppose), but it remains a hypothesis that this is the main reason for the differences so I think it is mandatory to write 'this may be due to'

REPLY: Totally agree with you. Changed to more open possibilities. "This may be due to…." is now stated.

REFEREE #2.8: Line 469: The meaning of the term 'meteorologically influenced patterns' is not completely clear here. I guess that it refers to the impact of long range transport (in contrast to the transport within the region mentioned afterwards), but please change the wording in the text.
REPLY: We clarified this important question in 2 paragraphs. The first is in the section of L422-425: "show relatively narrow diurnal variations and multiday episodes, with low or enhanced concentrations, according to meteorological fluctuations (accumulation and air mass renovation cycles of 3 to 12 days cause a wider O_3 and O_X concentrations range than the typical daily cycles evidenced in most of the other sites)." The second is in L469: "O_3 and O_X concentrations at the regional background site (MSY, 720 m a.s.l., green in Figure 5) depict also the meteorologically influenced patterns (in the sense previously described for BEG and MSC),….."

REFEREE #2.9: Lines 476-481: It is not clear how the 150 micrograms/m^3 were calculated. Please give the necessary details**.**

REPLY: We clarified the way it was calculated. Now we stated: "For these exceedances, an hourly contribution of up to 150 µg/m^3 of O_X (mostly O_3) both from fumigation of recirculated return layers (injected at an altitude of 1500-3000 m a.g.l. in the prior day(s)), and from transport and

photochemical generation of O_3 of the BMA plume, might be estimated based on the differences of the O_X early afternoon maxima recorded at the coastal BMA sites (CTL, PLR) and the ones in the Vic Plain (TON, MON, VIC). Thus, as shown in Figure 5, on 14-18/07/2016 midday maxima recorded at CTL (into BMA) range between 38-62 ppb O_X, on an hourly basis; whereas at TON (in the Vic Plain), these reach 102-115 ppb. Accordingly, differences of 50-73 ppb O_X (close to 100-150 $\mu g/m^3$ O_X) between CTL and TON can be estimated for these days."

Furthermore in L 488 we also clarified this issue: "As described above, this variation points to the process of O_3 and O_X formation with a mean O_X difference between the urban-coastal sites and the Vic Plain hourly maxima of up to 73 ppb O_X (around 150 $\mu g/m^3$) for the TON site when subtracted O_X hourly maxima from CTL (Figure 5), with a maximum average O_3 hourly levels of around 200 $\mu g/m^3$. These O_X differences are mostly due to O_3 differences (Figure 6). Accordingly, during these intense O_3 pollution episodes, more than 50% of the O_X and O_3 hourly maxima concentrations are attributable to….."

REFEREE #2.10: Lines 493-495: I do not understand the reasoning here: In my understanding not only the inland stations in the Vic plain but also the coastal sites should be subject to fumigation by recirculated strata.

REPLY: In the coastal sites the PBL height is markedly reduced when compared with the inland regions and then the capture of these high altitude O_3-rich layers by the PBL growth and the consequent fumigation on the surface is less probable in the coastal areas than in the inland ones. We added this comment in text.

REFEREE #2.11: Lines 583-586: The occurrence of layers where ozone and BC are uncorrelated is attributed to recirculation of aged air masses, possibly coming from "local-to-regional sources and more distant over the W-Mediterranean and also from hemispheric transport of air masses". However in the abstract it is suggested that these layers are "possibly due to a prevailing regional/hemispheric contribution of O_3 at those altitudes", i.e. transport at a much larger scale. As this is an important issue and as the abstract should reflect the contents of the paper, I think it would be relevant to discuss this possibility of an impact of long range transport.

REPLY: Thanks a lot for highlighting this important inconsistency. We modified this section to include "local-to-regional sources, more distant over the W-Mediterranean or even from hemispheric transport of air masses as reported by UNECE (2010)."

REFEREE #2.12: Line 591, 'ordered by importance': It is not clear to me how the relative importance of the three processes has been determined**.**

REPLY: We agree also with this. We cannot be completely sure of this order and then we deleted "(ordered by importance)" and we leaved it qualitatively: "…..attributable to fumigation, photochemical production and transport of high O_3 air masses, all controlled by insolation."

REFEREE #2.13: The basis for dividing the figures between the main paper and the supplementary information is not completely clear to me. I would suggest to put the figures that are most important for the discussion in the main paper. For instance, the maps of the synoptic meteorological situations that lead to the two episodes (type A and type B) are essential for following the discussion in the paper. I would thus suggest to move Figure S5 from the supplement into the main paper and also to replace the present figure with German text by a figure with English text. Also Figure S7 is important for the discussion and thus I find it more natural to have it in the main paper.

REPLY: OK, we have moved Figures S5 and S7 to main text and re-numbered all figures accordingly.

REFEREE #2.14: Line 180, 'The area is surrounded'. The sentence needs to be rephrased.

REPLY: Thanks a lot. Yes, we had two missing words. We added them to the text. "The area is surrounded by mountains and it is affected by thermal inversions during the night."

We added in addition a missing reference:

Gangoiti, G., L. Alonso, M. Navazo, J. A. García, and M. M. Millán (2006), North African soil dust and European pollution transport to America during the warm season: Hidden links shown by a passive tracer simulation, J. Geophys. Res., 111, D10109, doi: 10.1029/2005JD005941

PHENOMENOLOGY OF HIGH OZONE EPISODES IN NE SPAIN

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ABSTRACT

Ground level and vertical measurements (performed using tethered and non-tethered balloons), coupled with modelling, of ozone (O_3), other gaseous pollutants (NO, NO_2, CO, SO_2) and aerosols were carried out in the plains (Vic Plain) and valleys of the northern region of the Barcelona Metropolitan Area (BMA) in July 2015; an area typically recording the highest O_3 episodes in Spain. Our results suggest that these very high O_3 episodes were originated by three main contributions: (i) the surface fumigation from high O_3 reservoir layers located at 1500-3000 m a.g.l. (according modelling and non-tethered balloon measurements), and originated during the previous day(s) injections of polluted air masses at high altitude; (ii) local/regional photochemical production and transport (at lower heights) from the BMA and the surrounding coastal settlements, into the inland valleys; and (iii) external (to the study area) contributions of both O_3 and precursors. These processes gave rise to maximal O_3 levels in the inland plains and valleys northwards from the BMA when compared to the higher mountain sites. Thus, a maximum O_3 concentration was observed within the lower tropospheric layer, characterised by an upward increase of O_3 and black carbon (BC) up to around 100-200 m a.g.l. (reaching up to 300 µg/m^3 of O_3 as a 10-s average), followed by a decrease of both pollutants at higher altitudes, where BC and O_3 concentrations alternate in layers with parallel variations, probably as a consequence of the atmospheric transport from the BMA and the return flows (to the sea) of strata injected at certain heights the previous day(s). At the highest altitudes reached in this study with the tethered balloons (900-1000 m a.g.l.) during the campaign, BC and O_3 were often anti-correlated or unrelated, possibly due to a prevailing regional or even hemispheric contribution of O_3 at those altitudes. In the central hours of the days a homogeneous O_3 distribution was evidenced for the lowest 1km of the atmosphere, although

probably important variations could be expected at higher levels, where the high O_3 return strata are injected according to the modelling results and non-tethered balloon data.

Relatively low concentrations of ultrafine particles (UFP) during the study, and nucleation episodes were only detected into the boundary layer.

Two types of O_3 episodes were identified: Type A) with major exceedances of the O_3 information threshold (180 μg/m^3 on an hourly basis) caused by a clear daily concatenation of local/regional production with accumulation (at upper levels), fumigation and direct transport from the BMA (closed circulation); and Type B) with regional O_3 production without major recirculation (neither fumigation) of the polluted BMA/regional air masses (open circulation), and relatively lower O_3 levels.

To implement potential O_3 control and abatement strategies two major key tasks are proposed: (i) meteorological forecasting, from June to August, to predict recirculation episodes so that NO_X and VOCs abatement measures can be applied before these episodes start; (ii) sensitivity analysis with high resolution modelling to evaluate the effectiveness of these potential abatement measures of precursors for O_3 reduction.

Keywords: O_3, photochemistry, air pollution, air quality, NO_x

INTRODUCTION

Ozone (O_3) is an airborne secondary pollutant that is produced through the photo oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_X=NO+NO_2), with more intensive production in high insolation regions. It is well known that its formation processes are very complex and that the reaction and production rates are not linear (Monks et al., 2015 and references therein). According to EEA (2015) 97% of the European population is exposed to O_3 concentrations that exceed the WHO guideline (see below) for the protection of the human health. The complexity of this pollutant is also reflected in its air quality targets; thus, the European air quality directive 2008/50/EC establishes a number of O_3 target values (which are not legally binding, as opposed to the limit values set for the majority of pollutants):

- A human health target value fixed at 120 μg/m^3 as 8 hours maxima in a day that should not be exceeded in more than 25 days/year as a three-year mean. This target value was (arbitrarily) increased from the recommended 100 μg/m^3 in the WHO air quality guidelines (where no specific number of exceedances is recommended).
- A population information hourly threshold of 180 μg/m^3.
- A population alert hourly threshold of 240 μg/m^3.
- A vegetation protection target, AOT40 [expressed in μg/m^3·h], as the sum of the excess of hourly concentrations above 80 μg/m^3 along a given period using only hourly values measured between 8:00 and 20:00 h, Central Europe Time (CET), for every day. Hourly AOT40 from May to July should not exceed 18.000 μg/m^3·h O_3 as a mean for 5 years.

NO_x has a catalytic effect in O_3 generation, and is only removed from the system by either deposition or oxidation to nitric acid (HNO_3) and reaction with VOCs to yield secondary aerosols, such as inorganic and organic nitrates, which may sequester a significant fraction of NO_X. Consequently, O_3 generation involves not only local and regional air masses but also long-range transport. Thus, as a general observation, long range transport of O_3 and its precursors influence markedly the background O_3 levels in Europe (UNECE, 2010; Doherty et al., 2013). However, this

situation might be very different when considering the high summer O_3 episodes of Southern Europe (e.g. Millán et al., 1997, 2000; Palacios et al., 2002; Castell et al., 2008a, 2008b, 2012; Stein et al., 2005; Escudero et al., 2014; Pay et al., 2014; Querol et al., 2016).

In the Western Mediterranean basin the problem of tropospheric O_3 has been intensively studied since the early 1980s (Millán et al., 1991, 1996a, 1996b, 1996c, 2000, 2002; Millán, 2002a; Millán and Sanz, 1999; Mantilla et al., 1997; Salvador et al., 1997, 1999; Gangoiti et al., 2001; Stein et al., 2004, 2005; Doval et al., 2012; Castell et al., 2008a, 2008b, 2012; Escudero et al., 2014). Results have evidenced that (i) the meteorology driving O_3 fluctuation in this region is markedly influenced by a very complex orography with high mountain chains surrounding the basin; (ii) in summer, the lack of a marked synoptic advection caused by the presence of the Azores anticyclone and the Iberian and north African thermal lows, together with the sea and land breezes, give rise to air mass recirculation episodes (lasting for several days); and (iii) during these summer vertical and horizontal recirculations of air masses loaded with O_3 precursors and coinciding with high insolation and elevated biogenic VOCs (BVOCs) emissions (Seco et al., 2011), high O_3 concentrations may be recorded.

Millán's team results demonstrated that Western Mediterranean basin dynamics are very different from those in Central Europe. The latter are dominated by neutral-cloudy conditions, where O_3 episodes are usually associated with advection, and transformation takes place within large displacements of air masses. There, morning fumigation from a high O_3 residual (and stratified) boundary layer (BL) formed over the previous days, in addition to local formation in the sunny midday period may give rise to peak O_3 episodes if conditions persist after several days. In contrast, vertical re-circulations developed over all Western Mediterranean coastal areas, determine a very different O_3 dynamics. Air masses travel all the way from the sea to the continental divide, or to the top of the Apennines in the case of Italy. These air mass circulations create layers over the sea at various altitudes, with accumulated pollutants/precursors in several stages of transformation. These processes can occur during a few consecutive days (e.g. 10 days, Millán et al., 1997). The layers already over the basin descend from 1000-3500 m a.s.l. during the day and can reach the lower levels, providing a high background O_3 to coastal cities when the sea and up-slope breezes build up (Millán et al., 2000). Layers, by definition, are stratified and decoupled from each other so they can move in different directions and speeds at their own heights.

Rodriguez et al. (2002) and Cusack et al. (2013) showed that these high background O_3 episodes are characterised also by high particulate matter (PM) concentrations, mostly due to the formation of secondary organic and inorganic aerosols. Such episodes are very common from June to August, and are usually limited by the occurrence of episodic Atlantic or African advective conditions that help (especially the first) to ventilate the Western Mediterranean basin. Minguillón et al. (2015) demonstrated also the occurrence of very intense aerosol nucleation episodes under high insolation scenarios in the vertical column (from 200 to 1000 m.a.s.l.) over the city of Barcelona. As the surface air ascends, aerosols are diluted and levels of O_3 are expected to increase.

The Barcelona Metropolitan Area (BMA) is a highly industrialised and dense urban agglomeration extending over the Mediterranean side of northeast Spain. High anthropogenic NO_X and VOCs emissions arise both from road (and shipping) traffic and power generation, which combined with BVOCs emissions, very often cause severe O_3 episodes in the northern plains and valleys (Toll and Baldasano, 2000; Barros et al., 2003; Gonçalves et al., 2009; Seco et al., 2011; Valverde et al., 2016; Querol et al., 2016). The urban plume is transported inland by sea breezes, heading North

channelled by N-S valleys that cross the coastal and pre-coastal Catalan Ranges to an intra-mountain plain (the Vic Plain) where the cities of Manlleu, Vic and Tona lie, 40-65 km north of Barcelona (Figure 1). A mean of 15 annual exceedances of the hourly O_3 information threshold/site are recorded at the urban background monitoring sites of these cities (Querol et al., 2016). In 2015, 96 out of the 115 hours exceeding the O_3 information threshold in the whole Catalonia air quality monitoring network were recorded in the area within 40-90 km north of Barcelona (towards the Pyrenees), and 82 in the Vic Plain itself (http://www.gencat.cat/mediamb/qaire/ciozo.htm).

This work focuses on an intensive campaign on O_3 and particulate pollutants performed in and around the BMA during July 2015, when high O_3 episodes were recorded, with the aim of investigating the origin of the most intense O_3 events in north-eastern Spain. To this end, regional air quality monitoring network data, passive dosimeters at ground level, vertical profile measurements of O_3 and ultrafine particles (UFP) in the Vic Plain, and modelling tools were employed.

METHODOLOGY

Study area

This study is set in central Catalonia (Figure 1), in north-eastern Spain. The mountain ranges surrounding the area (Pyrenees and Catalan Coastal Ranges) protect the area from the advection of Atlantic and continental air masses but hamper dispersion of pollutants. The typical winds in the region are the Tramontana (northern winds), the Mistral or Cierzo (north-western winds channelled by the Ebro valley) and the sea breezes in the coastal region. In summer, daytime up-slope winds combined with sea breezes may result in air masses penetrating 120-160 km inland that are injected aloft the top of the mountains, and follow the return night flows towards the sea (Millán, 2014). This scenario of air mass regional recirculation during periods of several days prevails in summer (Millán et al., 1997 and 2000). Hence, summer pollution events are characterised by (i) the absence of large-scale forcing and the predominance of mesoscale circulations; (ii) the formation of a thermal low at a peninsular level (forcing the convergence of surface winds from the coastal areas towards the central plateau with strong levels of subsidence over the Western Mediterranean basin); and (iii) combined breeze dynamics, resulting in the recirculation and accumulation of pollutants over the whole Western Mediterranean basin, including the Eastern Iberian peninsula (Millán 2014 and Millán et al., 1997, 2000).

The region is characterised by important atmospheric pollutant emissions from road traffic, industries, biomass burning, livestock, and airport and shipping activities, which coupled with high solar radiation turns into a high rate of secondary PM and O_3 formation (Rodriguez et al., 2002). Industrial activities are mostly concentrated in the Barcelona and Tarragona provinces, and include 19 combustion/energy plants, 84 metallurgy plants and 70 mineral industries. Road traffic, airport and shipping emissions are concentrated in the Barcelona area with >3.5 10^6 vehicles (0.6 per inhabitant, with high diesel and motorbike proportions; DGT, 2014), >45 10^6 tons of shipping transportation, and >37 10^6 aircraft passengers in 2014 (Ajuntament de Barcelona, 2015).

Agriculture, livestock and biomass burning emissions are spread over the rural areas but concentrated in the core study area, the Vic Plain: a 30 km long depression in the north-south direction located 60 km to the north of Barcelona. The area is surrounded by mountains and it is

affected by thermal inversions during the night. The summer atmospheric dynamics dominated by sea breezes from the southern sector, channelled through the valleys formed by the coastal ranges, giving rise to the transport of pollutants from the BMA and the numerous surrounding highways.

Ground level measurements

Online measurements of gaseous pollutants

Measurements of gaseous pollutants were performed at 48 sites belonging to the regional air quality network (Figure 1, XVPCA; http://dtes.gencat.cat/icqa, Table S1) from 01 to 31/07/2015. Continuous measurements of O_3, NO, NO_2, CO and SO_2 were carried out using MCV 48AV UV photometry analysers, Thermo Scientific chemiluminescence analysers (42i-TL), Teledyne 300 EU Gas filter correlation analysers; and Teledyne 100 EU UV fluorescence analysers, respectively.

Measurements of gaseous pollutants with passive dosimeters

Diffusion tubes for NO_2 and O_3 sampling (Gradko Environmental) were deployed at 17 locations between the cities of Barcelona and Ripoll (Figure 1) covering strategic areas not monitored by the regional air quality network. The dosimeters were positioned along two main river basins in the study area (Besòs/Congost and Tordera), from the BMA to the Vic Plain. Sampling points were selected avoiding the direct influence of vehicular emissions and located at a height of approximately 2.5 m above ground level. One sample per site and sampling period (01-14 and 14-29/07/2015) were collected. After exposure, samples were stored at 4 °C until analysis.

Replicas were placed in 9 locations, showing good reproducibility of the results (relative errors of 5%±6% for O_3 and 4%±7% for NO_2). Dosimeters were collocated also at some XVPCA sites for comparison with reference measurements (6 samples for O_3 at Vic (VIC), Montcada (MON) and Montseny (MSY); and 10 samples for NO_2 at Santa María de Palau Tordera (SMPT), Palau Reial (PLR), Tona (TON), Manlleu (MAN), and Granollers (GRA)). Correction factors were obtained from the comparison between dosimeter and reference data (Dosimeter O_3 = 1.01*Reference O_3 + 17.43, R^2 = 0.97; and Dosimeter NO_2 = 1.27*Reference NO_2 + 1.14, R^2 = 0.90, in all cases in $\mu g/m^3$) and then applied to the dosimeter data (supplementary information Figure S1).

NH_3 passive samplers (CEH ALPHA, Tang et al., 2001) were also used in 30 specific points.

O_x concentrations

O_x values (NO_2+O_3) were calculated to complement the interpretation of O_3 concentrations. The concept of O_X was initially proposed by Kley and Geiss (1994) to analyse the O_3 spatial and time variability by diminishing the effect of titration of O_3 by NO ($NO+O_3 \rightarrow NO_2+O_2$, with the subsequent consumption of O_3) in highly polluted areas with high NO concentrations.

Laboratory van in Vic

A laboratory van was deployed next to the Vic air quality station during 10-17/07/2015. Eight-hour $PM_{2.5}$ samples were collected three times per day (00:00-08:00, 08:00-16:00, and 16:00-00:00 UTC) by means of Digitel DH80 high volume samplers (30 m^3/h) on Pallflex quartz fiber filters (QAT 150 UP). Filters were conditioned at 20-25°C and 50% relative humidity over at least 24 h before and after sampling to determine gravimetrically the $PM_{2.5}$ concentration. Subsequently a detailed chemical analysis following the procedure described by Querol et al. (2001) was carried out.

Hourly equivalent Black Carbon (BC) in $PM_{2.5}$ concentrations were determined by a multi-angle absorption photometer (MAAP, model 5012, Thermo). PM_1, $PM_{2.5}$ and PM_{10} hourly concentrations were determined by an optical particle counter (GRIMM 1107).

Vertical profiles

During 14-17/07/2015 several vertical profiles up to 1550 m a.s.l. (1000 m a.g.l.) were performed by means of a tethered balloon (details can be found in Table S2) in the city of Vic (Figure 1), at less than 200 m from the laboratory van and the Vic air quality station. The tethered balloon of 27 m^3 filled with helium was equipped with an instrumentation pack attached 30 m below the balloon. This setting has been successfully used in previous studies (Minguillón et al., 2015), hence the lack of a fixed support for the instrumentation pack is not expected to hinder the quality of measurements.

The instruments included in the pack were:

- A miniaturized condensation particle counter (Hy-CPC) measuring particle number concentration larger than 3 nm with a time resolution of 1 s and a flow rate of 0.125 L/min, using isopropyl alcohol as the working fluid (Lee et al., 2014). The particle number concentration measured by the Hy-CPC will be referred to as N_3. Prior studies have demonstrated the agreement of the Hy-CPC and conventional TSI CPCs (Minguillón et al., 2015).
- A miniaturized nano-particle sizer for the determination of the particle number size distribution (Hy-SMPS, Figure S2) in the range 8-245 nm with a time resolution of 45 s and a flow rate of 0.125 L/min (Lee et al., 2015). The instrument output agreed well with the results from a Scanning Mobility Particle Sizer (SMPS, 10-478nm), composed by a Differential Mobility Analyser (DMA, TSI 3081) coupled with a CPC (TSI 3772) (Figure S3, Hy-SMPS= 0.71*Reference SMPS + 999, R^2 = 0.88).
- A miniaturized optical particle counter (Hy-OPC, Figure S2) measuring particle number concentrations in the ranges 0.3-0.5 µm ($N_{0.3-0.5}$), 0.5-1.0 µm ($N_{0.5-1.0}$), 1.0-2.0 µm ($N_{1.0-2.0}$), and 2.0-5.0 µm ($N_{2.0-5.0}$), with a time resolution of 1 s and a flow rate of 1 L/min.
- A microaethalometer (MicroAeth AE51), which provided BC concentrations derived from absorption measurements on a 5 min basis with a flow rate of 0.15 L/min.
- A portable O_3 monitor that measures concentrations every 10 s based on UV absorption (POM^{TM} 2B Technologies, Figure S2). The personal POM O_3 monitor was compared with the O_3 concentrations from the nearby reference station, yielding good results (n=34 min data; POM O_3= 0.85* ReferenceO_3 +0.56, R^2 = 0.93) (Figure S1). The measured vertical O_3 concentrations reported in this study were normalized to standard temperature and pressure conditions (25 °C, 1013.2 hPa).
- A Global Position System (GPS).
- Temperature, relative humidity, pressure, wind direction and wind speed sensors.

Moreover, another sounding was carried out on the 16/07/2015 at 11:00 UTC. A free balloon was used with an instrumentation pack equipped with a Hy-CPC, a GPS, a temperature sensor, and a relative humidity sensor. The pack was placed in an insulated box (Figure S4).

Meteorological parameters

30-minute meteorological data from 11 sites located throughout the study area in the proximity of air quality monitoring sites were provided by Meteocat (Meteorological Office of Catalonia) (Figure 1 and Table S3). Hourly average wind components were calculated and used in polar plots with hourly O_3 and O_X concentrations, by means of the OpenAir software (Carslaw, 2012). These are bivariate polar plots where concentrations are shown to vary by wind speed and wind direction as a continuous surface.

Modelling system for O_3

The ambient O_3 concentrations were modelled using the ARAMIS (A Regional Air Quality Modelling Integrated System) high resolution modelling system that integrates the Weather Research and Forecasting model (WRF-ARW) version 3.1.1 (Skamarock et al., 2008) as a meteorological model, the High Resolution Emission Model (HIREM) (Soler et al., 2004, 2011 and 2015), and the Models-3 Community Multiscale Air Quality Modelling System (Models-3/CMAQ) (Byun and Ching, 1999) as a photochemical model. The modelling system was configured using four nested domains, D1, D2, D3, and D4 with horizontal grids of 27, 9, 3 and 1 km, respectively. For the coarser domain, initial and boundary conditions for the meteorological model were taken for the European Centre for Medium-Range Weather Forecast global model (ECMWF) with a 0.5º x 0.5º resolution using nudging and the boundary conditions are forced every 6 h, whilst for the photochemical model initial and boundary conditions model came from a vertical profile supplied by CMAQ itself. Domains are run in one-way nesting and 24 h spin-up was performed to minimize the effects of initial conditions for the inner domains. The output data is saved every hour. ARAMIS is continuously updated, it has been extensively evaluated (Soler et al., 2015) to simulate air quality over regional and local scales. In the present study the domain D3 was used, which covers the area of interest.

RESULTS AND DISCUSSION

Meteorological background and diurnal cycles of pollutants

Two types of episodes that will be discussed in the following sections were identified concerning the meteorological patterns and the O_3 concentrations recorded.

- Type A episode: Under "usual summer conditions", with the Azores High located west of Iberia, and a ridge of high pressures extending into southern France, air masses in the Western Mediterranean basin rotate clockwise (anticyclonic) during the day, following the combined sea breezes and upslope flows at eastern Iberia and a simultaneous generalized compensatory sinking is observed in the basin. During nighttime, drainage flows into the sea develop at the coastal strip, subsidence over the basin weakens and the wind over the sea is observed moving southward, transporting the coastal emissions almost parallel to the shoreline (Gangoiti et al., 2001). At the same time, Atlantic gap winds (through the Ebro and Carcassonne valleys), weaken during daytime due to inland sea breezes and become strengthened during nighttime (Millán et al. 1997; Gangoiti et al., 2001, Gangoiti et al., 2006 and Millán 2014). In such conditions, the air layers over the sea in front of Barcelona tend to move within the south-westerlies during the day, following the clockwise rotation, i.e. towards Southern France and the Gulf of Genoa, and within the northerlies (towards Valencia) during the night. Thus, direct transport of O_3 and precursors

from the Fos-Berre-Marseille-Piombino (Livorno) area towards the BMA is weak or null. However, indirect transport is more likely, first into the sea during nighttime conditions, and then following the daytime south-westerlies for the combined coastal sea-breeze and anticyclonic gyre at the coastal strip of Catalonia, which could bring a fraction of the referred O_3 and precursors originated in southern France, together with those emitted at the eastern coast of Iberia

- Type B episode: When the anticyclone establishes over Central Europe with relative low pressures to the West over the Atlantic, the flow pattern over the Western Mediterranean changeS: southerly winds blow at height over eastern Iberia, while at ground level, gap winds may weaken or stop the Mistral and the Tramontana winds in the Gulf of Lion, and Barcelona could then be directly affected by O_3 and precursors, coming with the easterlies blowing at the marine boundary layer (emissions from Corsica, Sardinia and Italy). However, under these atmospheric conditions O_3 levels did not reach the observed values found during episodes type A, and the O_3 daily records did not show the classical pattern of accumulation from one day to the next, characteristic of the highest O_3 episodes in the Western Mediterranean (Millán et al., 1997, 2000 and Castell et al., 2008a)

Under the above "usual summer conditions", Millán et al. (1991, 1996a, b, c, 1997, 2000, 2002), Gangoiti et al., (2001), and Castell, (2008a) demonstrated the vertical recirculation of O_3-rich masses in the western Mediterranean, with O_3 being formed from precursors transported inland by the combined up-slope and sea breeze winds. O_3 loaded air masses, elevated by topography and sea-mountain breezes will be transported back to the coastal area at a certain altitude during the day and accumulates in elevated stably stratified layers at the coastal areas during the late evening and night. During nighttime and at ground level O_3 depletion dominates mainly in urban and industrial centers, driven by reaction with new emissions, which at the coastal area are transported offshore within the stable surface drainage flows.

The synoptic atmospheric situation in July 2015 was characterized by an intense high pressure system over central and southern Europe during almost the whole month (Figure 2). Type A and B scenarios alternated, transporting warm air masses from North Africa towards higher latitudes by the anticyclonic dynamic and reaching extremely high temperatures in Europe. The stagnation of air masses induced a regional meteorological scenario in the area under study, characterized by local/regional re-circulations and sea-land breezes, both channelled by the complex topography. The flow pattern, together with the observed stably stratified layers developed up to a height of 2000-2500 m a.s.l. (Figure 3) associated with subsidence, enhanced the accumulation of pollutants and caused several pollution episodes in the north-eastern Iberian Peninsula. Coastal and pre-coastal locations (Barcelona) were mainly affected by daily sea breezes, starting blowing from the east (around 08:00 UTC) and turning progressively to south and southwest. The sea breezes were channelled through the valleys, which are mainly located following a north-to-south axis, and arrived to the monitoring stations predominantly from a southerly direction. However, during the night atmospheric conditions were much more stable with flow patterns dominated by land breezes from N-NW.

The VIC site was characterised by stagnant conditions during the day, reaching the maximum wind speed (4 m/s on average) at around 15:00 UTC, when sea-breeze intensity was at the highest (Figure 4). During the night very light winds blew from the north (Figure 4). During the periods 14-20/07/2015 (episode type A) and 03-06/07/2016 (episode type B) the sea breeze blew from 10:00 to 18:00 and 10:00 to 21:00 UTC, respectively; but in the first one the wind speed was higher (maximum of 2.7 m/s as an average for the period) and maximal at 14:00 UTC, whereas in the

second wind speed was lower, with a maximum mean value for the period of 2.4 m/s at 17:00 UTC, but only 1.5 m/s at midday.

Averaged ground O_3 concentrations during type A episode recorded at VIC were clearly influenced by these wind patterns, showing a typical midday peak, followed by a higher peak at 13:00-14:00 UTC probably caused by the transport of BMA air masses by the breeze (Figure 4). Mean O_3 levels during this A episode reached 195 µg/m^3 at 13:00 UTC. During type B episode averaged O_3 levels were also very high (142 µg/m^3 at 14:00 UTC) but clearly lower than during the A episode (Figure 4).

Intensive surface measurements were only available for 10-17/07/2015 (when the mobile laboratory was working at VIC). Average SO_2 levels for this period (included in the type A episode) showed a similar daily pattern to that of O_3 (Figure 4) pointing to a probable Hewson's-type I fumigation process (Hewson, 1964, Geiger et al., 1992) when midday convective flows that abate to the surface a SO_2 rich layer accumulated in the limit of the boundary layer. Ground level concentrations of BC, NO_2 and PM_x showed a similar daily pattern driven by stagnation and traffic rush hour, with maxima concentrations around 06:00 UTC (08:00 h local time, Figure 4). Finally, extremely high concentrations of NH_3 (this is one of the most intensive farming regions of Spain and mean values of the Vic Plain dosimeters reached 30 µg/m^3 NH_3 for 01-31/07/2015) followed the typical midday maximum due to evaporative emissions from fertilisers, but the rapid increase of the wind speed and dilution by the growth of the PBL thickness (see vertical profiles of temperature, aerosols and O_3 at VIC in following sections) probably account for a reduction of ground level NH_3 concentrations during the central hours of the day (Figure 4).

The varying diurnal and nocturnal air mass patterns in the Vic Plain are also shown by the $PM_{2.5}$ chemical composition. Figure S5 shows the 8-h concentration patterns of selected components during the week period of 10-17/07/2015, including several days (14 to 17/07/2016) of the type A episode defined above, affected by polluted air masses from the BMA.

In addition to the regionally transported O_3, concentrations of elemental carbon (EC) and traffic and industry-related metals (including Zn, Cu, Pb, Sn and Sb) were notably enhanced at the end of the week, and were attributed to local sources. This enhancement was most obvious during the 00:00-08:00 UTC period (Figure S5), under calm or northerly low wind (drainage slope winds) carrying metallic pollutants from the Cu-smelter located 13 km to the north of Vic, and leading to high Cu, Zn, Sn, W, Pb and Sb concentrations on the nights of 15 and 16/07/2015 (Figure S5). The increase in EC was related to local traffic emissions during the morning rush hour as deduced from the peaking MAAP BC concentrations during 05:00-08:00 UTC (07:00-10:00 h local time), up to 5 µg/m^3 hourly BC, when compared to 3 µg/m^3 recorded as maximum traffic rush hour concentrations in the preceding days (data not shown). In contrast, the rise of organic carbon (OC) concentrations observed during 08:00-16:00 UTC is attributed to the formation of secondary organic aerosols (SOA).

Sulphate concentrations did not show any trend, as expected from secondary inorganic components present in relatively homogeneous concentrations on a regional scale, whereas nitrate (and a minor proportion of ammonium) concentrations increased during the 00:00-08:00 UTC periods as a result of gas to particle partitioning (Figure S5) due to the thermal instability of ammonium nitrate (Hertel et al., 2012), under typical high daytime temperatures reached in July 2015. Interestingly, the stronger southerly winds during the daytime in the second part of the week (see below) appear to have brought polluted air from the BMA as signalled by slightly higher V concentrations (tracer of fuel oil combustion); but also the fumigation from high strata (polluted for air masses that were injected the previous day-s) might account for these SO_2 and V increases.

The concentrations of mineral matter and all its components (Al, Fe, Mg, Li, Ti, Rb, Sr, Ti, As) were constant during the week, with relatively higher concentrations in the 08:00-16:00 UTC samples (Figure S5), indicating a higher resuspension caused by stronger afternoon winds. The increment on the 15/07/2015 (08:00-16:00 UTC) was attributed to resuspension of local dust, given that the occurrence of African dust outbreaks was not observed during this period.

The free sounding measurements carried out at 11:00 UTC on 16/07/2015 revealed stratified air masses up to 3000 m a.g.l. (Figure 3). The vertical profiles of potential temperature, water vapour and aerosol concentration distributions can be used for the identification of atmospheric layers presenting different properties: a lower layer up to about 1100 m a.g.l. characterised by a relative high aerosol concentration, well mixed and with a relative high and uniform water vapour content. A clear discontinuity between 1100 to 1500 m a.g.l limits the mentioned lower layer and a series of stably stratified layers up to a height of 3000 m a.g.l. This layering of pollutants is probably related to the development of regional and mesoscale convective cells driven by the combined upslope and sea breeze flows developed the day before (Millán et al., 1997).

O_3 and O_X episodes

Figure S6 shows the average O_3 and O_X ground level concentrations recorded in July 2015 in the study area at the XVPCA air quality monitoring network and with the passive dosimeters. O_X maximum concentrations were recorded at the Vic Plain area and in the coastal sites at the northeast of Barcelona. This may be due to the high O_3 concentrations in Vic and to a higher proportion of primary NO_2 (emitted mainly from diesel engines, and not formed in the atmosphere from NO titration by O_3) in the coastal cities, respectively.

In July 2015, the O_3 hourly information threshold was exceeded a total of 74 times at the XVPCA stations of Catalonia, 57 taking place in the Vic Plain stations (TON, VIC and MAN), and 69 in the surrounding areas (pre-Pyrenees, High Llobregat river and Montseny).
Figure 5 shows hourly O_3 concentrations for the study period from selected monitoring sites. O_3 concentrations recorded at a coastal (Begur, BEG; blue, 200 m a.s.l.) and a remote inland western pre-Pyrenean site (MSC, light green, 1570 m a.s.l.) (Figure 5a) show relatively narrow diurnal variations and multiday episodes, with low or enhanced concentrations, according to meteorological fluctuations (accumulation and air mass renovation cycles of 3 to 12 days cause a wider O_3 and O_X concentrations range than the typical daily cycles evidenced in most of the other sites). O_3 variations at the coastal BEG are opposed, in periods such as 01-03, 10-12 and 26/07/2015 and several periods from 14-20/07/2015, to those at the inland MSC. As shown by the polar plots from Figure 6, relatively low O_3 concentrations (but still high in absolute terms) were recorded at the BEG coastal site (easternmost site in this figure) when the wind blows from the sea, whereas polluted air masses are transported towards the inland remote MSC (westernmost location in the figure) site under the same meteorological conditions. Conversely, when westerly winds blow, the inland remote MSC site received relatively clean air masses with low O_3 (Figure 6), which are progressively loaded with regional pollution as these are transported towards the coastal BEG site.

Data from two urban background sites of Barcelona (PLR and CTL, 81 and 5 m a.s.l., grey and black in Figure 5b) show evidence of a high nocturnal O_3 consumption, with differences due to local NO_x traffic emissions. Following the transport of air masses by combined breezes, the two sites located in the northern periphery of the BMA, along the Besòs river valley (GRA and MON, 140 and 33 m a.s.l., orange and yellow in Figure 5c; 20 and 6 km from BMA in NE an NNE directions, respectively)

show local O_3 production, with higher midday concentrations, while very low nocturnal levels reflect again the intensive O_3 consumption (in a densely populated basin). O_3 concentrations were closer between GRA and MON than between the two Barcelona urban sites (PLR and CTL).

Relevant O_3 net production and fumigation can be readily seen in the inner Vic Plain (TON, VIC and MAN; 620, 498, 460 m a.s.l.; red, pink and violet in Figure 5d; 45, 55 and 62 km from BMA in a NNE direction, respectively) as well as at the remote eastern pre-Pyrenean site of Pardines (PAR, brown, 1226 m a.s.l, 102 km from BMA in a NNE direction), where O_3 formation and fumigation seems to have already reached its maximum, and similar O_3 concentrations were recorded at all sites during the midday increase. This suggests that the intensity of O_3 formation and fumigation was clearly reduced in the Vic Plain-Pyrenees transect with respect to the Barcelona-Vic Plain (an intermediate production place would be MSY (720 m a.s.l.; green in Figure 7, 39 km from BMA in a NE direction). Polar plots of GRA, TON, MSY, VIC, MAN show clearly that the highest O_3 levels were recorded with wind blowing from the Direction where BMA is located (Figure 6).

As it can be observed in Figures 5 and 7, during two periods (01-02 and 07-20/07/2015) O_3 concentrations increased progressively from the Barcelona city towards the northern BMA (GRA and MON), the intermediate MSY regional background area and towards the northern Vic Plain sites; and from there it slightly decreased towards the eastern pre-Pyrenees (PAR) following the midday-afternoon combined breeze transport (Figures 5 and 7). During these days, no exceedance of the information threshold was produced in the urban environment; only sporadic measurements above the human protection target value were recorded in the close surroundings of Barcelona. However, frequent exceedances of both thresholds were recorded in a regional transport context towards the north of the BMA.

While differences in O_3 concentrations between TON, GRA, MSY, BEG and CTL were observed during the period 03-06/07/2015 (B type episode), O_X concentrations show a very similar behavior along the Vic Plain, both qualitative and quantitative (Figure 7, O_X is not reported at BEG due to the lack of NO_2 measurements). Conversely, in the period 07-20/07/2015 (that includes the A type episode), characterized by a change in the synoptic conditions, differences in daily maximum O_X values resemble the same behavior of O_3 alone, with a positive and marked inland gradient. O_3 concentrations at BEG, a coastal site far in the northeast were higher during the former period and showed low intra-day variation, indicating a probable long range transport of polluted air masses (Figure 7).

O_3 and O_X concentrations at the regional background site (MSY, 720 m a.s.l., green in Figure 7) depict also the meteorologically influenced patterns (in the sense previously described for BEG and MSC), but with a clear overlapped and pronounced daily fluctuation, with marked higher concentrations indicating O_3 generation from a regional origin, especially on 01-02 and 07-20/07/2015 (Figure 7).

Diurnal O_3 concentrations in the Vic Plain (around 460-620 m a.s.l.) were markedly higher than at the coastal (CTL, PLR) sites, and slightly higher than at mountain sites (MSY, PAR and MSC, from 720, 1226 and 1570 m a.s.l.) during the 01-02 and 07-20/07/2015 periods. The O_3 hourly information threshold of 180 $\mu g/m^3$ was exceeded 55 times in the Vic Plain (3 sites), with 50 of these exceedances taking place during 01/07/2015 and 14-20/07/2015. For these exceedances, an hourly contribution of up to 150 $\mu g/m^3$ of O_X (mostly O_3) both from fumigation of recirculated return layers (injected at an altitude of 1500-3000 m a.g.l. in the prior day(s)), and from transport and photochemical generation of O_3 of the BMA plume, might be estimated based on the differences of the O_X early afternoon maxima recorded at the coastal BMA sites (CTL, PLR) and the ones in the Vic Plain (TON, MON, VIC). Thus, as shown in Figure 7, on 14-18/07/2016 midday

maxima recorded at CTL (into BMA) range between 38-62 ppb O_X, on an hourly basis; whereas at TON (in the Vic Plain), these reach 102-115 ppb. Accordingly, differences of 50-73 ppb O_X (close to 100-150 µg/m^3 O_X) between CTL and TON can be estimated for these days.

Type A episode (14-20/07/2015)

During this episode, a progressive time shift of the daily hourly O_3 and O_X maxima was observed from the Barcelona area (10:00 UTC, at CTL into the BMA) towards the metropolitan periphery (11:00, at GRA), the intermediate mountain sites (13:00, MSY, 39 km from BMA), the Vic Plain (12:00, 13:00 and 14:00, TON, VIC and MAN, 45, 55 and 62 km from the BMA, respectively) and the northern pre-Pyrenean site (16:00, PAR, 102 km from BMA) (Figure 8). As described above, this variation points to the process of O_3 and O_X formation with a mean O_X difference between the urban-coastal sites and the Vic Plain hourly maxima of up to 73 ppb O_X (around 150 µg/m^3) for the TON site when subtracted O_X hourly maxima from CTL (Figure 7), with a maximum average O_3 hourly levels of around 200 µg/m^3. These O_X differences are mostly due to O_3 differences (Figure 8). Accordingly, during these intense O_3 pollution episodes, more than 50% of the O_X and O_3 hourly maxima concentrations are attributable to (i) O_3 contributions from the previously referred surface fumigation of recirculated strata (over the VIC-MAN-TON area) containing the polluted air masses injected the day before by complex topographic induced circulations; and to (ii) the local O_3 generation and surface transport of the BMA plume into inland valleys. Attributing these O_3 exceedances to local/regional causes is also supported by the spatial distribution of the hourly O_3 maxima, the number of hourly exceedances of the information threshold, the time shift of the exceedances at the different sites (as moving towards the north) (Figure 9), and the polar plots of hourly O_3 concentrations pointing towards the BMA as main source region (Figure 6). It is important to note that in the coastal sites the PBL height is markedly reduced when compared with the inland regions and then the capture of these high altitude O_3-rich layers by the PBL growth and the consequent fumigation on the surface is less probable in the coastal areas than in the inland ones.

Thus, during the A episode, O_3 has mostly a major local/regional origin (with O_X maximum hourly levels progressively increasing from 166 to 246 µg/m^3 from the BMA to the Vic Plain). The concatenation of daily cycles of regional/long range recirculation of air masses and regional/local O_3 production in the A episode accounted for the accumulation of O_X and the consequent exceedance of the hourly information threshold. Castell et al. (2008a) have already reported a correlation between their 'recirculation factor' (a meteorological parameter devised to increase with the concatenation of days with regional vertical recirculation of air masses) with the occurrence of O_3 episodes in 2003. The relevance of these recirculations in originating these high O_3 episodes in Southern Europe was highlighted already, not only by scientific papers by the CEAM's team but also assumed by the European Commission (EC, 2004).

Figures 10 and 11 show results for the vertical profiles (0-1100 m a.g.l.) of O_3 concentrations, particle number concentrations for particles > 3 nm (red), 0.3-0.5 µm (blue), 0.5-1.0 µm (brown), ambient temperature, relative humidity and wind direction, obtained at the beginning of the A type episode (from 14 to 17/07/2015).

In the profiles from 07:06 to 08:21 UTC on the 14/07/2015, a boundary layer (150 to 250 m thick) with relatively high levels of N_3 (0.8 to 2.0 10^4 #/cm^3) was differentiated from the free troposphere (0.2 to 0.8 10^4 #/cm^3) (Figure 10). However, in the profile obtained from 09:42 to 10:52 UTC on 17/07/2015, the growth by convective turbulence accounts for a homogeneous boundary layer

and profile of $N_{0.3-0.5}$ below 1000 m a.g.l. (Figure 10). Inside the boundary layer nucleation occurred (yellow to red areas in Figure 12 for 16/07/2015) regionally driven by photochemical processes. Minguillón et al. (2015) showed the occurrence of these nucleation events into the mixing layer as convective transport elevates and dilutes air masses from polluted areas under high insolation in Barcelona. During 14-16/07/2015 nucleation episodes occurred occasionally, but only inside the boundary layer. On the 17/07/2015 at 9:42-10:52 UTC new particle formation occurred probably at relatively high altitudes, also inside the boundary layer, as deduced from the high N_3 levels measured from 400 to 1000 m a.g.l., with concentrations reaching 1 10^4 #/cm^3, while simultaneously low concentrations (< 0.3 10^4 #/cm^3) were measured at ground level (Figure 10). This vertical gradient is not observed for the coarser particles ($N_{0.3-0.5}$ and $N_{0.5-1}$) and O_3 (Figures 10 and 11, for which relatively constant levels were measured inside the boundary layer), suggesting new particle formation.

On 14/07/2015 07:06-08:21 UTC a well stratified atmosphere (Figure 11) with both thermal and O_3 layers is observed, with a general upward increasing trend for O_3 from 40 µg/m^3 at ground level to much higher levels in different strata, such as one reaching 150 µg/m^3 in strata at 500 and others with 140, 100 or 40 µg/m^3, such as the ones at 300, 800-1000 or 400 m a.g.l., respectively, reflecting, in addition to stratification of O_3 concentrations in altitude, the effect of surface depletion by NO titration and by deposition during the night (see in Figure 11 the progressive O_3 depletion from 150 µg/m^3 at 500 m a.g.l. to 40 µg/m^3 at surface levels). From 13:49 to 15:03 UTC on the 14/07/2015 (Figure 11) the vertical profile changed substantially, with an already unstable atmosphere near the ground, showing very high surface O_3 concentrations of 217 µg/m^3 that increase up to 330 µg/m^3 in a layer around 100 m a.g.l., decreasing again through an upper layer with values of 240 µg/m^3 until 300 m a.g.l. (where measurements were not available due to instrumental problems). This 100-200 m a.g.l. very high O_3 layer agrees with the modelled O_3 concentrations for the study area (Toll and Baldasano, 2000; Barros et al., 2003; Gonçalves et al., 2009) and reflects elevated O_3 concentrations due to local production and transport of O_3, that decrease from 100 m a.g.l. to the surface due to its titration, consumption and deposition. On 15 and 16/07/2015, a similar upward increasing O_3 gradient was observed in the early morning (Figure 12). On 17/07/2015 7:39-08:40 UTC O_3 concentrations were relatively constant, but showing also a strongly stratified profile, in the range of 100-165 µg/m^3 in the lower 500 m. In the last profile from 09:42 to 10:52 UTC, O_3 concentrations increased from 140 to 200 µg/m^3 from 200 to 1000 m a.g.l., but again a maximum close to 200 µg/m^3 was observed at the same height around 100 m a.g.l. (Figure 11).

Thus, vertical profiles of the type A episode are characterised in the early morning by a strong stratification, showing low ground level O_3 concentrations, due to low production (low insolation) and/or consumption (titration and deposition), and increasing concentrations with altitude. This variation is related to prevailing meteorological conditions enhancing local recirculation or larger scale transport with high O_3 masses injected (the day before) at certain altitudes by vertical recirculations into the residual layer, above the nocturnal surface stably stratified boundary layer. Nevertheless, during specific days, homogeneous O_3 vertical profiles up to 1000 m a.g.l. (the maximum height reached with captive sounding) were also evidenced, but probably not maintained at higher levels (where we were not able to measure with our system). Thus, as shown by the 4500 m profile measured with the free sounding on 16/07/2016 (Figure 3), high PM (and probably O_3) strata are present between 1500 and 3000 m a.g.l., these being probably the polluted air mases injected the day before in the northern mountain ranges and recirculated to the coast at certain altitudes (see modelling outputs below). On the other hand, with constant southerly winds (from the coastal area to the Vic Plain) usually associated with the combined sea-breeze and up-

slope flows, O_3 was enriched in the lower 100-200 m atmospheric layer, generated by the intensive local photochemical production. O_3 concentrations reached maximal values (up to 330 µg/m^3) on the top of this layer, while they decreased at lower heights by titration and deposition, although hourly levels of 225 µg/m^3 were still recorded. These results are consistent with the gradient of O_3 concentrations between the Vic Plain (around 500 m a.s.l.) and the MSY mountain site (720 m a.s.l., and more close to the sea) during the episodes, (Figures 7 to 9). At higher altitude, O_3 concentrations decreased but were still high (150-240 µg/m^3) due to the O_3 formation in air masses constantly transported from the coastal area, which also incorporates O_3 and precursors recirculated the day before, as it is shown next.

Interesting results are also obtained by comparing the vertical profiles of BC and O_3 (Figure 13). BC is a tracer of local primary pollution at ground level, and of the potential transport and stratification of regional/local primary pollutants (together or not with regional O_3) when present at high altitude. On 14/07/2015 07:06-08:21 UTC, at 350 m a.g.l. (and similarly on 15-17/07/2015 but at varying heights, 100-350 m a.g.l.) a clear discontinuity is evidenced with sudden and simultaneous decreases of BC and O_3 above these heights. The relatively high BC levels within the lower layer suggest the nocturnal accumulation, while O_3 appears in strata (with low values near the ground due to titration and deposition) and with a high concentration just above that level (350 m), now with low BC concentrations. There is a further upward decrease of BC and an increase of O_3 up to the limit of the sounding (870 m).

The occurrence of an O_3 maximum layer around 100-200 m a.g.l., on top of the nocturnal stably stratified boundary layer reinforces the idea of an important local production contributing to an upward increase of O_3 inside the layer. Finally, at the highest altitudes reached in this study (900-1000 m a.g.l.), BC and O_3 concentrations were often anti-correlated or unrelated, possibly more related with aged air masses re-circulated within the whole region and with a mixed origin: including local-to-regional sources, more distant over the W-Mediterranean or even from hemispheric transport of air masses as reported by UNECE (2010).

Figure 14 shows mean O_3 hourly concentrations recorded at VIC for the episodes A and B, as well as mean wind speed and direction. Mean hourly concentrations are characterized by an increase until 10:00-11.00 UTC, followed by an inflexion point and a more marked increase, with a maxima between 13:00 and 14:00 h UTC, and then a progressive decrease, more marked in the episode A. As stated above, processes contributing to increase levels were attributable to fumigation, photochemical production and transport of high O_3 air masses, all controlled by insolation. Millán et al. (2000) described this characteristic diurnal O_3 pattern typically for inland valley stations (as in our case around 75 km from the coast), where the first O_3 increase is attributed to O_3 contributions from surface fumigation of high recirculated return strata as well as from the arrival of higher O_3 air masses transported by sea-breeze and the local photochemical production from precursors. On the other hand, the second O_3 concentration 'hump' is coincident with maximum wind speed and probably corresponds to a more intensified sea breeze transport compared with local photochemical formation and fumigation. Figure 14 shows that the two O_3 increases (and consequently the contributions from the 3 above processes) are more pronounced in the type A compared to the type B episode, and that the second maxima (more associated to inland surface transport by sea breeze) is wider, coinciding with a shift of the maxima wind speed towards the late afternoon, in the B episode.

Modelling outputs for the A episode points to light winds from the south, transporting pollutants from the BMA towards northern areas (including the Vic Plain), and triggering the hourly O_3 exceedances under the effect of the sea and land breeze transport. Thus, Figures 15 and 16 show

the horizontal wind vector at 10 m a.g.l. and NO_2 and O_3 concentrations both at ground level and at a height above the surface layer, at different hours for two representative days of the type A and B episodes, respectively. During the type A episode day (15/07/2015), the effect of the land breeze transport accumulates NO_2 over the sea during the night, starting intense O_3 production when sun rises and sea breezes start the inland transport. Maximum concentrations of O_3, exceeding 180 $\mu g/m^3$ were calculated by the model and measured at the stations located in the Vic Plain (TON, VIC and MAN, Figure 16), although the model overestimated maximum O_3 concentrations in TON and VIC and delayed the hourly maximum value in all stations. The vertical distribution shows an important accumulation of around 110 $\mu g/m^3$ trapped in a reservoir layer at around 1500 m a.s.l. during the night (Figure 17), which will fumigate downwards into the new developing mixing layer during the following hours. Local O_3 production from fresh precursors accumulated during the night in the stably stratified surface layer and then progressed inland along the midday hours. This results in an O_3 enriched plume within a layer of 1000-1500 m depth in the late afternoon, following the model results (Figure 17). This mixing layer also incorporates O_3 from upper reservoir layers after fumigation during the inland travel. The O_3 located at upper levels can re-circulate back into the sea and it will be potentially available to be transported inland (Millán et al., 1997 and 2002), to re-start a new cycle the following day.

Type B episode (03-06/07/2015)

As opposed to episode A, during the type B episode and 22-31/07/2015, despite the high O_3 and O_X concentrations, these concentrations were very similar in the urban and remote coastal sites and all along the northern sites, including the Vic Plain. Hence, the averaged O_X hourly concentrations of all the study sites were close to those at the coastal urban site in Barcelona CTL (and in the case of the O_3 close to the remote coastal site of BEG) compared with the large differences reported for the A episode (Figure 8). The high O_X peak measured at the urban site during the mornings of the B period (Figure 8) and from 8:00 to 10:00 UTC in the average hourly patterns (Figure 9) is due to the contribution of primary NO_2. According to Carslaw et al. (2016) the Euro 1 to Euro 2 diesel engines in Europe (early 1990s) emitted 5-10% of primary NO_2 and 90-95% of NO, whereas the Euro 4 to Euro 5 equivalent engines (2004 and 2009 onwards) emit 16-29% of primary NO_2 and 71-84% of NO.

Also as opposed to the A episode, during the B episode, O_X levels varied in a very narrow range from East (coastal) to West (mountains, MSC site) and from South (BMA) to North (Vic Plain) and at different heights (from Barcelona and BEG at sea level to MSC at 1570 m a.s.l.). Following the results of the model in the Figures 15 and 17, O_3 does not re-circulate around the region in this period. There is no accumulation from one day to the next in reservoir layers located over the region. Southerly winds blow at height during the whole period and the combined sea breeze and upslope winds developed at lower layers during daytime, after coupling with the southerlies, vent out the O_3 production and the rest of pollutants to the north. The circulation is open, as opposed to the type A episode, which show a closed circulation (it is never completely closed) (Millán et al., 1997, 2000). Unfortunately, vertical profiles of O_3, UFP, PM and BC profiles were not obtained for this episode.

Model outputs also evidence a net night and early morning transport of O_3 at lower layers from east and north-east during the B episode, supporting the hypothesis of a regional transport from Southern France, advecting aged air masses to the whole region, while O_3 and its precursors from the BMA were transported during the morning to the south-west regions (Figure 15) giving rise to hourly O_3 exceedances in some stations situated in this area. Figure 15 also shows that during this episode (03/07/2015) the combined sea-breeze and upslope wind transported O_3 and precursors

674 to the western pre-Pyrenees area, and values lower than 180 µg/m^3 were measured and modelled
675 in all monitoring stations and mainly in the Vic Plain. The vertical distribution of O_3 also shows
676 relatively low concentrations over most of the domain (Figure 17).

677

678 **CONCLUSIONS AND IMPLICATIONS FOR AIR QUALITY**

679 Very high levels of O_3 were recorded in the plains and valleys of the northern regions surrounding
680 the Barcelona Metropolitan Area (BMA) during July 2015, where 69 out of the 74 exceedances of
681 the hourly O_3 information threshold measured in the entire air quality monitoring network of
682 Catalonia were recorded. This represents a major environmental problem for which air quality
683 managers must implement European and national legislation.

684 Both experimental measurements and modelling exercises suggest that these very intense O_3
685 episodes were originated by the concatenation of daily cycles of vertical recirculation of air masses
686 that accumulated photochemically generated pollutants (Millán et al., 1997, 2000, 2002; Gangoiti
687 et al., 2001 and Castell et al., 2008a, Valverde et al., 2016), favoured by the high BVOCs and
688 anthropogenic NO_X emissions in the BMA region. The lower 1000 m a.g.l. were highly enriched in
689 O_3 by fumigation from precursors and O_3 located at upper levels (1500-3000 m a.g.l). Additionally,
690 local contributions of O_3 to these episodes were also demonstrated by soundings of the lower
691 layers (0-1000 m a.g.l.). Thus, slightly higher concentrations of O_3 were measured in stations
692 located at the plains and inland valleys than at higher altitudes (up to +30-40/µg/m^3 added to
693 180µg/m^3 reached in the mountain sites), due to the local photochemical production from fresh
694 precursors emitted during the night and early morning, and their channelling within the combined
695 upslope and sea breeze circulation that transports O_3 and precursors from the BMA. Thus vertical
696 profiles identified a high O_3 layer at 100-200 m a.g.l., produced by these local processes and also
697 by the high deposition and titration of O_3 at the lower 100m depth layer. In our (mostly rural)
698 study low concentrations of ultrafine particles were recorded at this high O_3 100-200 m a.g.l. layer
699 and nucleation episodes were only detected into the boundary layer, most of the days at the
700 lower atmospheric levels.

701 Two types of high O_3 episodes (A and B) were identified in the area:

702 Type A episode: Characterized by major local/regional O_3 recirculation, fumigation, production and
703 transport, superimposed on the typical regional/long range transport, and by the occurrence of
704 major exceedances of the O_3 information threshold (14-20/07/2015). Surface fumigation from
705 high O_3 return (to the sea) layers injected the day(s) before at altitudes of 1500-3000 ma.g.l., and
706 recirculated over the VIC-TON-MAN area, as well as direct surface transport and formation of
707 local/regional polluted air masses (with O_3 and precursors) from the BMA towards the north,
708 decisively contributed to these exceedances. Thus, this atmospheric scenario is governed by poor
709 ventilation under local breeze circulations and vertical recirculation of air masses over the study.

710 Type B episode: With a major regional transport O_3 contribution, yielding similar O_X levels at all
711 monitoring sites of the study area, with the arrival of aged air masses from the east/northeast
712 (high O_3 levels entering through the coast), but without major transport from BMA to the Vic Plain
713 (3-6/07/2015), and without vertical recirculation of air masses over the study area. When sunlight
714 activates atmospheric photochemistry in the early morning, the northern regions were loaded
715 with air masses with lower content of O_3 precursors, since air masses were transported from the
716 BMA to the southwest (parallel to the coast) from 00:00 to 09:00 h UTC. The combined breeze at
717 midday favored the transport towards the northwest, rather than to the north, as described for
718 the type A episode. In addition the aged air masses are not vertically recirculated and leave the

719 region towards the north-east (to France). Thus, O_3 concentrations were still relatively high
720 (exceeding 120 µg/m^3 but below 180 µg/m^3) due to local production from fresh precursors and
721 background O_3 contributions from the western Mediterranean, but not enough to exceed the
722 information threshold.

723 From the perspective of possible precursor abatement strategies, direct mitigation measures at
724 the BMA would have had a minor effect on O_3 concentrations at the Vic Plain area during the type
725 B episode. However, during the type A episode, a reduction of NO_x and/or VOCs emissions in the
726 BMA, some days before and during the episode, might have an effect on O_3 concentrations
727 recorded in the Vic Plain. Nonetheless, due to the non-linearity of the O_3 generation processes,
728 sensitivity analysis with high resolution modelling is necessary to evaluate the possible effects in
729 terms of absolute concentrations.

730 The use of O_X data from strategically selected monitoring sites in the east coast, western and
731 central mountain areas, urban background sites of the BMA and sites in the Vic Plain, tracking the
732 natural routes of pollutant transport, is a useful tool to assess the different regimes leading to high
733 O_3 concentrations, and to differentiate between type A and type B episodes, with important
734 implications in the design of potential abatement strategies.

735 We are aware that we only analysed the most intense O_3 episodes occurring in July 2015, and that
736 there might be other scenarios, different to type A and B, yielding high O_3 events, such as the
737 transport of aged air masses from other regions of Europe or the transport of the BMA emissions
738 in meteorological scenarios different to those described here. However in a recent study (Querol
739 et al., 2016) we demonstrated with the analysis of the 2000-2015 O_3 data series, that the Vic Plain,
740 (40-50 km north of Barcelona) is the area in Spain recording the highest number of annual
741 exceedances of the O_3 information threshold, orders of magnitude higher that the surrounding
742 areas of the axis BMA-Vic Plain-Pre-Pyrenean ranges. Thus it is clear that the BMA emissions and
743 the vertical re-circulations caused by the local complex orography have an important role in the
744 occurrence and development of intensive O_3 episodes in the region.

745 To implement potential (and difficult) abatement strategies two major key tasks are proposed:

746 1. Meteorological forecast from June to August to predict recirculation episodes in order to
747 apply abatement measures for O_3 precursors before a recirculation episode starts. As state
748 above, the relevance of these recirculations in originating these high O_3 episodes in
749 Southern Europe was assumed already by the European Commission in 2004 (EC, 2004).
750 2. Sensitivity analysis with high resolution modelling to evaluate the effectiveness of NO_x and
751 VOCs abatement measures on O_3 reduction.

752

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754

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FIGURE AND TABLE CAPTIONS

Figure 1. Top: Study area and location of monitoring sites (regional air quality monitoring sites XVPCA, dosimeters, meteorological stations and vertical measurements). BMA: Barcelona Metropolitan Area. Bottom: Topographic profiles across the study area, red arrows point to the valleys connecting BMA with the Vic Plain and the Pre-Pyrenean regions.

Figure 2. Geopotential and temperature at 850 hPa (left) and 500 hPa (center). Potential temperature (K) of the atmospheric sounding in Barcelona (WMO 08190) at 12:00 UTC (right). Meteorological figures are reported for 03/07/2015 (top) and 14/07/2015 (bottom).

Figure 3. Data from the non-tethered balloon measurements (at VIC) of temperature, relative humidity, and particle number concentrations performed from 10:00 to 11:30 UTC on 16/07/2015. Red lines identifies the limit between diferrent atospheric layers.

Figure 4. Top: Mean hourly (UTC) values for meteorological parameters and O_3 ambient air concentrations measured during 03-06, 14-20 and 10-17/7/2015 recorded at the permanent VIC XVPCA station (O_3) and at the Gurb meteorological station (temperature, humidity and wind patterns, Meteocat) located 1 km to the north of Bottom: Mean hourly concentrations of other gaseous and particulate pollutants measured at VIC with the laboratory van (only during 10-17/07/2015) co-located with the XVPCA station.

Figure 5. O_3 hourly concentrations recorded at the coastal (BEG, blue) and remote inland western pre-Pyrenean (MSC, clear green, 1570 m a.s.l.) sites, 2 urban background sites of Barcelona (PLR, CTL, grey and black), 2 urban sites in the northern periphery of the Barcelona's metropolitan area (GRA, MON, orange and yellow), the inner Vic Plain sites (TON, VIC and MAN, red, pink and violet) and the remote eastern pre-Pyrenean site of PAR (brown), along July 2015.

Figure 6. Polar plots of hourly O_3 concentrations in the real-time measurement sites.

Figure 7. O_3 and O_X (O_3+NO_2) hourly concentrations recorded at the coastal (BEG, blue, at this site only O_3 is available due to the lack of NO_2 measurements), an urban background site of Barcelona (CTL, black), an urban site in the northern periphery of the Barcelona's metropolitan area (GRA, orange), the intermediate inland rural site of MSY (720 m a.s.l., green), and the inner Vic Plain site (TON, red) along July 2015. The pink and blue squares mark the A and B O_3 and O_X episodes distinguished in this study, respectively.

Figure 8. Mean hourly levels of O_3 and O_X (O_3+NO_2) for sites in a south (coast) to north (inland) transect (CTL, GRA and BEG, and MSY, TON, VOIC, MAN and PAR, respectively) following the inland transport of pollutants from the coast, and maxima time shift according to the sea breeze transport (right) for the periods 3-6/07/2015 (B type episode, left) and 14-20/07/2015 (A type episode, right). Time is UTC.

Figure 9. Top: Hourly O_3 maxima (and number of hours exceeding 180 $\mu g/m^3$) in the study sites with real time O_3 measurements (shadowed areas indicate 2 different degrees of exceedances, 1-3

h and 13-23h). Bottom: Frequency of occurrence of hourly (UTC) O_3 exceedances of 180 µg/m^3 along the day; both for July 2015.

Figure 10. Vertical profiles of particle number concentrations for particles >3 nm (red, N_3), 0.3-0.5 µm (blue, $PM_{0.3-0.5}$), 0.5-1.0 µm (maroon, $PM_{0.5-1}$) and wind direction obtained with the tethered balloon measurements on 14 and 17/07/2015.

Figure 11. Vertical profiles of O_3, temperature and relative humidity obtained with the tethered balloon measurements on 14 and 17/07/2015.

Figure 12.Time variation of altitude, temperature, relative humidity, N_3, particle number size distributions and O_3 concentrations during the tethered balloon measurements on 16/07/2015. 1 to 3 illustrate the nucleation episode recorded at surface level with particle number size distributions, and 4 the typical regional background N size distribution at around 300 m over the ground.

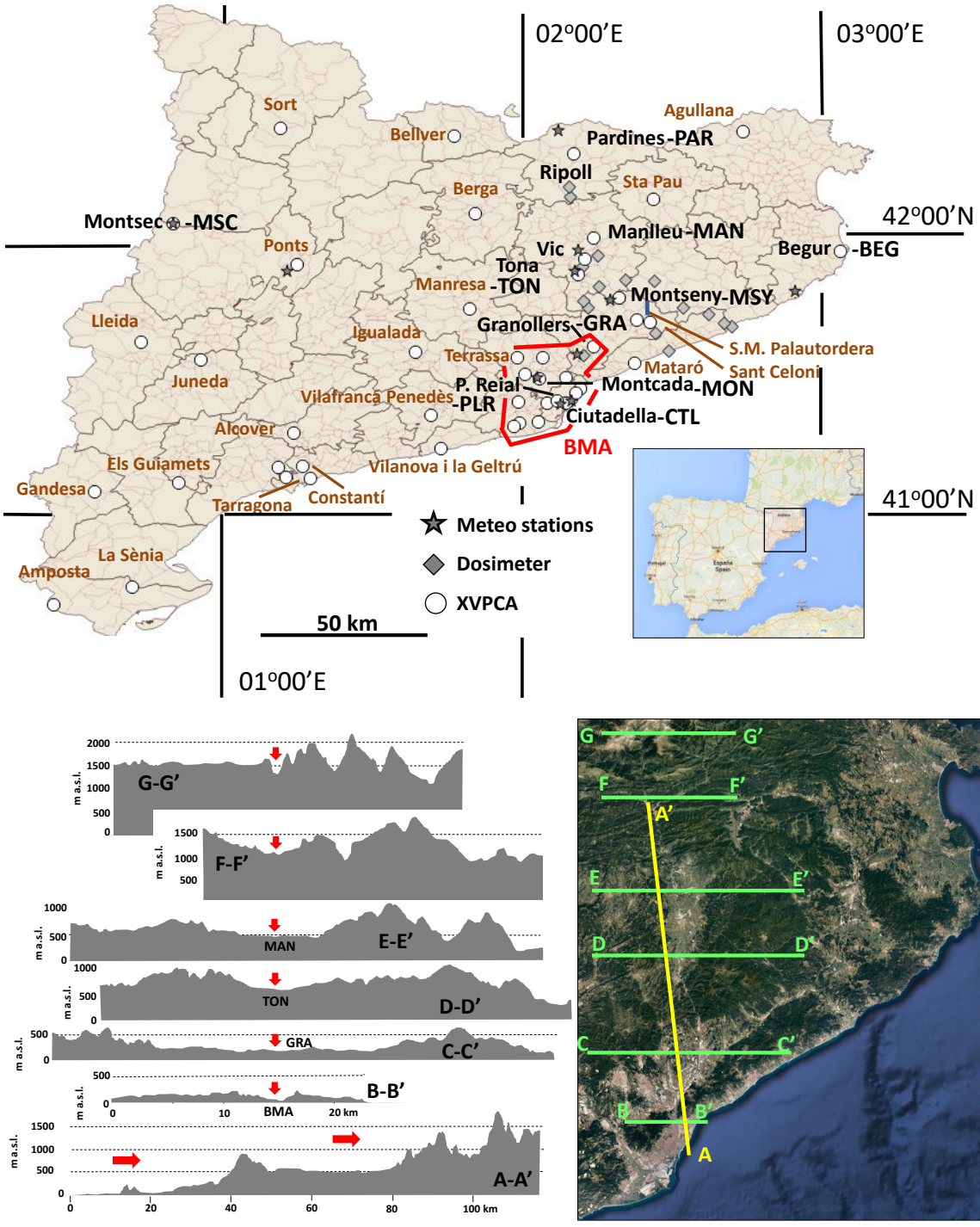
Figure 13. Vertical profiles of BC (5 min time resolution) and O_3 (10 seconds time resolution) at VIC.

Figure 14. Mean hourly O_3 concentrations, and wind speed and wind direction for the episodes A and B, showing higher levels in the A episodes for the two O_3 maxima.

Figure 15. Maps of simulated NO_2 and O_3 concentrations at ground level and 1000m a.g.l., and horizontal wind fields at 10 m a.g.l. for selected hours on 03/07/2015.

Figure 16. Maps of simulated NO_2 and O_3 concentrations at ground level and 1000m a.g.l., and horizontal wind fields at 10 m a.g.l. for selected hours on 15/07/2015.

Figure 17. Spatial distributions of simulated O_3 concentrations and wind field vectors in the south–north vertical cross-section for different hours on 03 and 15/07/2015.



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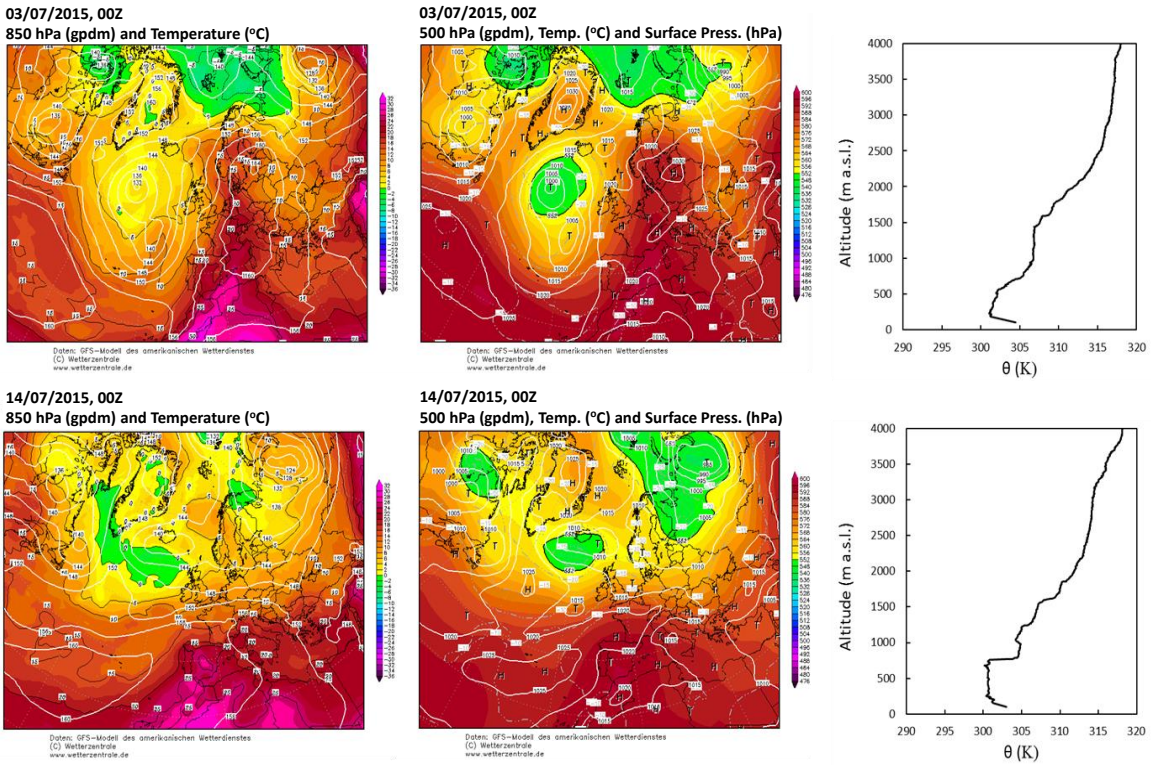

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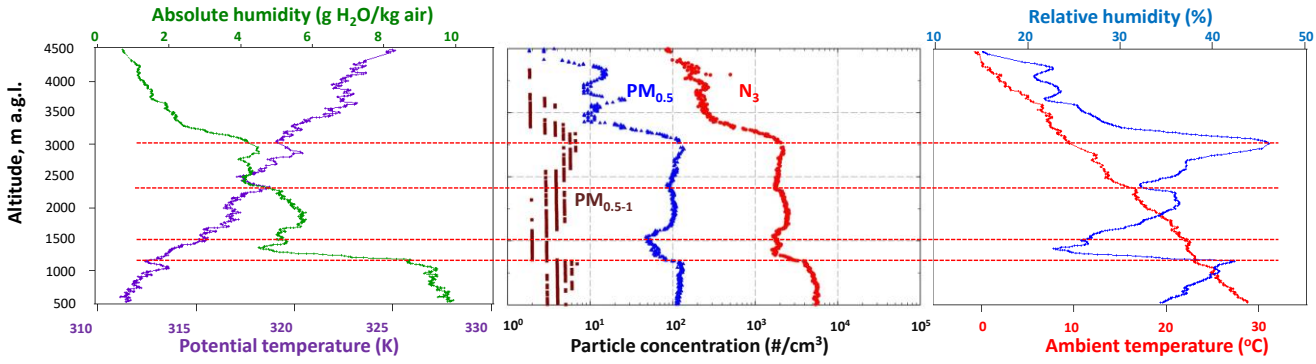

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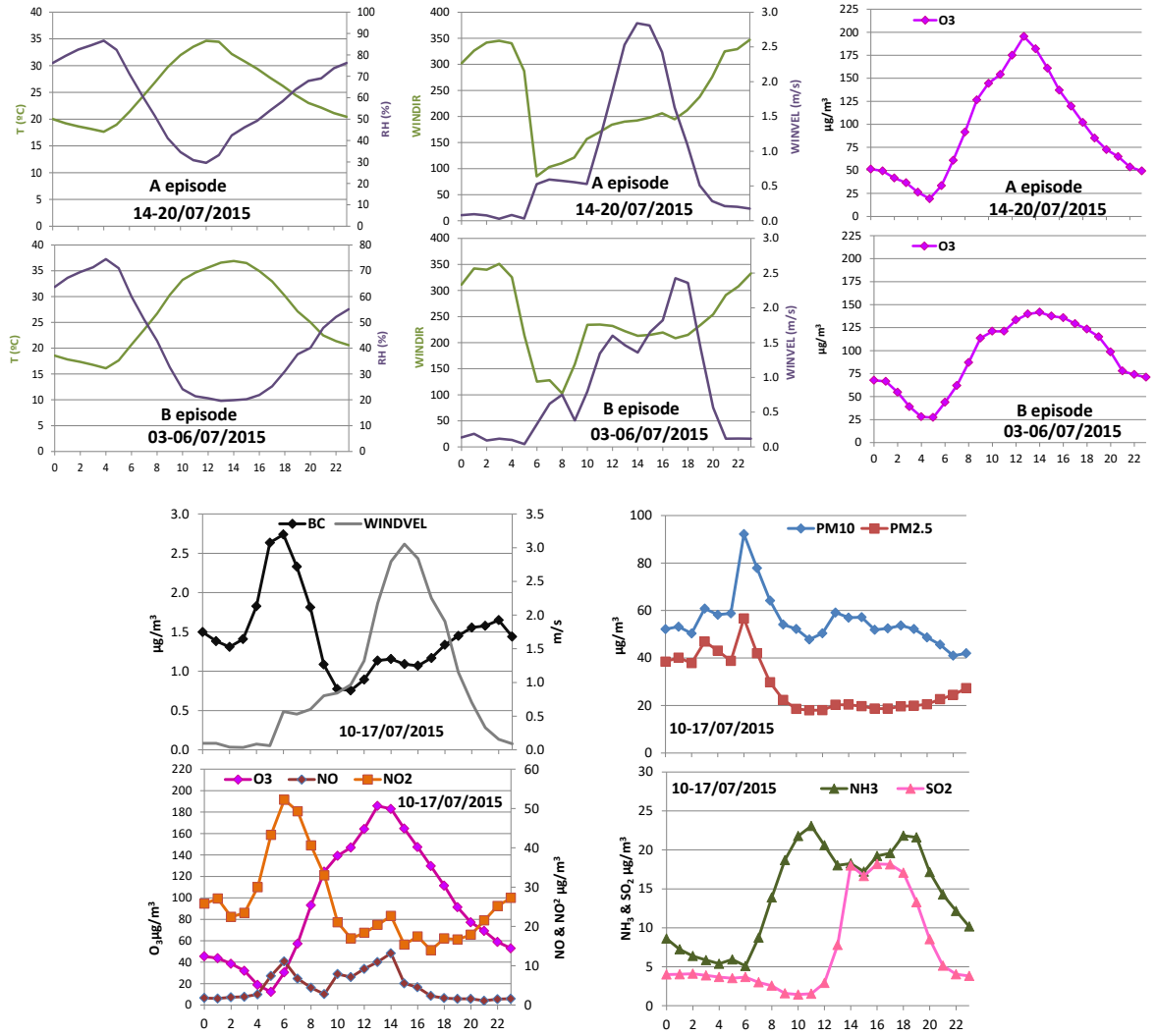

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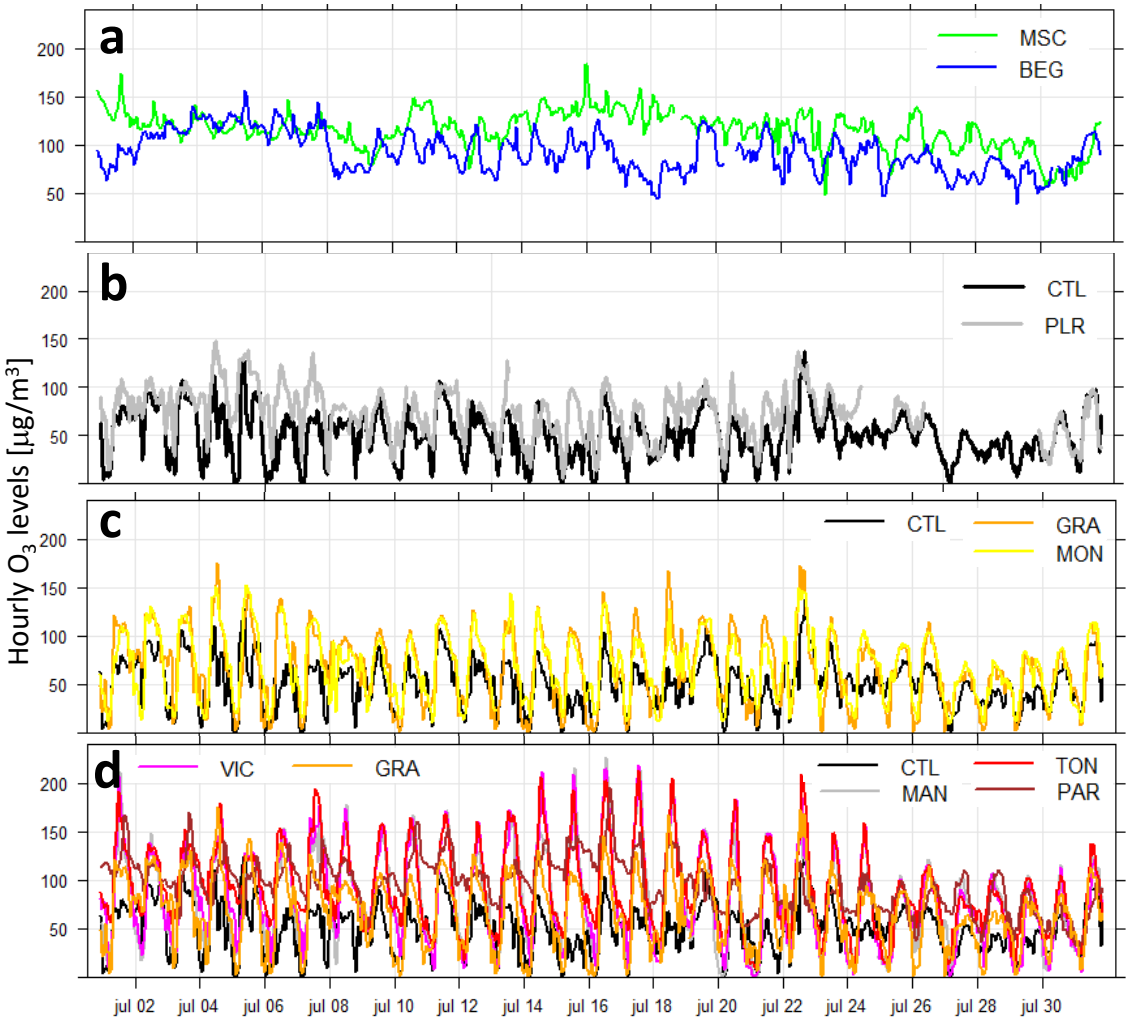

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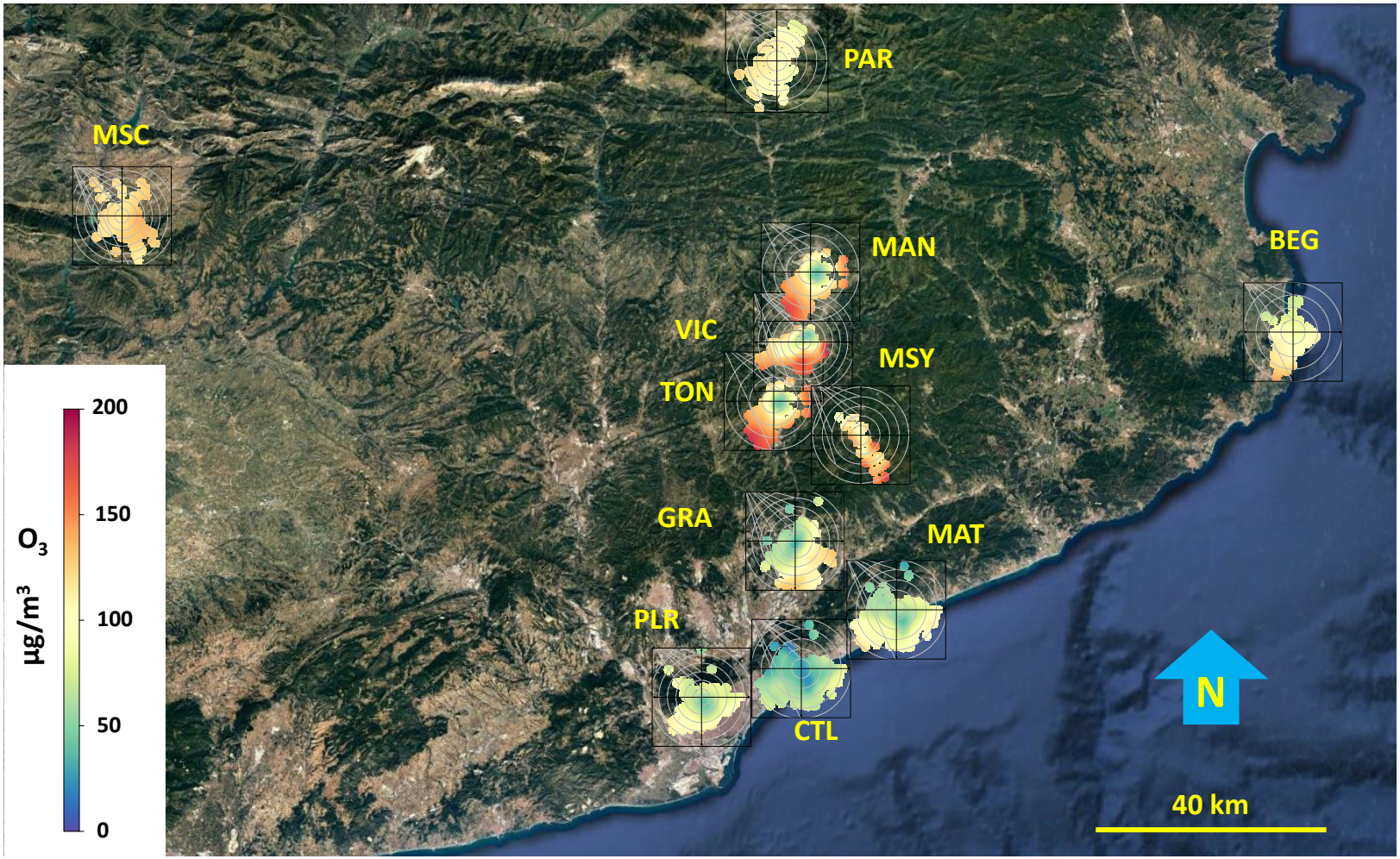
PAR
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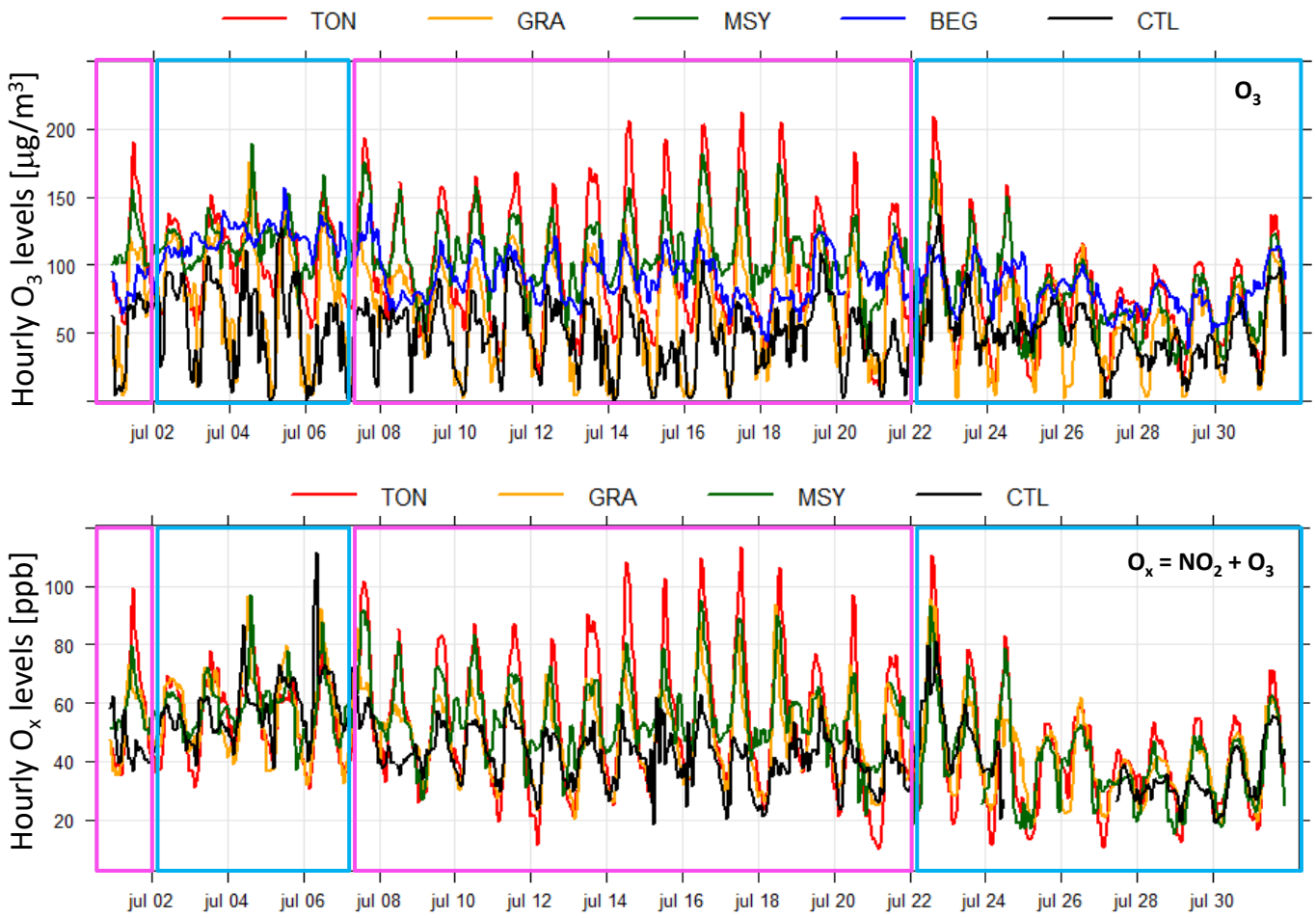
40 km
200
150
100
50
0
O3
µg/m3

Figure 6



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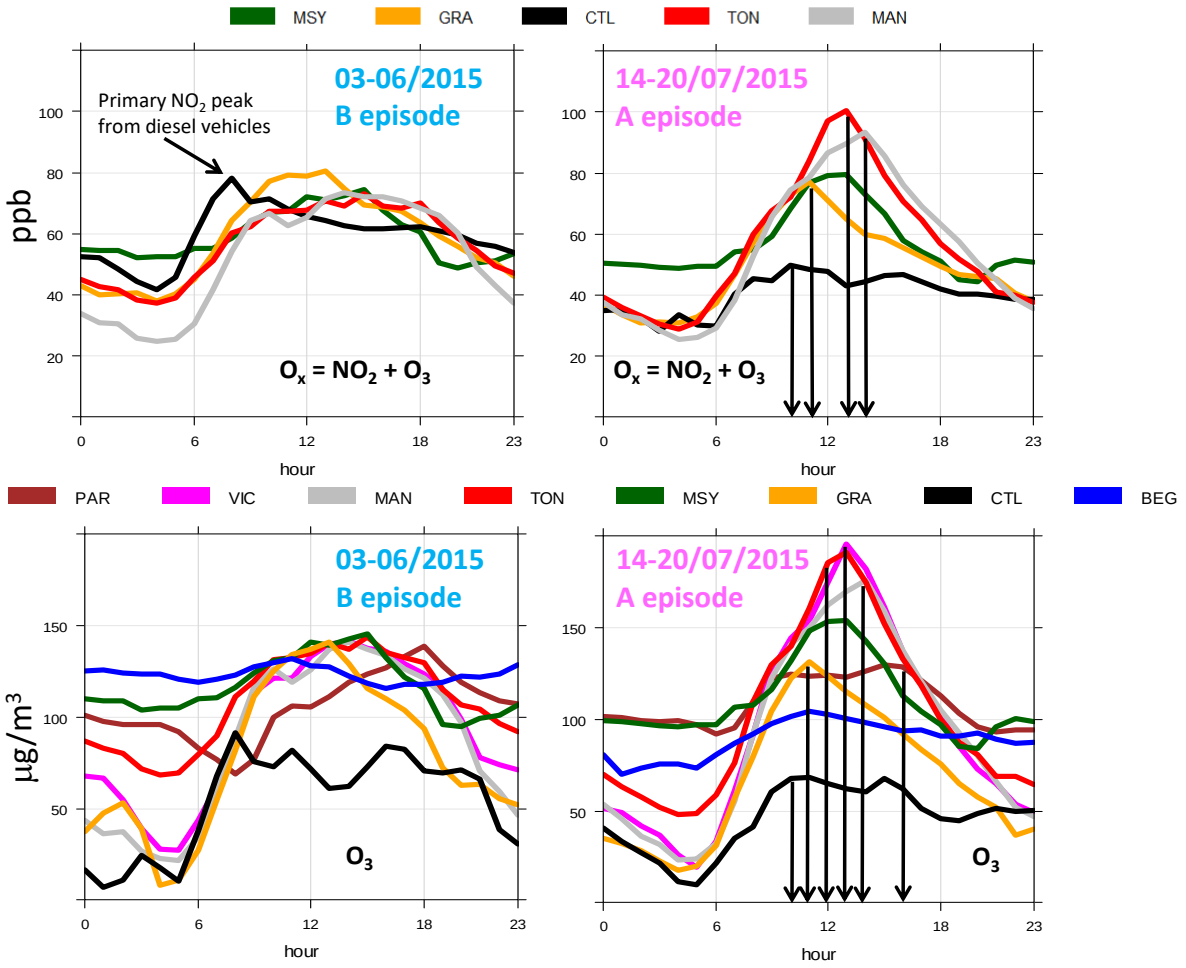

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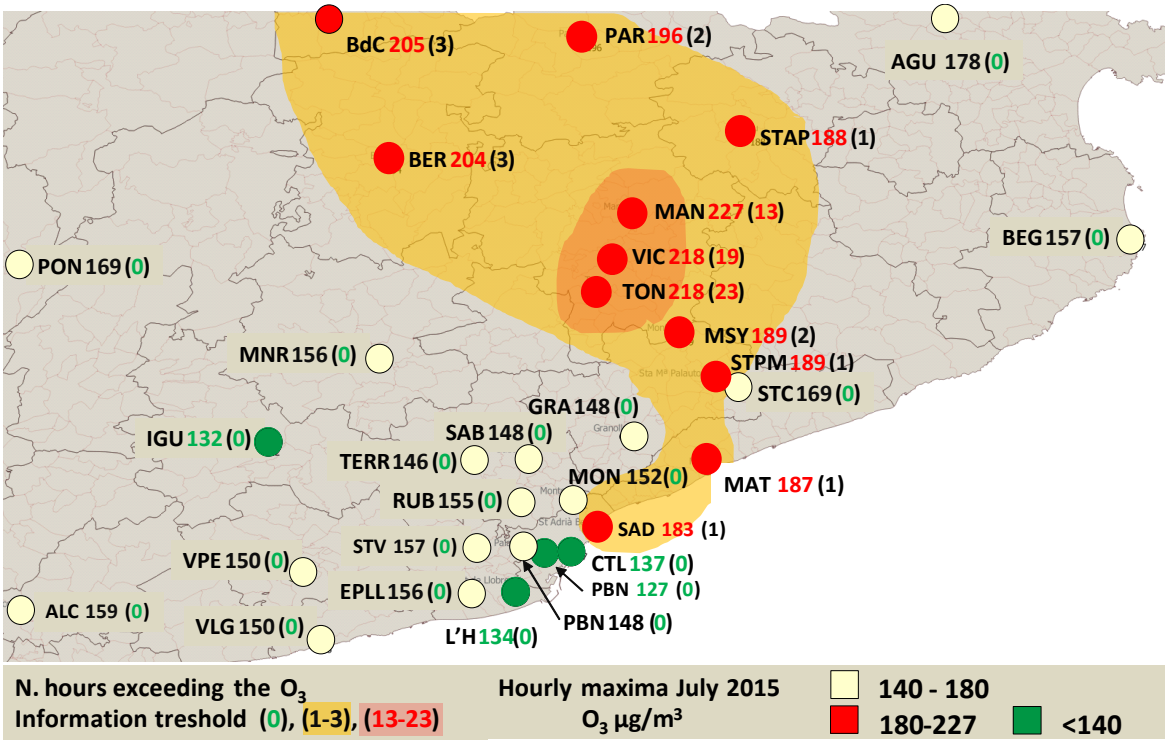

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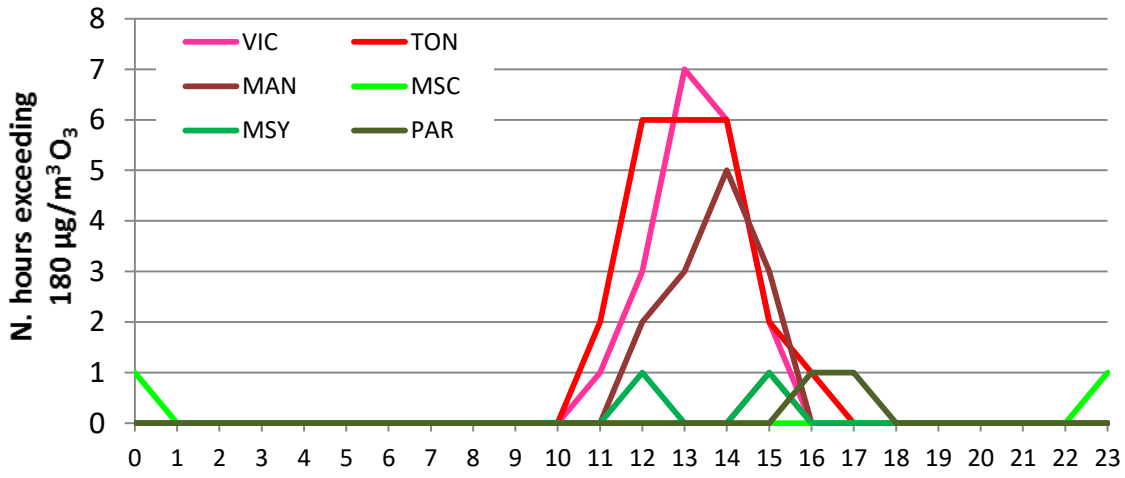

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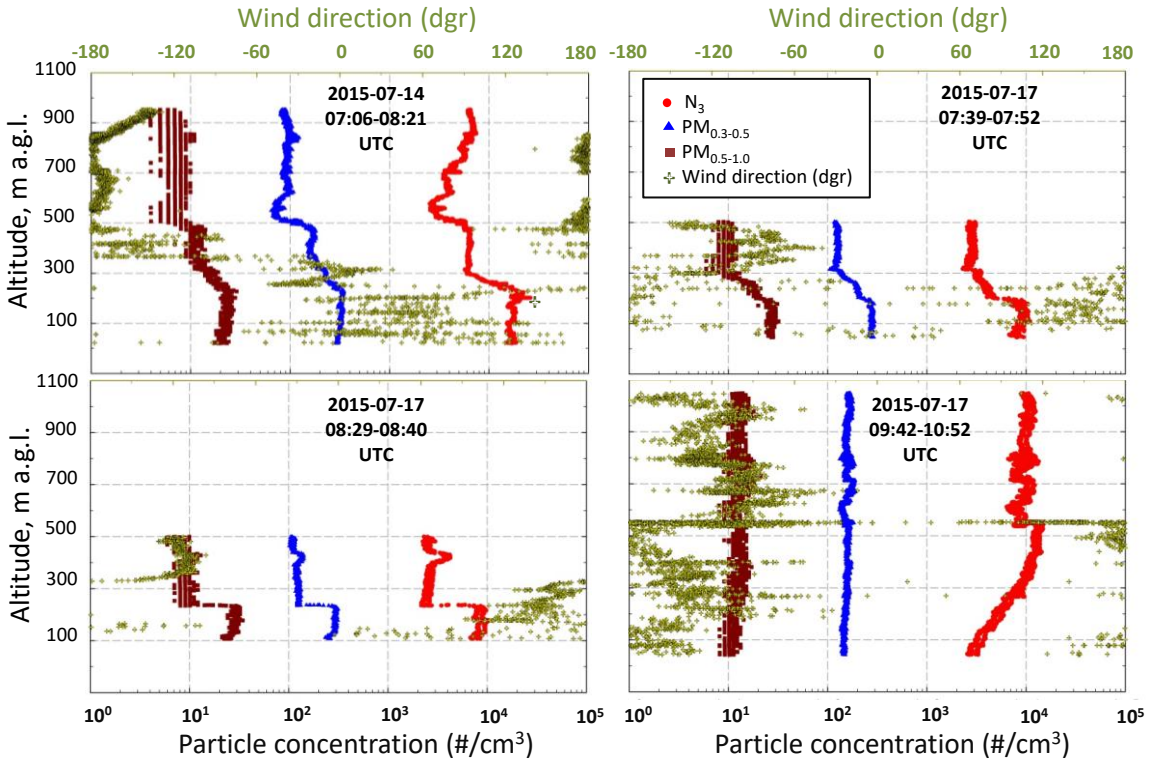

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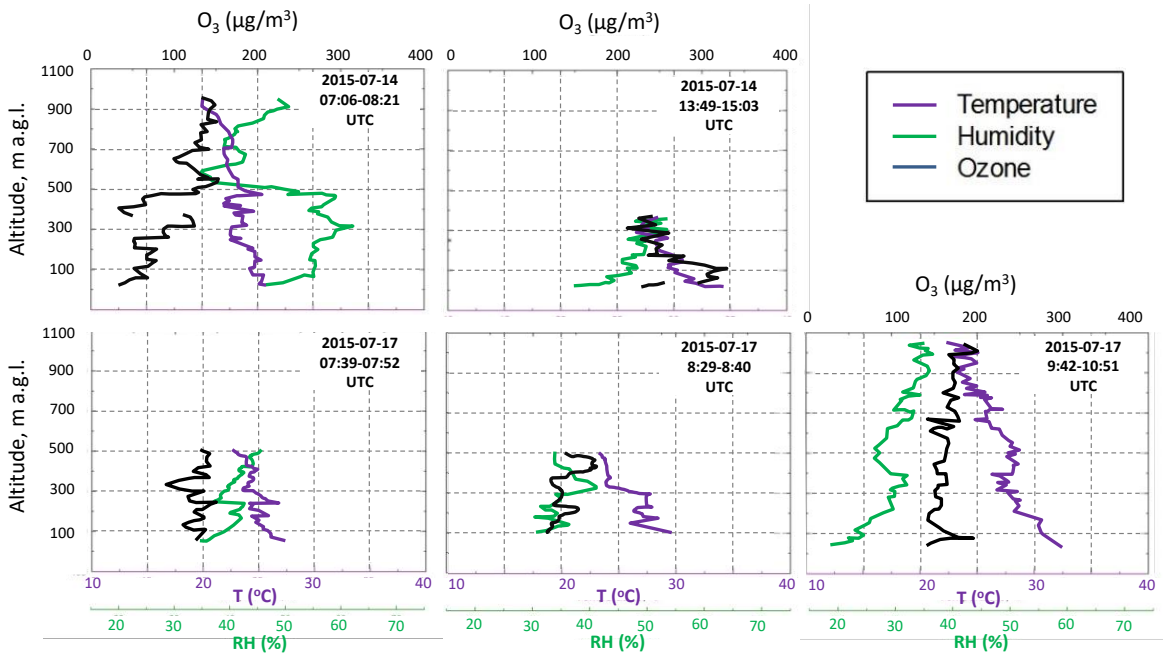

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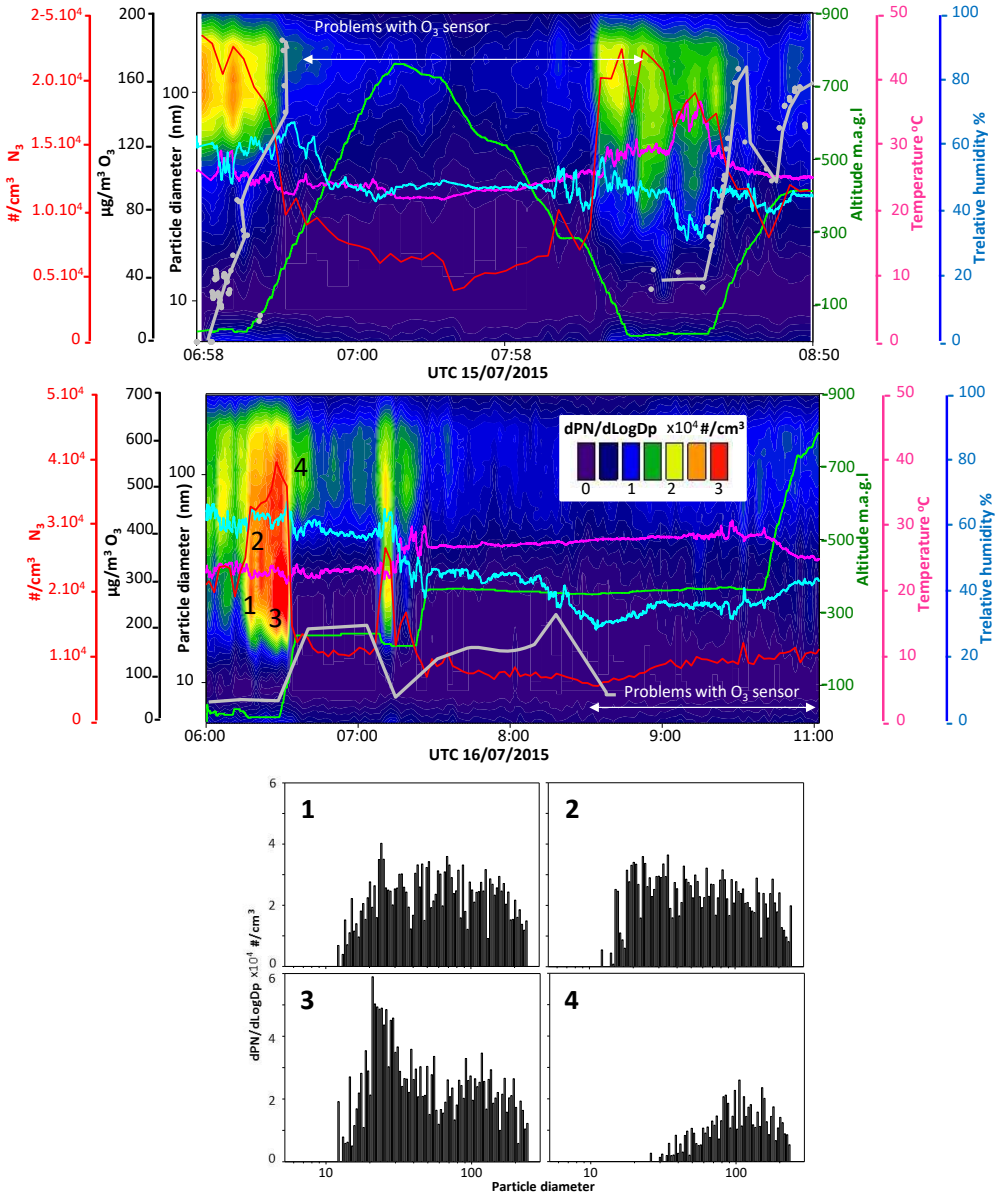
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µg/m³ O_3
Particle diameter (nm)
Altitude m.a.g.l
Temperature °C
Trelative humidity %
UTC 15/07/2015
dPN/dLogDp x10⁴ #/cm³
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Problems with O_3 sensor
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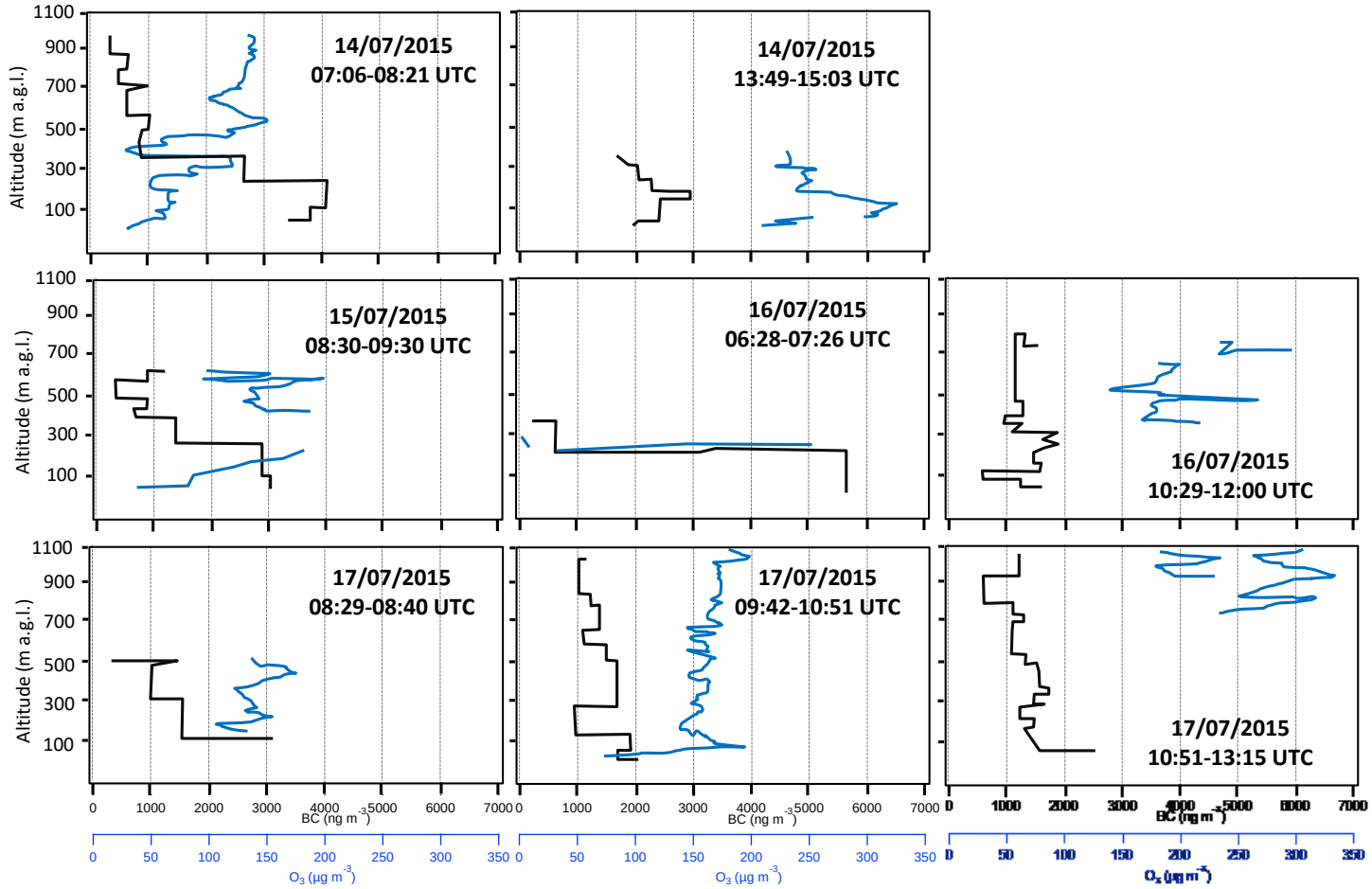
Particle diameter

Figure 12



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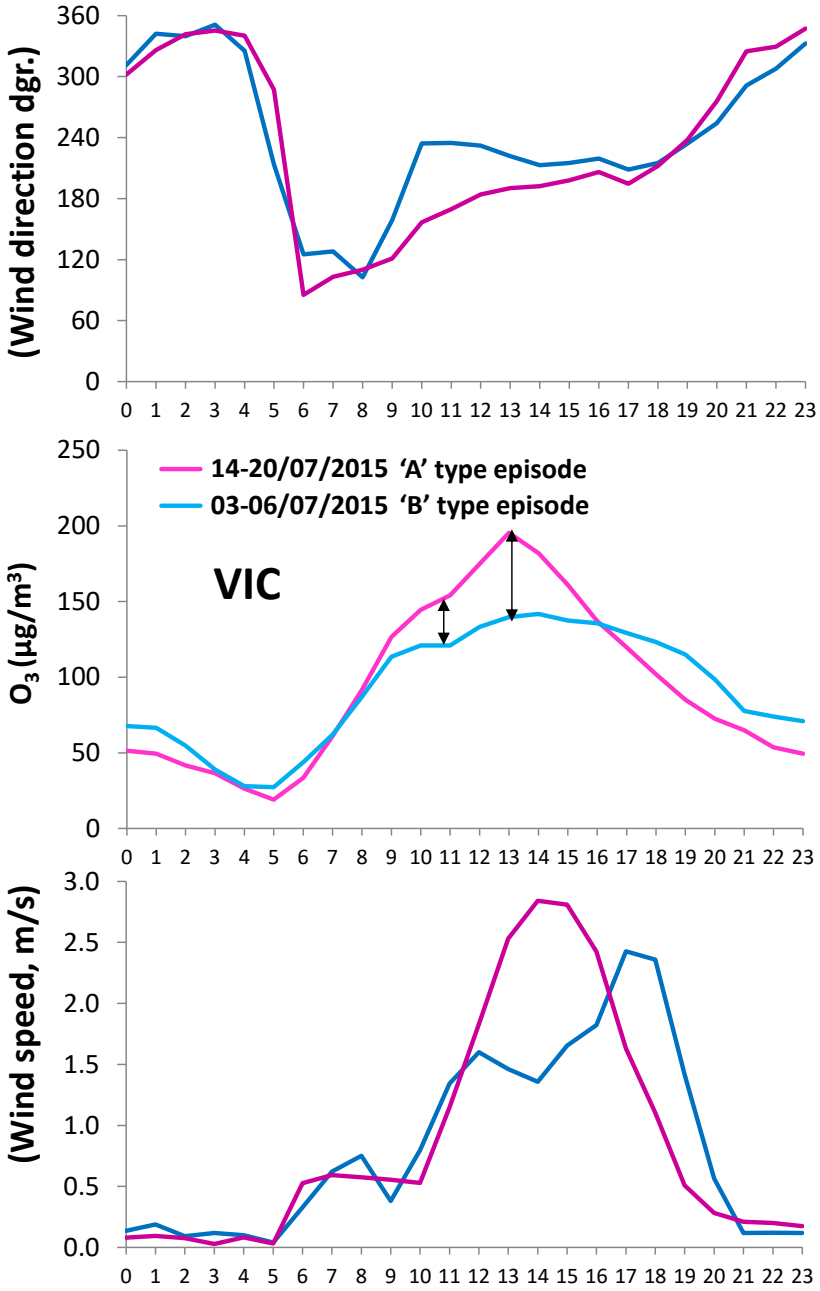

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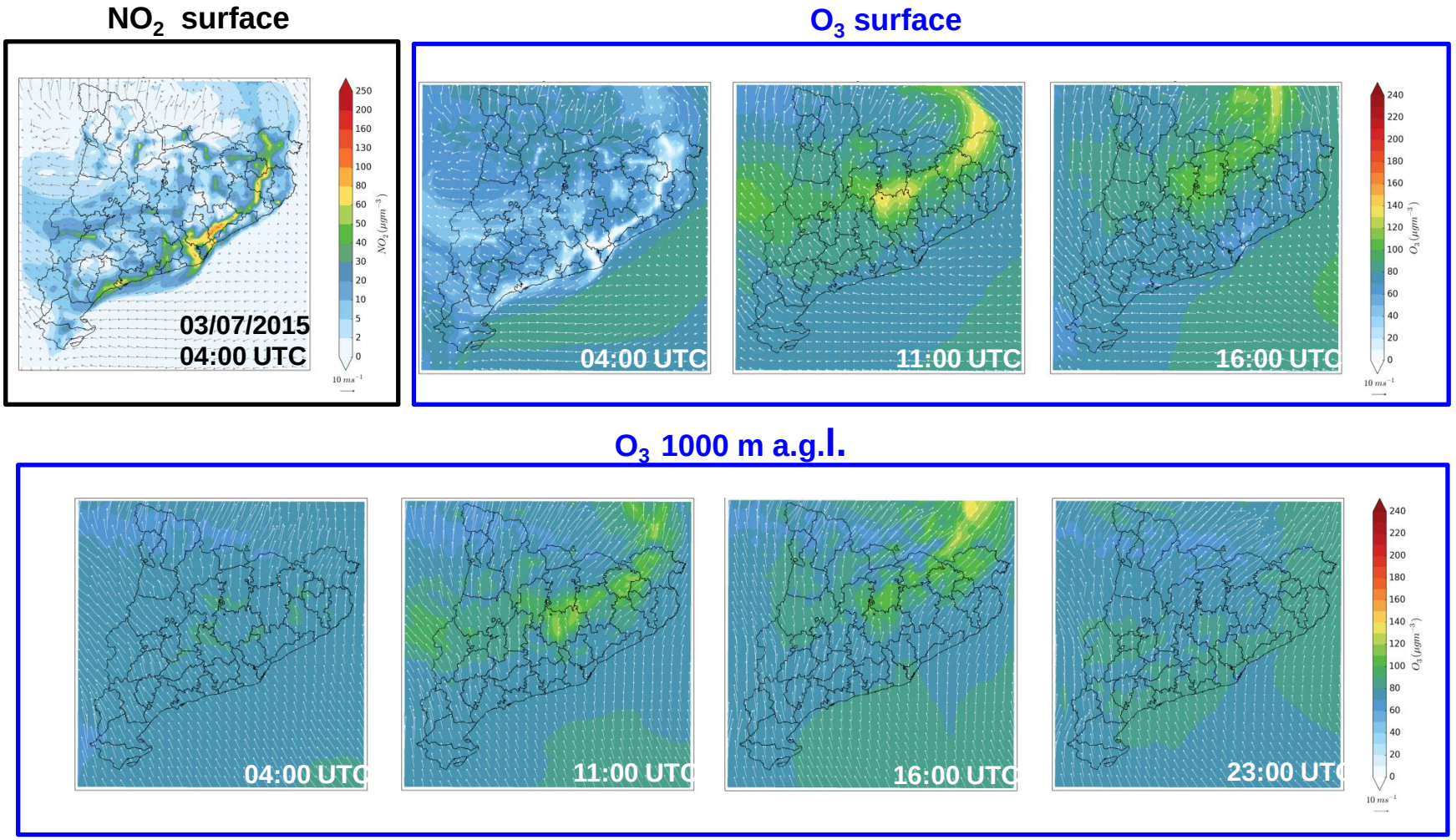
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Figure 15

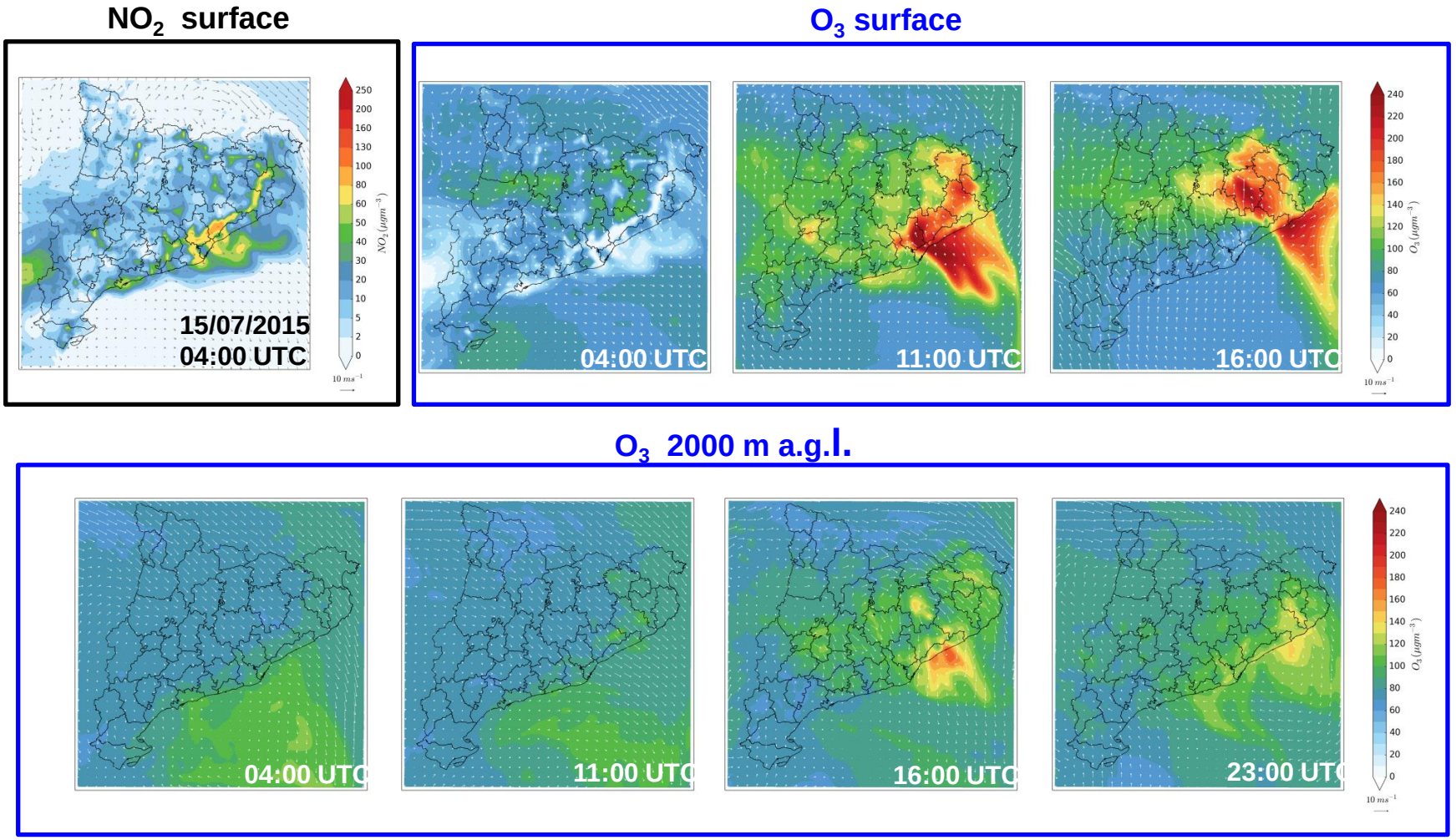
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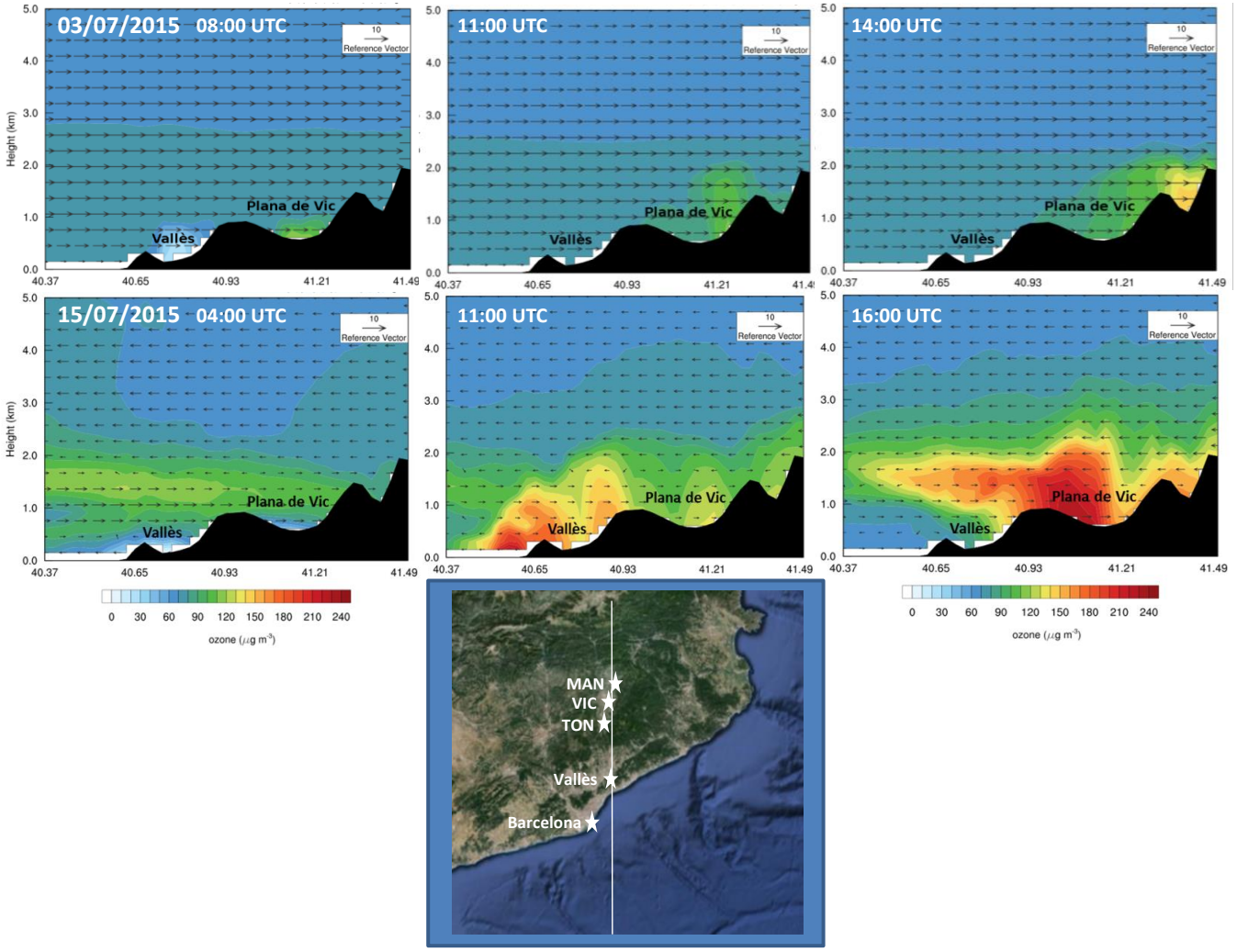
Figure 16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Reference Vector
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ozone (μg m-3)
MAN
VIC
TON
Vallès
Barcelona

Figure 17

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