

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 O₃ 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 O₃ 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 NO_x but also VOCs anthropogenic emissions occur in the BMA. Seco et al., 2011 showed also prevalence of BVOCs in the rural area where high O₃ 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 O₃ 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 O₃ and O_x concentrations range than the typical daily cycles evidenced in most of the other sites)." The second is in L469: "O₃ 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/m³ 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/m³ of O_x (mostly O₃) 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 $\mu\text{g}/\text{m}^3$ 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 $\mu\text{g}/\text{m}^3$) 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 $\mu\text{g}/\text{m}^3$. 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