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