

Final author replay to the editor

Dear editor, thank you for the opportunity to revise our submission and provide responses to the points raised by both anonymous reviewers. We acknowledge them for fruitful critics and for their suggestions that helped us to improve our work.

In the document attached we provide point-to-point responses to each of their questions and comments. The author comments are structured according to ACP guidelines and follow the recommended sequence: comments from the referees (RC1 and RC2) are shown in blue, then we provide our responses in black and the main changes made in the manuscript are included in red. We respond to both reviewers in the same document. Although we provide a common response to the points raised in some cases we duplicate the corresponding explanations to facilitate the work of both reviewers.

Since we made substantial changes throughout the document, we include the revised version of our submission in full (manuscript and supplementary material with changes highlighted in red) at the end of this document for the sake of clarity.

RC1

The manuscript “summertime tropospheric ozone source apportionment study in Madrid (Spain) by de la Paz et al. presents a ozone source apportionment study using ISAM in the CMAQ model over the Madrid region for July 2016.

While the topic of the paper is very interesting and fits into the scope of ACP, the manuscript lacks many important information and the results are discussed in an insufficient way. Therefore, I recommend to reject the manuscript. Please find below a more detailed review given some major and minor comments the authors should consider before the plan to resubmit the publication.

Thank you for the time devoted to our manuscript and for pointing out potential ways to improve our work and specific issues that need further discussion or clarification.

Reading the paper I had several major concerns which needs to be clarified.

1) The authors apply a new version of ISAM in CMAQ 5.3.2 which (to my knowledge) has not been used in similar publications before. According to the authors this new version attributes ozone to all involved precursors and NOT to the limiting precursor (e.g. NO_x or VOC). Sadly, the manuscript is lacking any details on the new method. I guess the method is somehow similar to the method presented by Grewe et al., 2017? The results presented in the manuscript heavily depend on this method. Therefore, the method either needs to be presented before in a scientific publication (e.g. an update of Kwok et al., 2015 and not a youtube video) which is cited by the authors or the manuscripts needs to include a detailed presentation/discussion of the revised method.

To our knowledge this is, in fact, one of the early applications of this version of CMAQ-ISAM and constitutes one of the novelties of the paper. However, there is a now publication, which became available during the review process of our work, that fully details the latest implementation of CMAQ-ISAM, provides a sample application, and compares results to other apportionment techniques. Additionally, the manuscript was modified to provide some brief explanation of CMAQ-ISAM, and more importantly to direct the reader to Shu et al., (2023) for a more detailed view of the model. This replaces the reference to the “youtube video”, which is a recording of an invited presentation at the CMAS Annual Conference (a highly regarded scientific event among CMAQ users worldwide) that accompanies the conference proceedings. So, Napelenok et al. (2020b) has been replaced by the reference to this paper published in Geoscientific Model Development. Consequently, Napelenok et al. (2020a) is referred as Napelenok et al. (2020) in our revised manuscript (line 136). Considering the comments from the reviewers, we included a brief discussion of source apportionment techniques and recent applications in the introductory section (lines 75-87) and focus on the description of CMAQ ISAM specifically in section 2.1 (lines 135 to 153 of the revised manuscript).

The paragraph included in section 1 reads:

“... relevant from air quality management perspective. Furthermore, information on the relative importance of emission sources on ambient levels should be considered when designing plans and measures, especially when they target highly non-linear secondary pollutants such as O₃ (Cohan and Napelenok, 2011).

There are different source apportionment techniques that may support air pollution research and decision making (Thunis et al., 2019). Approaches based on sensitivities, such as single-perturbation or brute force methods (Borge et al., 2014, Tagaris et al., 2014, Zhang et al., 2022, Qu et al., 2023) may be useful to anticipate the potential effect of a given intervention. However, tagging methods (Grewe et al., 2017, Butler et al., 2018) provide fully mass conservative apportionment at receptors of interest and may be better suited for diagnosis purposes (Borge, 2022). These pollution tracking capabilities have been integrated into modern air quality models to provide attribution information together with the standard concentration and deposition output fields, can be successfully applied to study pollution dynamics (Simon et al., 2018; Pay et al., 2019, Li et al., 2022). This approach may be particularly interesting to describe how O₃ levels are linked to emission sources under unfavorable meteorological conditions (Cao et al., 2022; Zohdirad et al., 2022) or specific local atmospheric circulation patterns (Zhang et al., 2023) that may lead to high concentration events (Lupaşcu et al., 2022)”

References added:

- Butler, T., Lupaşcu, A., Coates, J., and Zhu, S.: TOAST 1.0: Tropospheric Ozone Attribution of Sources with Tagging for CESM 1.2.2, *Geosci. Model Dev.*, 11, 2825–2840, <https://doi.org/10.5194/gmd-11-2825-2018>, 2018.
- Cao, J., Qiu, X., Liu, Y., Yan, X., Gao, J., and Peng, L.: Identifying the dominant driver of elevated surface ozone concentration in North China plain during summertime 2012–2017, *Environmental Pollution*, 300, 118912, <https://doi.org/10.1016/j.envpol.2022.118912>, 2022.

- Grewe, V., Tsati, E., Mertens, M., Frömming, C., and Jöckel, P.: Contribution of emissions to concentrations: the TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52), *Geosci. Model Dev.*, 10, 2615–2633, <https://doi.org/10.5194/gmd-10-2615-2017>, 2017.
- Lupaşcu, A., Otero, N., Minkos, A., and Butler, T.: Attribution of surface ozone to NO_x and volatile organic compound sources during two different high ozone events, *Atmos. Chem. Phys.*, 22, 11675–11699, <https://doi.org/10.5194/acp-22-11675-2022>, 2022.
- Qu, K., Wang, X., Cai, X., Yan, Y., Jin, X., Vrekoussis, M., Kanakidou, M., Brasseur, G. P., Shen, J., Xiao, T., Zeng, L., and Zhang, Y.: Rethinking the role of transport and photochemistry in regional ozone pollution: insights from ozone concentration and mass budgets, *Atmos. Chem. Phys.*, 23, 7653–7671, <https://doi.org/10.5194/acp-23-7653-2023>, 2023.
- Tagaris, E., Sotiropoulou, R.E.P., Gounaris, N., Andronopoulos, S., and Vlachogiannis, D.: Impact of biogenic emissions on ozone and fine particles over Europe: Comparing effects of temperature increase and a potential anthropogenic NO_x emissions abatement strategy, *Atmospheric Environment*, 98, 214-223, <https://doi.org/10.1016/j.atmosenv.2014.08.056>, 2014.
- Zhang, S., Zhang, Z., Li, Y., Du, X., Qu, L., Tang, W., Xu, J., and Meng, F.: Formation processes and source contributions of ground-level ozone in urban and suburban Beijing using the WRF-CMAQ modelling system, *Journal of Environmental Sciences*, 127, 753-766, <https://doi.org/10.1016/j.jes.2022.06.016>, 2023.
- Zhang, Y., Yu, S., Chen, X., Li, Z., Li, M., Song, Z., Liu, W., Li, P., Zhang, X., Lichtfouse, E., and Rosenfeld, D.: Local production, downward and regional transport aggravated surface ozone pollution during the historical orange-alert large-scale ozone episode in eastern China, *Environ Chem Lett*, 20, 1577–1588, <https://doi.org/10.1007/s10311-022-01421-0>, 2022.
- Zohdirad, H., Jiang, J., Aksoyoglu, S., Namin, M. M., Ashrafi, K., and Prévôt, A. S. H.: Investigating sources of surface ozone in central Europe during the hot summer in 2018: High temperatures, but not so high ozone, *Atmospheric Environment*, 279, 119099, <https://doi.org/10.1016/j.atmosenv.2022.119099>, 2022.

And the changes made in section 2.1 regarding model description are as follows:

~~Source attribution provides information on the relative importance of emissions sources on ambient concentration levels which can be particularly useful for highly non-linear secondary pollutants such as O₃ (Cohan and Napelenok, 2011). In this study, the Integrated Source Apportionment Method (ISAM) (Kwok et al., 2015; Kwok et al., 2013) implemented in CMAQv5.3.2 (Napelenok, 2020) is used. This mass transfer method tracks the contribution of all the precursors and proportionally attributes the products to the corresponding sources (Shu et al., 2023). While this approach is based on the same conceptual basis, it substantially differs from the implementation of previous versions (including CMAQv5.0.2) that attribute the formation of a secondary pollutant to the sector contributing the limiting reactant. While other source apportionment approaches (Thunis et al., 2019) based on sensitivities may be better suited to investigate the potential of abatement measures (Borge et al., 2014), tagging methods such as ISAM~~

~~can serve better for diagnosis purposes (Borge et al., 2022) and thus, can be successfully applied to study pollution dynamics (Simon et al., 2018; Li et al., 2022; Pay et al., 2019).~~

In this study, the Integrated Source Apportionment Method (ISAM) (Kwok et al., 2013, ~~Kwok et al., 2015~~) implemented in CMAQv5.3.2 (~~Napelenok, 2020b~~, Napelenok, 2020; Shu et al., 2023) is used. ISAM provides apportionment capability of the full concentration and deposition output arrays including the gaseous photochemically active species such as O₃ as well as inorganic and organic particulate matter. The CMAQ-ISAM implementation used in this study attributes source identity to secondary pollutants based strictly on reaction stoichiometry with all reactions playing a role that are relevant to the formation and destruction of any species in the chemical mechanism. ISAM is highly customizable for any number of user-specified combinations of emissions source sector and geographical source areas. For O₃, this implementation differs from the previous ISAM versions (including CMAQv5.0.2) that attribute the formation of secondary pollutants to source sectors based on chemical regime – NO_x- or VOC-limited O₃ formation (Kwok et al., 2015) and from other studies where precursor attribution is directed by the user to either NO_x or VOC emissions, such as Butler et al. (2020). Regime-based methods are useful to attribute secondary species that depend on multiple precursors. However, the regime determination relies on predefined thresholds of different metrics, often the H₂O₂/HNO₃ ratio (Sillman, 1995) that dynamically depend on location and time specific parameters (Li et al., 2022). By strictly following stoichiometry of all chemical reactions in the mechanism, this version of ISAM avoids the necessity to make decisions and assumption regarding ozone formation regimes. Decisions on tagging method selections are highly dependent on the specific application and the scientific and/or regulatory aims of each individual study. As the needs of the scientific and regulatory communities evolve, so do the apportionment methodologies. Since the conclusion of this study, CMAQ-ISAM has been expanded to include the regime-based, the stoichiometry-based, as well as other configuration options. More information on ISAM as well sample application and comparison results can be found in Shu et al. (2023).

References added/removed:

- ~~• Napelenok, S., Bill Hutzell, C. Hogrefe, B. Murphy, J. Bash, K. Baker, K. Foley, Q. Shu, AND R. Mathur. CMAQ 5.3.2: Updates to Integrated Source Apportionment Method (ISAM). CMAS Annual Conference 2020, Chapel Hill, NC, October 19–21, <https://youtu.be/959IveSeEf4>, 2020b~~
- Shu, Q., Napelenok, S. L., Hutzell, W. T., Baker, K. R., Henderson, B. H., Murphy, B. N., and Hogrefe, C.: Comparison of ozone formation attribution techniques in the northeastern United States, *Geosci. Model Dev.*, 16, 2303–2322, <https://doi.org/10.5194/gmd-16-2303-2023>, 2023.
- Sillman, S.: The use of NO_y, H₂O₂, and HNO₃ as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, *Journal of Geophysical Research*, 100, 14175-14188, <https://doi.org/10.1029/94JD02953>, 1995.

2) Given the new method, I am missing a detailed discussion of the method and the results in comparison to previous publications (see for example Butler et al., 2018 for a detailed discussion of

many ozone tagging methods). Moreover, I am missing a critical discussion of the model results. As example, Fig.4 shows a contributions of more than 14 % of SNAP6 (solvents) to ozone over the mountain range north of Madrid. Given my understanding of the method and results of similar methods I wonder about this high contribution. How can this be explained? Moreover, I wonder about the small contribution of biogenic emissions, even though they account for a large fraction of the VOC emissions. If the method attributed ozone to all precursors, they should account for a larger fraction (?) Please clarify.

As pointed out in the previous response, we further discuss the CMAQ-ISAM version used in our study and include a reference for a more detailed view of the model (Shu et al., 2023). To provide a better context of this study, we included a more elaborated discussion of source apportionment techniques and recent applications in the introduction.

As for the critical discussion of our results, we have revised our paper to provide a better insight and explain our results. To clarify the two specific points raised by Reviewer #1 in this comment, we elaborate and discuss our results in section 3.2 (3.1 in the original submission) about the contribution of the main VOC sources, both anthropogenic and biogenic. Regarding the first, we would like to clarify that Figure 4 (Figure 5 in the revised manuscript) shows that emissions from the SNAP 6 sector (solvents) may contribute more than 14% to O₃ P90 (close to 20% in some points), but this refers to the anthropogenic contribution, so it is in the range of 2% of total O₃ P90 levels. From the scientific literature and the speciation profiles used for VOC emissions in this sector, we propose that this contribution relates to the high reactivity of individual species within these emissions such as aromatics, that have a large ozone formation potential (OFP). In our discussion we cite other studies that point in that direction too. As for the spatial distribution of this contribution, it reaches the maximum impact (in absolute values) 20-30 km away from Madrid City center in the southwest direction (see Figure AC1, included in the supplementary material as Figure S2 in our revised submission). Of note, that does not correspond exactly with the mountain range north of Madrid, but the southside mountain foothills (Figure 1). However, the maximum relative contribution is found in the northwest direction (Figure 5 in the revised manuscript) because the total contribution of anthropogenic emissions -dominated by NO_x- is smaller in that area. This is related to the slowest chemistry of VOCs in comparison with that of NO_x and similar results have been found for other urban environments such as New York City.

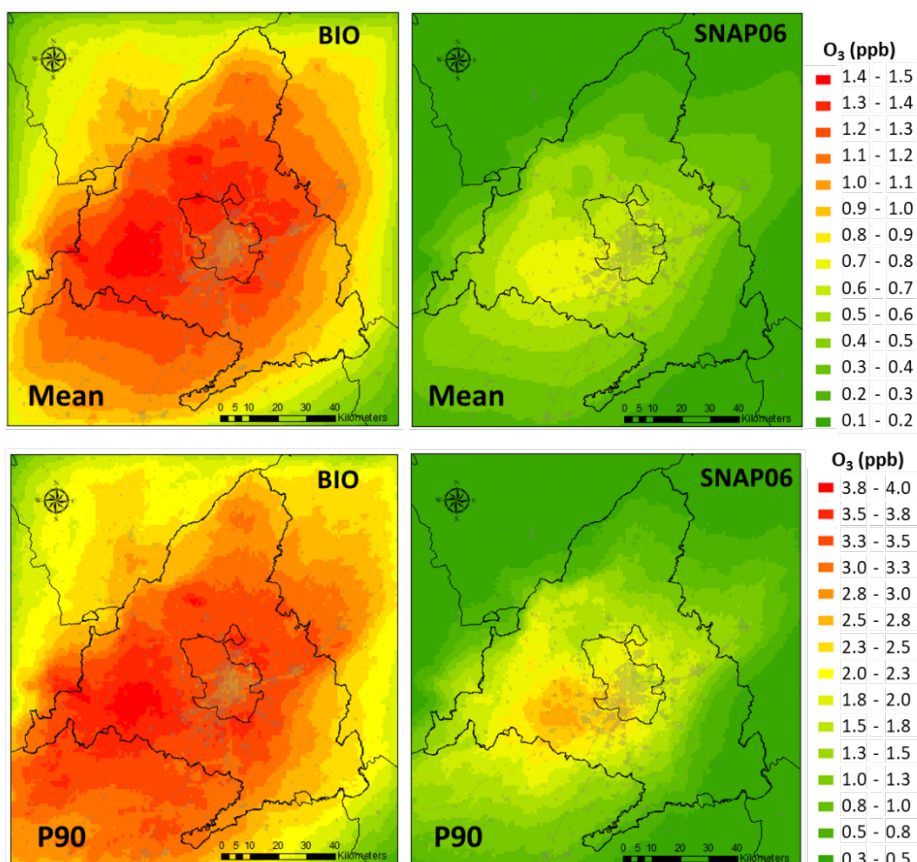


Figure AC1. Absolute contribution (ppb) to the monthly mean 1-hour 90th O₃ percentile of the SNAP 06 sector (use of solvents and other products) and biogenic emissions.

This is discussed in the passage between lines 325 and 340 within section 3.2 of our revised manuscript:

“... of the Adolfo Suárez Madrid-Barajas airport. This suggests that NO_x emissions play a more important role than VOC emissions in the photochemical production of ozone, in concurrence with previous source apportionment studies (Dunker et al., 2016; Butler et al., 2018; de la Paz et al., 2020). Nonetheless, the importance of controlling anthropogenic VOC emissions to prevent high O₃ episodes has been noted in previous studies (Cao et al., 2022), even in regions with strong biogenic emissions (Coggon et al., 2021). In addition to the contribution of BVOC previously discussed, anthropogenic VOC had also an influence on O₃ levels during July 2016 in the Madrid region. While the spatially-averaged attribution of O₃ to SNAP 06 is only 1.5 ppb with maximum contributions of 3 ppb at specific locations (southwest of Madrid as shown in Figure S2 and Figure S5), emissions from the use of solvents and other products can reach values up to 20% of total anthropogenic contributions to O₃ P90 (Figure 4c). This is comparable to the contribution of all industrial sources combined (SNAP01-03-04). This may be related to the high OFP of aromatics within SNAP 06 VOC (Meng et al., 2022) and is consistent with the findings of Oliveira et al., (2024) that attributed 64% or total OFP to the solvent sector (relative to that of total anthropogenic VOC) in densely urbanized areas such as Madrid. Coggon et al., (2021) also found that consumer and industrial products

(included in SNAP 06 group) are important precursors of ozone in urban areas, were typically present a VOC-sensitive regime. Nonetheless, they found that O₃ formation may take a few hours and the maximum contributions of VOC emitted in New York City to occur a few tens of km away, close to NO_x-limited areas. Our high-resolution analysis indicates that a similar process may take place in Madrid too. The rest of the sectors analyzed (SNAP05 and SNAP09) have negligible contributions (around 0.05 ppb as an average over the Madrid region).”

We also reflect on our results regarding the contribution of biogenic emissions and discuss them in the context of previous studies. We reformulated the narrative not to underestimate the influence of biogenic VOCs (BVOC) and compare our results with the findings of previous studies in the literature. We make clear that the direct comparison is not possible since the interpretation depends on the specific source apportionment methodology used and the specific model domain and scale of application. As shown in Figure AC1 (=Figure S2), the maximum contribution to O₃ of biogenic emissions occurs in the central area of the Madrid region, even though vegetation emissions in that more densely populated area are smaller. That is consistent with previous studies that reported stronger contributions of BVOC to O₃ levels in VOC-limited areas. On the contrary, the production of O₃ away from anthropogenic high-intensity areas is limited due to the unavailability of NO_x.

As for the relative importance in comparative terms with other sources, we found that global and continental studies usually attribute a more important role to BVOC in the explanation of O₃ budgets. Nonetheless, our results seem consistent for other studies in the Iberian Peninsula or the Madrid region specifically. Nonetheless, we highlight the need to use caution comparing results from different studies, so the reader is not misled by methodological differences. We connect this discussion with the reactivity of specific VOCs for a more consistent view of the role of VOCs, focusing on isoprene -see response to first general from Reviewer #2, when we compare CMAQ predictions with observed values for this specie (see Figure AC2, included in the supplementary material of our revised submission as Figure S3)- as one of the key BVOC in the atmospheric photochemistry. We believe this discussion helps to clarify why the contribution of BVOC is smaller than that of all anthropogenic sources combined but larger than that of the SNAP 06 alone.

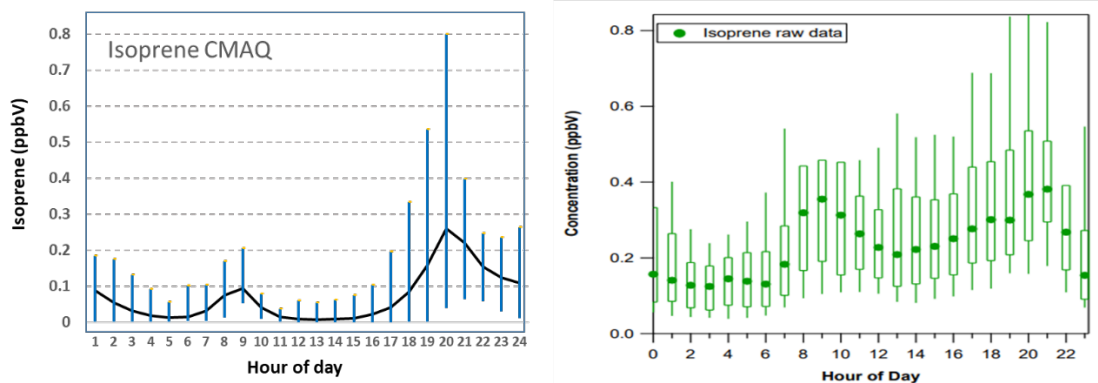


Figure AC2. Comparison of isoprene ground-level mixing ratios predicted by CMAQ (left) and measurements made in Majadahonda (suburban site) by Querol et al., (2018) (right). Both graphs present the hourly values during the day averaged over the period July 5th and July 19th. The source of the right-hand panel is Pérez et al., (2016).

Reference (added to the supplementary material):

- Pérez, N., A. Alastuey, C. Reche, M. Ealo, G. Titos, A. Ripoll, M.C. Minguillón, F. J. Gómez-Moreno, E. Alonso-Blanco, E. Coz, E. Díaz, B. Artíñano, S. García dos Santos, R. Fernández-Patier, A. Saiz-López, F. Serranía, M. Anguas-Ballesteros, B. TemimeRoussel, N. Marchand, D. C. S. Beddows, R. M. Harrison y X. Querol. Campaña intensiva de medidas de UFP, O₃ y sus precursores en el área de Madrid: medidas en superficie., https://www.miteco.gob.es/content/dam/miteco/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/anexo_informea33_madrid_tcm30-561368.pdf (last access: [January 22, 2004]), 2016.

The discussion about biogenics is included at the beginning of the revised section 3.2 and it reads as it follows:

“Figure 4 shows the contribution to ground-level O₃ concentration of the BC and that of all local anthropogenic emissions combined for both, monthly average and high values (illustrated by the 90th percentile, hereinafter P90). O₃ apportionment to biogenic emissions is not considered in Figure 4 because i) they have less interest from the point of view of possible abatement measures (Oliveira et al., 2023) and ii) their contribution is relatively small (below 4% to total O₃ levels in this period). However, it is not a negligible apportionment since biogenic emissions account for 27% (monthly mean) and 22% (P90) of total O₃ averaged over the Madrid region when BC and IC are not considered (Figure S1). In other words, their contribution represents around 21% and 28% of that of local anthropogenic emissions. This is a similar relative importance to that reported by Sartelet et al. (2012) at European scale. As well as Collet et al., (2018), they argue that the influence of BVOC becomes stronger on VOC-limited areas which is consistent with our findings (Figure S2), since the Madrid region is predominantly NO_x-limited in summer, except for the metropolitan area of Madrid city and surroundings, that remains VOC-limited all year round (Jung et al., 2022, Jung et al., 2023). Pay et al. (2019) did not quantify explicitly the contribution of biogenic emissions to ozone in the Iberian Peninsula. However, the contribution of “other”, that included emissions from SNAP 11

along with other sectors was around 5% in the center of the Iberian Peninsula, even though biogenic emissions represent a large fraction of total VOCs.

The contribution of BVOC to ozone levels in Europe reported by Tagaris et al. (2014), Karamchandani et al. (2017) or Zohdirad et al. (2022) are slightly larger (below 6%) and are even more according to some source apportionment at global scale for this latitude (Grewe et al. 2017; Butler et al., 2020). It should be noted that different experimental design and apportionment algorithms would lead to significant differences (Zhang et al., 2017; Borge et al., 2022) preventing the direct comparison of the results from different studies. Nonetheless, the contribution of biogenic emissions found in our work is not remarkably different than those previously reported, especially for this same geographical area.

Previous studies suggested that relatively low contributions of biogenic VOCs to O₃ levels may relate to underestimations of isoprene levels (Lupaşcu et al., 2022), a very relevant specie for O₃ chemistry (Dunker et al., 2016) that constitutes more than 25% of global biogenic VOC emissions Guenther et al. (2012). Nonetheless, it is widely recognized that BVOC emission estimates involve large uncertainties (Poupkou et al., 2010; Wang et al., 2017; Zhang et al., 2017) and the MEGAN model used in this study has been found to overestimate isoprene emissions (Wang et al. 2017 and references within). According to our inventory, isoprene represents 48% of total BVOC. While isoprene ambient measurements are not made routinely, Querol et al., (2018) recorded an average level of isoprene around 0.2 ppb in Majadahonda, a suburban site ~15 km away from downtown Madrid (in the west, northwest direction) between July 5th and July 19th, 2016. That is in relatively good agreement with the results of CMAQ in our simulation, that predicted slightly less than 0.1 ppb for that location and period and reproduced quite accurately the average daily pattern (see Figure S3).

Arguably, the relatively low contribution of BVOC in our and previous studies in this area (Valverde et al., 2016; Pay et al., 2019) may be a consequence of the underestimation of isoprene mixing ratios. However, that is compatible with the stronger influence of other anthropogenic VOC species reported elsewhere. Querol et al., (2018) estimated the total ozone formation potential (OFP) applying the maximum incremental reactivity (MIR) proposed by Carter (2009) to the VOC measurements made in their campaign for the same period and location than our study. Based on this methodology, they identified formaldehyde as the single most important compound (35.5% of total OFP) while isoprene was ranked 7th with an OFP below 5%. By family, primary BVOCs represented 6% of total OFP as an average during the experimental campaigns in this period. Similar studies elsewhere (e.g. Meng et al., 2022 in the Pearl River Delta region) conclude as well that the ozone formation potential of BVOCs is lower than that of anthropogenic VOCs applying a similar reactivity scale (Carter and Atkinson, 1989). That may be consistent with the apparent insensitivity of O₃ to isoprene emissions reported in other studies (Simpson, 1995; Jing et al., 2019; Ciccioli et al., 2023).“

References added:

- Butler, T., Lupascu, A., and Nalam, A.: Attribution of ground-level ozone to anthropogenic and natural sources of nitrogen oxides and reactive carbon in a global chemical transport

model, *Atmos. Chem. Phys.*, 20, 10707–10731, <https://doi.org/10.5194/acp-20-10707-2020>, 2020

- Carter, W. P. L., and Atkinson, R.: Computer modeling study of incremental hydrocarbon reactivity, *Environmental Science & Technology*, 23(7), 864-880, <https://doi.org/10.1021/es00065a017>, 1989.
- Carter, William PL.: Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications. California Air Resources Board Contract, vol. 339, <https://ww2.arb.ca.gov/sites/default/files/barcu/regact/2009/mir2009/mir10.pdf>, 2009
- Ciccio, P., Silibello, C., Finardi, S., Pepe, N., Ciccio, P., Rapparini, F., Neri, L., Fares, S., Brilli, F., Mircea, M., Magliulo, E., and Baraldi, R.: The potential impact of biogenic volatile organic compounds (BVOCs) from terrestrial vegetation on a Mediterranean area using two different emission models, *Agricultural and Forest Meteorology*, 328, 109255, <https://doi.org/10.1016/j.agrformet.2022.109255>, 2023.
- Dunker, A. M., Koo, B., and Yarwood, G.: Ozone sensitivity to isoprene chemistry and emissions and anthropogenic emissions in central California, *Atmospheric Environment*, 145, 326-337, <https://doi.org/10.1016/j.atmosenv.2016.09.048>, 2016.
- Jiang, J., Aksoyoglu, S., Ciarelli, G., Oikonomakis, E., El-Haddad, I., Canonaco, F., O'Dowd, C., Ovadnevaite, J., Minguillón, M. C., Baltensperger, U., and Prévôt, A. S. H.: Effects of two different biogenic emission models on modelled ozone and aerosol concentrations in Europe, *Atmos. Chem. Phys.*, 19, 3747–3768, <https://doi.org/10.5194/acp-19-3747-2019>, 2019
- Jung, D., de la Paz, D., Notario, A., and Borge, R.: Analysis of emissions-driven changes in the oxidation capacity of the atmosphere in Europe, *Science of The Total Environment*, 827, 154126, <https://doi.org/10.1016/j.scitotenv.2022.154126>, 2022.
- Jung, D., Soler, R., de la Paz, D., Notario, A., Muñoz, A., Ródenas, M., Vera, T., Borrás, E., and Borge, R.: Oxidation capacity changes in the atmosphere of large urban areas in Europe: Modelling and experimental campaigns in atmospheric simulation chambers, *Chemosphere*, 341, 139919, <https://doi.org/10.1016/j.chemosphere.2023.139919>, 2023.
- Karamchandani, P., Long, Y., Pirovano, G., Balzarini, A., and Yarwood, G.: Source-sector contributions to European ozone and fine PM in 2010 using AQMEII modeling data, *Atmos. Chem. Phys.*, 17, 5643–5664, <https://doi.org/10.5194/acp-17-5643-2017>, 2017.
- Meng, Y., Song, J., Zeng, L., Zhang, Y., Zhao, Y., Liu, X., Guo, H., Zhong, L., Ou, Y., Zhou, Y., Zhang, T., Yue, D., and Lai, S.: Ambient volatile organic compounds at a receptor site in the Pearl River Delta region: Variations, source apportionment and effects on ozone formation, *Journal of Environmental Sciences*, 111, 104-117, <https://doi.org/10.1016/j.jes.2021.02.024>, 2022.
- Poupkou, A., Giannaros, T., Markakis, K., Kioutsioukis, I., Curci, G., Melas, D., and Zerefos, C.: A model for European Biogenic Volatile Organic Compound emissions: Software development and first validation, *Environmental Modelling & Software*, 25(12), 1845-1856, <https://doi.org/10.1016/j.envsoft.2010.05.004>, 2010.
- Sartelet, K. N., Couvidat, F., Seigneur, C., and Roustan, Y.: Impact of biogenic emissions on air quality over Europe and North America, *Atmospheric Environment*, 53, 131-141, <https://doi.org/10.1016/j.atmosenv.2011.10.046>, 2012.

- Simpson, D.: Biogenic emissions in Europe: 2. Implications for ozone control strategies, *Journal of Geophysical Research*, 100 (D11), 22891-22906, <https://doi.org/10.1029/95JD01878>, 1995.
- Valverde, V., Pay, M. T., and Baldasano, J. M.: Ozone attributed to Madrid and Barcelona on-road transport emissions: Characterization of plume dynamics over the Iberian Peninsula, *Science of the total environment*, 543, 670-682, <https://doi.org/10.1016/j.scitotenv.2015.11.070>, 2016.
- Wang, P., Schade, G., Estes, M., and Ying, Q.: Improved MEGAN predictions of biogenic isoprene in the contiguous United States, *Atmospheric Environment*, 148, 337-351, <https://doi.org/10.1016/j.atmosenv.2016.11.006>, 2017.
- Zhang, R., Cohan, A., Biazar, A. P., and Cohan, D. S.: Source apportionment of biogenic contributions to ozone formation over the United States, *Atmospheric Environment*, 164, 8-19, <https://doi.org/10.1016/j.atmosenv.2017.05.044>, 2017.

In addition, the manuscript is lacking an overview of the definition of the different source attribution sectors (e.g. as table etc). From Fig 11 it seems that 12 different source sectors are considered.

Tagged sectors, i.e. emission sources O₃ is attributed to, are presented in Figure 2. The discussion in lines 158-166 included in the original manuscript has been slightly revised to clarify the sectors tagged as well as other O₃ sources (not related to emitting activities) discussed in Figure 11 (Figure 12 in the revised manuscript). That passage now it reads:

“The share of NO_x and VOCs emissions of each SNAP (Selected Nomenclature for Air Pollution) groups is summarized in Figure 2. Emissions from power generation and industrial activities (SNAP 01, SNAP 03 and SNAP 04) were merged due to their limited presence in this modeling domain (and noted as S13 in Figure 12). Since emissions from agriculture (SNAP 10) in the region are only significant for VOCs from plants, they have been tagged along biogenic VOC (BVOC) emissions from vegetation (SNAP 11) (and labeled as BIO in Figure 12). Consequently, 8 emission sources were tagged for the source apportionment analysis of ambient O₃ in the region, as reflected in Figure 2. They account for the totality of emissions in the modeling domain although the main precursors originate from road traffic (SNAP 07) and solvent use (SNAP 06), with a total share of 65% NO_x and 49% VOCs, respectively. While emissions from the residential, commercial and institutional sector (SNAP 02) account for nearly 19% of annual NO_x emissions, they are produced almost exclusively in winter and are therefore, negligible in summer.

In addition to the attribution of O₃ ambient levels to the emissions within the modeling domain, hereinafter referred to as local sources, the contribution of boundary conditions (BC) and initial conditions (IC) are also estimated in this study (labeled as BCO and ICO in Figure 12). Considering the typical O₃ daily patterns and the variability of circulation patterns, the latter refer to the initial mixing ratios on a daily (24 hour) basis, i.e., each day is run separately using the outputs from the previous day as IC.”

Besides making an explicit reference to Figure 12 (Figure 11 in the original submission) for the sake of clarity, we added the following paragraph when Figure 12 is introduced (Lines 423-427 or the revised manuscript):

“The results are summarized in Figure 12. As previously discussed, it shows the contribution of all anthropogenic emission sources (S13 to S08), biogenic emissions (BIO) as well as boundary and initial conditions (BCO, ICO) and O₃ stratospheric transport (PVO3). Although 100% of emitting sectors have been tagged, Figure 12 shows as well the contribution from “others” (OTH). This relates to second-order interactions between sources (U.S. EPA, 2022). This represents a negligible fraction in this study, i.e. ISAM could attribute the virtual totality of O₃ to any of the other sources.”

Reference added:

- U.S. EPA: Community Multiscale Air Quality (CMAQ) model v5.4 User Guide, Office of Research and Development, U.S. EPA, https://github.com/USEPA/CMAQ/tree/5.4/DOCS/Users_Guide (last access: [January 22, 2004]), 2022.

3) I am missing any new results. The large importance of boundary conditions to ozone levels over the Iberian Peninsula have been reported by e.g. Pay et al., 2019. Also the larger importance of regional emissions to high ozone values have been presented in previous publications (maybe not focusing on Madrid). I like the detailed investigation of source attribution results for specific weather patterns, however, for a scientific publication in ACP more detailed analyses are needed in my opinion and the author need to highlight new findings in more detail.

We believe that this paper contributes to improve current knowledge about the attribution of air pollution to emission sources in general and adds considerable value to understand ozone pollution dynamics in the Madrid region in particular. We have revised our manuscript to highlight the main novelties of our work. They are as follows:

- Pay et al. (2019) presented a countrywide source apportionment analysis for a typical high-O₃ summer period. While they used the same chemical-transport model (CMAQ), there are relevant differences (see summary in Table AC1) that allow us to further delve into the specific O₃ dynamics for the Madrid region. Both studies agree on the dominant role of BC and consistently identify road traffic as the main local contributor to the production of O₃, especially regarding peak levels. However, we provide an estimate of the contributions of other sources not explicitly considered in previous studies, including solvent use, BVOC emissions or stratospheric transport. More importantly, our approach allows us to identify different apportionment structure depending on local circulation conditions and demonstrates the influence of O₃ generated in the previous 24 hours under stable atmospheric conditions (accumulation pattern). In addition, we report significant differences across our modelling domain depending on these meteorological patterns as well. Our study is by no means redundant of previous ones. On the contrary, it makes perfect sense considering the recommendation of Pay et al., (2019) or Escudero et al., (2019) regarding the need for detailed quantification of contributions to high O₃ concentrations considering the influence of local sources and topographical and meteorological conditions to effectively inform local strategies as well as exploring the apportionment for different phenomenology of high-O₃ episodes. In addition, we think our

methodology may be illustrative for other regions worldwide to perform local source apportionment studies that may support subsequent O₃ plans.

- This is one of the first applications of this CMAQ-ISAM implementation (Shu et al., 2023) and may support future source apportionment studies elsewhere using this tool
- Our study quantifies for the first time the implications of local circulation patterns identified in previous studies (Querol et al., 2018, Escudero et al., 2019) for O₃ source apportionment, providing useful information for the future development of plans and strategies, specially for short-term action plans
- For instance, we provide a first estimate of the theoretical maximum reduction of maximum O₃ ambient levels (approximately 25 ppb for 1-hour maximum) under unfavorable conditions, a result of large significance for the design of local strategies to reduce O₃ levels
- Considering these new findings, we propose some options for future research that may further improve our understanding of complex O₃ dynamics and effectively inform new policies

Table AC1. Comparison of the methodology of this study with that of Pay et al. (2019)

Feature	Pay et al. (2019)	Our study
Domain and resolution	Spain, 4 km x 4 km	Madrid region, 1 km x 1 km
Temporal domain	10 days (21 - 31 July 2012)	1 month (July 2016), 24-hours runs to identify the role of IC Specific analyses for relevant weather patterns
SA method	CMAQ-ISAM based on sensitivity regime (Kwok et al., 2015) - option 5 in current release of CMAQ (v 5.4)-	CMAQ-ISAM based on equal assignment for all reactants (Shu et al., 2023) -option 1 in current release of CMAQ (v 5.4)-
Tagged sectors	5 (power generation, industry, road transport, off-road mobile sources, others) + IC + BC	8 (power generation and industry, non-industrial combustion plants - residential, commercial and institutional emissions-, road transport, off-road mobile sources, waste treatment, agriculture and nature emissions) + IC + BC + stratospheric transport
Model performance assessment	Aggregated	Aggregated and individual (42 monitoring stations)
Analysis at specific monitoring-sites/locations	2	18

We have revised our paper to provide a more comprehensive analysis of the results (see changes made related to previous questions) and tried to highlight the contribution of our work. This is specifically reflected in the revised version of the conclusions, copied below:

“A high-resolution chemical-transport model has been used to investigate O₃ dynamics for a typical summer month (July 2016) in the Madrid Region. The model presents an acceptable performance and succeeds in reproducing the phenomena described in previous studies (Querol et al., 2018, Escudero et al., 2019), confirming that O₃ dynamics are conditioned by regional circulation patterns. Nonetheless, we found that model errors are larger for accumulation days and concentration peaks are underestimated. This may be related to an inadequate performance of the meteorological model under stagnation conditions. A novel implementation of CMAQ-ISAM (Shu et al., 2023) that attributes O₃ based reaction stoichiometry with all production and destruction reactions involved has been applied to perform a source apportionment of this non-linear, secondary pollutant under specific weather patterns. Our simulation shows that O₃ levels are dominated by non-local contributions (i.e., boundary conditions), representing around 70% of mean values across the region. Ozone reservoirs from previous days (label as initial conditions in our methodology) in the mid troposphere are also important to build up high O₃ levels in accumulation episodes, representing the main difference with advective periods. The analysis, however, points out that precursors emitted by local sources play a more important role regarding the highest mixing ratios values, illustrated in this study by the 90th percentile. This suggests that the implementation of emission reduction strategies in the region may be more effective to control O₃ concentration peaks than average values. This is particularly true under unfavorable, stagnation conditions associated with accumulation patterns when the highest O₃ values occur. According to our results, up to 35% of total O₃ may be originated from local sources, giving a theoretical maximum reduction potential of 1-h values of approximately 25 ppb under these conditions. Among local sources, road traffic is the main contributor, accounting for 55% of local sources. Our results suggest that NO_x emissions play a more important role than VOC emissions in the photochemical production of ozone. Nonetheless, we found that the use of solvents and other products, a significant source of VOCs emissions with high ozone formation potential, can explain up to 20% of the O₃ originated from local anthropogenic emissions in some locations. At the same time, our results suggest that the contribution of biogenic emissions is lower than that of anthropogenic sources (below 4% to total O₃ levels in this period), although they are responsible for 42.4% of total VOCs in the modeling domain. Emissions from other sectors play a minor role and O₃ transported from the Stratosphere within the model domain is negligible.

We also found significant variations in source apportionment patterns across station types and relative locations. This implies that high-resolution simulations under specific meteorological conditions should be performed to anticipate the potential outcome on O₃ levels in different locations of the Madrid region.

Considering these results, future modeling efforts should be oriented to simulate the effect of specific measures both, local and in cooperation with other administrations, to identify optimal emission abatement strategies. The modeling platform used in this study may be also helpful to assess sensitivities to different factors, including photochemical regimes or NO_x and VOCs speciation for specific sources. “

4) The authors mix the physical quantities “concentration” and “mixing ratio”. They use the term concentration and use the unit ppb which suggest a (volume) mixing ratio. Please clarify the used physical quantity. Similarly, Fig. 2 does not give any physical quantities for the emissions. In addition,

please clarify what emissions of NO_x and VOC are. Are they given in amount of N, NO, NO₂ and C or NMHC?

It is usual in the scientific literature and even in the air quality regulation to use the term “concentration” to refer to near-ground relative abundance of a given pollutant both, when volume/volume (ppb) or $\mu\text{g}/\text{m}^3$ are used. Nonetheless, we agree that mixing ratio is the correct term, especially when discussing vertical profiles. Following the reviewer’s suggestion, we refer to “concentration” only when discussing the results of our model with observed values (expressed in $\mu\text{g}/\text{m}^3$, standardized at a temperature of 293 K and an atmospheric pressure of 101,3 kPa) to reduce ambiguity. Consequently, we have revised the caption of original Figures 5, 6, 7, 8, 9 and 10 (as well as Figures in the supplementary material: S1, S2, S3, S4, S5, S6, S7, S8 and S9). Please, see the revised version of our manuscript included after the response to reviewers.

As for Figure 2, we revised the corresponding caption to clarify that shows the contribution as a percentage over total emissions in the region for each pollutant. The purpose of that figure is to illustrate the emission share and the relative importance of each source in our inventory and not present emissions in absolute terms. Just for clarification, the emission inventories used in this research are compiled according to the EMEP/EEA methodology: EMEP/EEA air pollutant emission inventory guidebook 2019. Technical guidance to prepare national emission inventories (<https://www.eea.europa.eu/publications/emep-eea-guidebook-2019>), which is a standard in Europe. In addition to the references to the specific inventories used, we included this one in the revised manuscript to let the reader understand the conceptual basis of the emission estimates (line 192). According to this methodology, NO_x emissions account for both NO and NO₂ emissions collectively expressed as NO₂ mass. According to the technical definition of NMVOC emissions for inventory reporting, they “comprise all organic compounds except methane which at 273.15 K show a vapor pressure of at least 0.01 kPa or which show a comparable volatility under the given application conditions” (AQEG, 2020) and intends to represent the total mass of organic compounds that are capable of producing photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight.

References:

- European Environmental Agency (EEA). EMEP/EEA air pollutant emission inventory guidebook 2019. Technical guidance to prepare national emission inventories. EEA Report No 13/2019. doi:10.2800/29365, <https://www.eea.europa.eu/publications/emep-eea-guidebook-2019> (last access: [January 22, 2004]), 2019.
- Air Quality Expert Group (AQEG). Non-methane Volatile Organic Compounds in the UK. Report prepared for the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of Agriculture, Environment and Rural Affairs in Northern Ireland. https://uk-air.defra.gov.uk/assets/documents/reports/cat09/2006240803_Non_Methane_Volatile_Organic_Compounds_in_the_UK.pdf (last access: [January 22, 2004]), 2020.

The first paragraph of section 2.4 now reads:

“Emissions for this modeling exercise result from the combination of the official national (MMA, 2018), regional (CM, 2021) and Madrid’s city local inventory (AM, 2022), **These inventories are compiled according to the EMEP/EEA standardized methodology (EEA, 2019) and are conveniently adapted, spatio-temporally resolved for modeling purposes (Borge et al., 2008; Borge et al., 2018) and consistently combined for the different modeling domains (Borge et al., 2014).**”

Both, the caption and the legend in Figure 2 have been updated too:

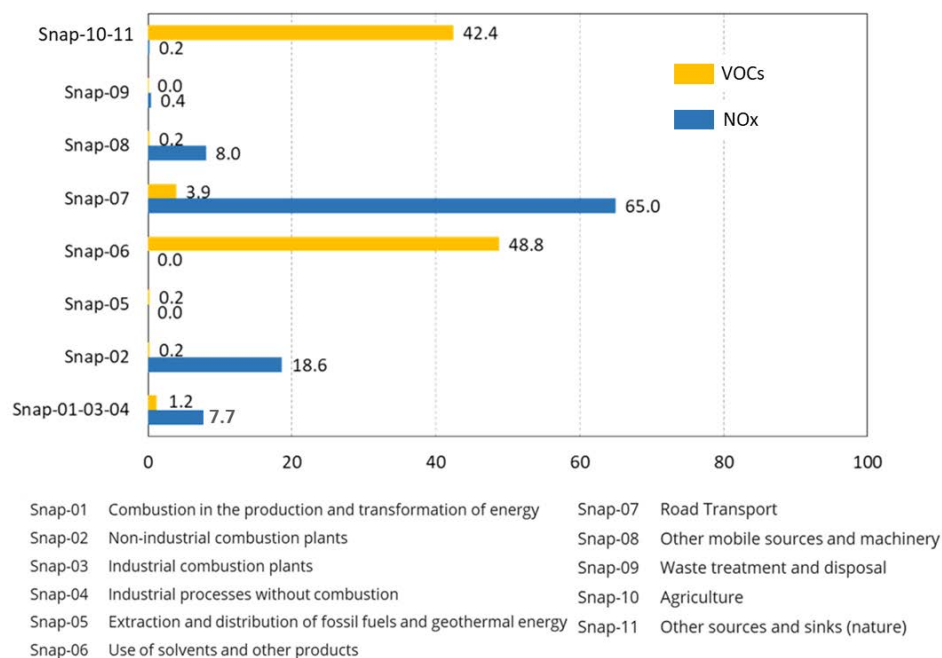


Figure. 2. NOx and VOCs emissions of tagged sectors (percentage on an annual basis) for the source apportionment analysis.

5) Parts of the manuscript are confusing and missing a proper proof-reading. As example, on P51197 the authors write that Fig. 4 shows “average contributions”. The description of Fig.4, however, indicates that contribution to the 90th percentile of ozone are given. Moreover, I find it very confusing, that the authors only show contributions to ozone attributed to anthropogenic origin. I suggest to always show contributions with respect to total ozone. Otherwise results are very hard to compare to other studies and readers might be confused.

We can confirm that the caption of Figure 4 (Figure 5 in the revised version of our manuscript) is correct. The reference to Figure 4 (page 5, line 197) read in the original submission “Figure 4 shows

the apportionment of each emission sector for local sources. Road transport (SNAP07) is the most influential sector, with an average contribution in the Madrid region of 41% and with maximum contributions of around 55%, located in the proximity of the main communication routes (Figure 4d).” The discussion here refers to high O₃ values, illustrated by the 90th percentile. We slightly changed the paragraph to avoid confusions like the one pointed out by reviewer #1. Now it reads:

“Figure 5 shows the apportionment to P90 of each emission sector for local sources. Road transport (SNAP07) is the most influential sector, contributing 41% to P90 as an average over the Madrid region. The contribution of this sector (relative to local sources) reaches values up to 55% in the proximity of the main communication routes (Figure 5d).

We appreciate the second suggestion made by Reviewer #1, but we think the current approach may be more effective to communicate our findings. Since contribution from sources outside the modeling domain dominate O₃ levels, the apportionment of specific sectors is presented as a percentage of the total contribution of local sources. At the same time, we provide information on the absolute contribution, in terms of ppb. We think this may make the interpretation easier and it may be more informative to support the design of strategies. We believe that the clarifications made regarding this issue, as well as the interpretation of initial conditions (see response to comment #7) and an extended discussion of source apportionment methods (see response to comment #1) have help clarifying our methodology and results.

The paper has been proofread again trying to make the discussion more accessible considering the example highlighted by Reviewer #1. We also corrected several typos and mistakes in the text (see revised version after RC2).

6) In the last subsections the authors present a comparison with measurements. This comparison shows an underestimation of ozone simulated by the model under accumulation conditions during 13 -19 UTC, however the authors do not discuss this model bias. How does it affect the source apportionment results? It seems that the model underestimated local ozone production under this stagnant conditions. To my opinion, the manuscript should start with a model evaluation and discuss the source attribution results critically with respect to the model performance.

Following the suggestions from both reviewers, we included a new section (3.1) to provide a better view of the model performance assessment. We keep the detailed results of model assessment for each air quality monitoring station in the supplementary material (Table S3 in the revised version of our submission) because we think it helps the interpretation of site-specific results and complements the information given by aggregated statistics (Table 1). All statistics have been revised and harmonized. In addition to this, we added two new tables (Table S4 and Table S5) to illustrate the differences on model performance (both CMAQ and WRF) depending on the circulation pattern. Following the suggestion of Reviewer #2 we also show the comparison of observed and modeled O₃ series for 3 representative sites (pinpointed now in the revised version of Figure 1) as Figure 3. Besides illustrating the capabilities of the model and the reason for the statistical results obtained, it serves to present the features of the study period. Although a detail investigation of the causes for model discrepancies with observation is out of the scope of this contribution, we think it helps understanding potential reasons for performance differences found.

As discussed in this new section, the difficulty of the meteorological model to reproduce wind fields under very weak forcing conditions (accumulation patterns) may contribute to the larger bias found in CMAQ outputs for that circulation type. We acknowledge this limitation and put our results in context with a critical discussion of our results and those from other relevant studies. We think this new section demonstrates a reasonable performance to study ground-level O₃. Furthermore, the results shown in Figure 8 (Figure 9 now) suggest a robust model performance also to describe O₃ mixing ratios aloft. We think this is enough to build confidence in the ability of the system to accurately describe ozone typical features and thus, we believe the modeling tool is fit for the purpose of the research at hand.

The new section 3.1 is as follows:

“3.1 Ozone levels during the study period and model evaluation

While this period was hotter and dryer than most of recent summers, July 2016 may be representative of typical summer conditions in the Madrid region and included a concatenation of characteristic local circulation patterns (Plaza et al., 1997) with direct implications on ground-level O₃ (Querol et al., 2018; Escudero et al., 2019). Figure 3 presents both observed and modeled concentration series at representative points (Figure 1), and shows the venting and accumulation days identified in Querol et al., (2018). The time series demonstrate that O₃ levels are significantly lower under venting conditions, although significant differences are found depending on the location, which supports the need to use high-resolution modeling systems to analyze pollution dynamics in the Madrid region. On the other hand, accumulation patterns tend to produce higher concentrations (up to 175 µg/m³), especially during July 27th.

It can be observed that the model is able to reproduce the temporal patterns, as confirmed by the high correlation coefficients (*r*) and index of agreement (IOA) shown in Table 1. The statistical evaluation demonstrates a reasonable model performance, yielding better statistical results than recent simulation studies in this domain. Pay et al. (2019) reported an aggregated correlation coefficient of 0.66 and mean bias (MB) of 22.5 µg/m³ for the central region of the Iberian Peninsula. In this study, we obtained an average *r* value of 0.74 and a MB of 6.2 µg/m³. Of note, 95.2% and 66.7% of the *r* values for the locations of the 42 monitoring stations used in this study are larger than 0.6 and 0.7, respectively while the overall normalized mean bias (NMB) is only 9%. The results for a series of common statistics (Borge et al., 2010) for each of the monitoring sites in our modeling domain can be found in Table S3. The model, however, may have some difficulties capturing the amplitude of observed O₃ series and fails to accurately reproduce concentration peaks on some days. This is evidenced by the relatively large error in comparison with the bias (23% and 9%, respectively as an average over the 42 monitoring stations in the modeling domain). In the supplementary material (Table S4), we present a separate model performance assessment for accumulation and advective patterns showing that the main differences among them relate to errors, both MGE and RMSE that are systematically higher for accumulation periods. This may be related to the limitations of the meteorological model to depict atmospheric circulation during stagnant conditions suggested by Pay et al., (2019). Even when WRF was found to outperform other

models for this particular episode (Escudero et al., 2019), the ability to reproduce wind direction and wind speed clearly deteriorates for accumulation periods, as shown in Table S5,

As expected, results are poorer for urban background and traffic locations, since the typical spatio-temporal representativeness of the measurements in such locations is not comparable with that of a mesoscale modeling system, even with 1 km² spatial resolution.”

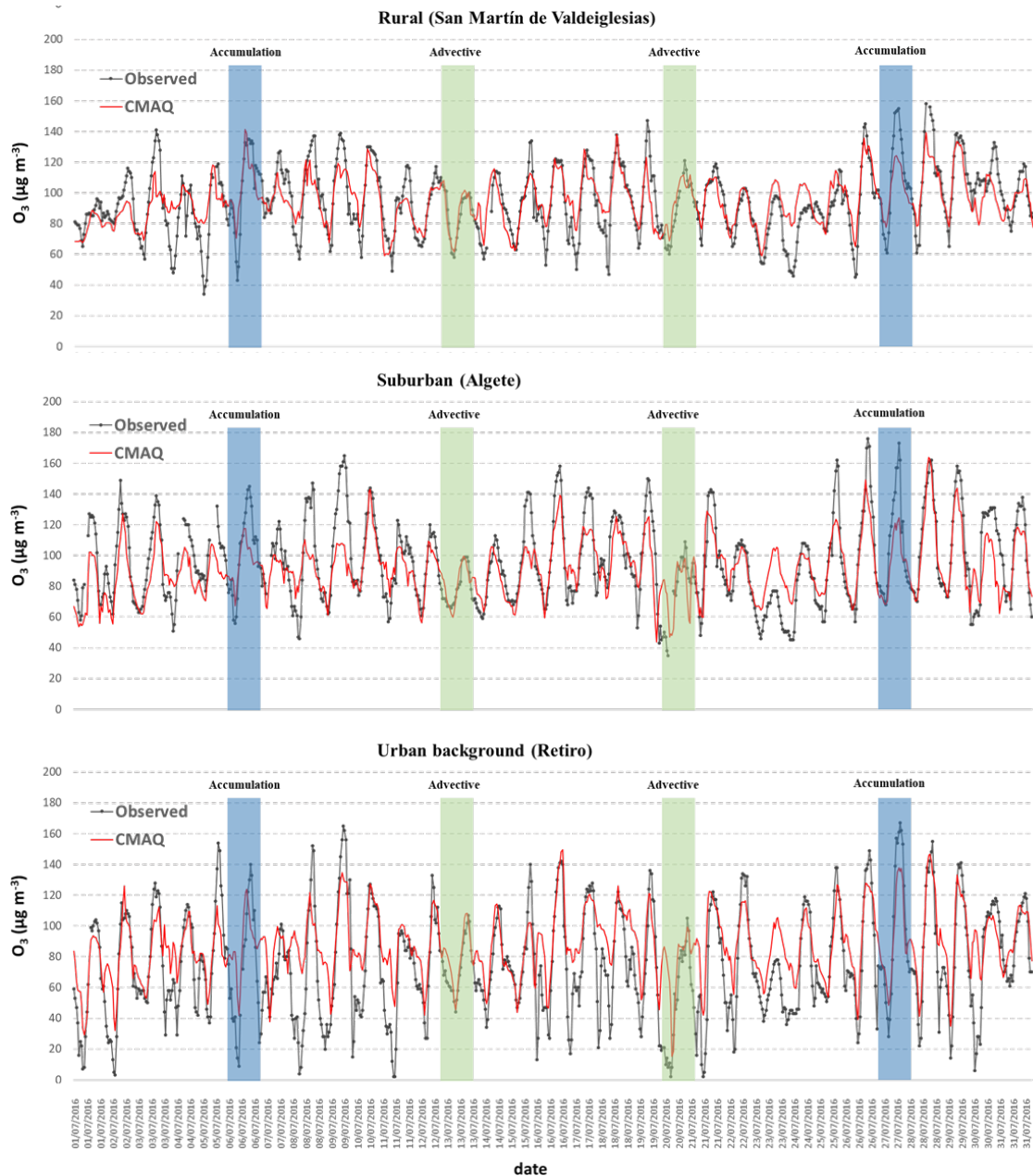


Figure 3. Observed and predicted concentration series for selected locations (1-SMV: a rural location in the southwestern area of Madrid region, 2-ALG: a suburban location in the northeastern area of Madrid region and 3-RET: an urban background site in Madrid city center).

And the new tables included in the supplementary material are:

Table S4. Model performance statistics (dimensionless unless noted otherwise) by station type and circulation pattern for ground-level O₃ concentration.

Station	Pattern	n	FAC2	MB (µgm ⁻³)	MGE (µgm ⁻³)	NMB	NMGE	RMSE (µgm ⁻³)	r	IOA
Rural	Accumulation	240	0.98	-6.7	15.29	-0.06	0.14	18.83	0.83	0.66
	Advection	232	0.98	3.1	9.31	0.04	0.11	12.97	0.83	0.73
	Other	3211	0.98	-3.0	14.01	-0.03	0.15	18.30	0.75	0.67
Suburban	Accumulation	474	0.96	-4.8	20.24	-0.05	0.20	26.69	0.76	0.68
	Advection	468	0.92	7.3	13.59	0.10	0.19	19.69	0.75	0.68
	Other	6412	0.94	2.6	17.18	0.03	0.20	23.22	0.73	0.68
Urban background	Accumulation	669	0.89	2.4	23.46	0.03	0.26	31.04	0.69	0.66
	Advection	670	0.89	11.4	16.95	0.17	0.25	22.34	0.72	0.60
	Other	9014	0.89	8.5	20.41	0.11	0.25	27.08	0.68	0.65
Industrial	Accumulation	96	0.95	4.7	16.40	0.05	0.18	20.15	0.86	0.73
	Advection	96	0.97	9.1	12.55	0.13	0.18	15.26	0.82	0.65
	Other	1278	0.95	7.9	14.54	0.10	0.18	18.79	0.83	0.71
Urban traffic	Accumulation	510	0.91	3.5	20.09	0.04	0.22	25.81	0.79	0.69
	Advection	522	0.87	15.8	18.22	0.25	0.28	24.55	0.69	0.55
	Other	7086	0.87	11.0	19.98	0.14	0.25	26.72	0.73	0.65

Table S5. Model (WRF) performance statistics by circulation pattern for basic meteorological variables

Variable	Pattern	FAC2	MB	MGE	NMB	NMGE	r	IOA
Temperature (T2)	Accumulation	1.00	-1.4 K	2.0 K	-0.05	0.07	0.92	0.81
	Advection	1.00	-0.5 K	1.5 K	-0.02	0.06	0.96	0.86
	Other	1.00	-0.8 K	1.6 K	-0.03	0.06	0.96	0.85
Wind speed (WS10)	Accumulation	0.63	0.9 m/s	1.7 m/s	0.31	0.63	0.30	0.33
	Advection	0.78	0.7 m/s	1.5 m/s	0.17	0.37	0.59	0.55
	Other	0.71	0.5 m/s	1.3 m/s	0.18	0.46	0.58	0.55
Wind direction	Accumulation	0.61	-34.3 °	90.7 °	-0.24	0.63	0.26	0.55
	Advection	0.87	6.5 °	34.5 °	0.05	0.25	0.79	0.81
	Other	0.77	-9.2 °	60.8 °	-0.06	0.38	0.53	0.68

7) Given the importance of emissions from the previous day for ozone formation I wonder why the authors attribute them to "IC". Wouldn't it be better to account them also sectorwise?

That is the approach followed by other source apportionment studies, but we think our methodology serves us better considering the temporal span of the period analyzed (a whole month), the typical diurnal cycle of O₃ and the goal of characterizing this attribution under specific meteorological conditions. This is another novelty of our methodology that may be better suited to provide useful information for decision making, especially for the design of short-term action plans intended to control ozone peaks. This is an important point and we added an explicit discussion at the end of section 2 (lines 209-217) to make it clear before discussing the results:

“In addition to the attribution of O₃ ambient levels to the emissions within the modeling domain, hereinafter referred to as local sources, the contribution of boundary conditions (BC) and initial conditions (IC) are also estimated in this study (labeled as BCO and ICO in Figure 12). Considering the typical O₃ daily patterns and the variability of circulation patterns, the latter refer to the initial mixing ratios on a daily (24 hour) basis, i.e., each day is run separately using the outputs from the previous day as IC. This is a difference with most previous source apportionment studies that analyze shorter periods (Pay et al., 2019) or specific high concentration events (Lupaşcu et al., 2022; Zhang et al., 2022). While this may hinder the comparability of our results, this methodological option may be appropriate considering the temporal span of the period analyzed (a whole month), the typical diurnal cycle of O₃ and the goal of characterizing this attribution under specific meteorological conditions. This helps understanding differences on O₃ source apportionment depending on regional circulation patterns (Zhang et al., 2023) and explicitly considering the influence of vertical transport of O₃ from residual layers from previous days that may lead to rapid increases of O₃ concentrations near the surface (Qu et al., 2023 and references within). Therefore, this approach may be better suited to provide useful information for decision making, especially for the design of short-term action plans intended to control ozone peaks.”

References added:

- Lupaşcu, A., Otero, N., Minkos, A., and Butler, T.: Attribution of surface ozone to NO_x and volatile organic compound sources during two different high ozone events, *Atmos. Chem. Phys.*, 22, 11675–11699, <https://doi.org/10.5194/acp-22-11675-2022>, 2022.
- Qu, K., Wang, X., Cai, X., Yan, Y., Jin, X., Vrekoussis, M., Kanakidou, M., Brasseur, G. P., Shen, J., Xiao, T., Zeng, L., and Zhang, Y.: Rethinking the role of transport and photochemistry in regional ozone pollution: insights from ozone concentration and mass budgets, *Atmos. Chem. Phys.*, 23, 7653–7671, <https://doi.org/10.5194/acp-23-7653-2023>, 2023.
- Zhang, S., Zhang, Z., Li, Y., Du, X., Qu, L., Tang, W., Xu, J., and Meng, F.: Formation processes and source contributions of ground-level ozone in urban and suburban Beijing using the WRF-CMAQ modelling system, *Journal of Environmental Sciences*, 127, 753-766, <https://doi.org/10.1016/j.jes.2022.06.016>, 2023.
- Zhang, Y., Yu, S., Chen, X., Li, Z., Li, M., Song, Z., Liu, W., Li, P., Zhang, X., Lichtfouse, E., and Rosenfeld, D.: Local production, downward and regional transport aggravated surface ozone pollution during the historical orange-alert large-scale ozone episode in eastern China, *Environ Chem Lett*, 20, 1577–1588, <https://doi.org/10.1007/s10311-022-01421-0>, 2022.

Nonetheless, to provide additional information on the question raised by Reviewer #1, we looked at the source apportionment structure at the end of each day (used as initial condition for the following) to understand what the contribution within the “ICO” label is sectorwise. As an average, the virtual totality of O₃ at midnight comes from BC (as already shown is Figures 11, S11, S12 and S13 in our original submission). The trace of IC from local sources after 24 hours is very weak, specially under advective conditions, when the influence of the ozone from the day before is negligible (Figure AC3).

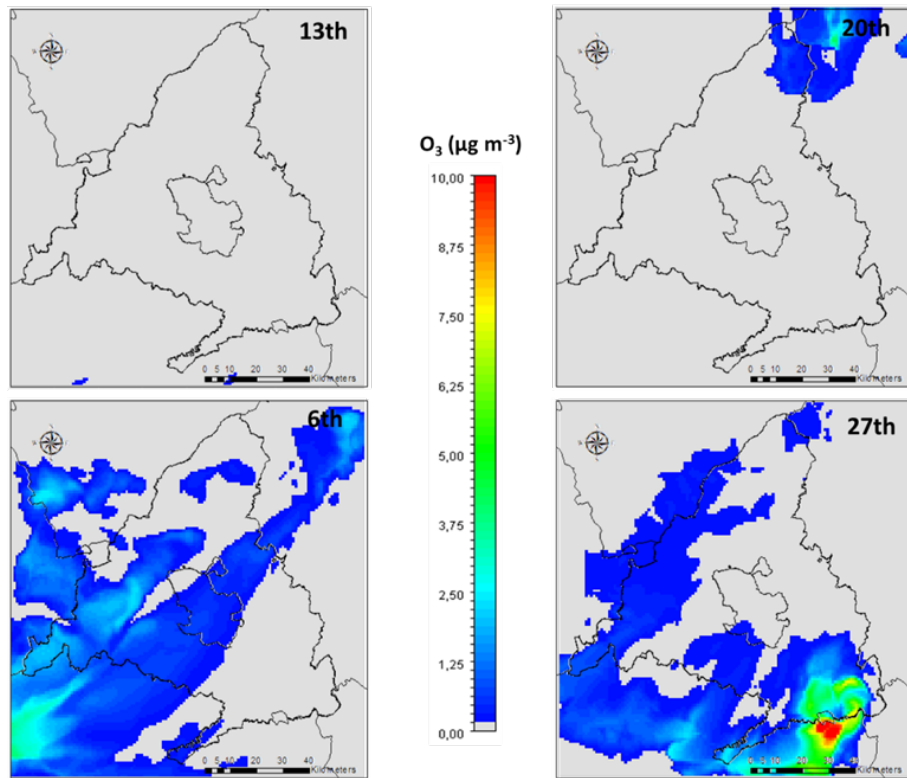


Figure AC3. Contribution of anthropogenic sources at the end of the day (23:59 PM) for advective conditions (July 13th and July 20th) and accumulation conditions (July 6th and July 27th)

However, we identified the moments and locations when the contribution of the remaining sources was higher at the end of the day and looked into the apportionment structure. The results, shown in Figure AC4 reveal that the breakdown of IC is very similar to that discussed throughout the paper for the mean and P90 levels. Therefore, we conclude that the approach follow for IC was key to track the relative importance of O₃ from previous days, but it does not distort the sectoral analysis.

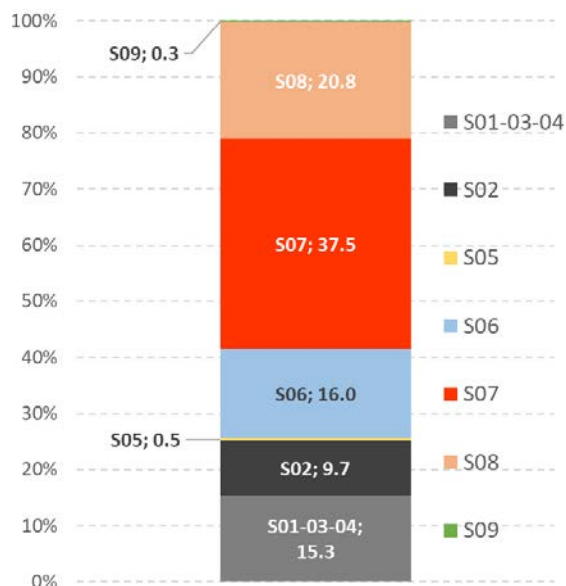


Figure AC4. Sectoral breakdown of the contribution of IC (BC excluded)

8) Some of the reference seems to be not adequate. As an example, P3I118 cites Borgee et al., 2022 (<https://doi.org/10.1016/j.scitotenv.2013.07.093>), but I can't find "tagging" nor "ISAM" in the whole paper. Maybe I misunderstood something, but the authors should check the manuscript carefully.

We carefully checked all the references in the manuscript and made minor changes, conveniently tracked in the revised version. In addition to a significant number of new references, we added missing cites in the original submission such as Butler et al. (2020) <https://doi.org/10.5194/acp-20-10707-2020> to the references list. However, the particular reference pointed out by Reviewer #1 seems to be correct. <https://doi.org/10.1016/j.scitotenv.2013.07.093> is the DOI of Borge et al. (2014) that presents the first source apportionment study made in Madrid using a sensitivity approach (brute force). However, Borge et al. (2022) refers to a comparison of the single-perturbation method (or brute force) with two implementations of CMAQ-ISAM; that of version 5.0.2 and the one used here, corresponding to version 5.3.2, that is completely pertinent for the discussion at hand. Thanks to this comment we realized the year was missing in the reference, something we corrected in the revised version of our manuscript. We also realized that <https://doi.org/10.1016/j.atmosenv.2022.119258> was mistakenly included within the references and was removed since it is not adequate here.

Correct reference for Borge et al. (2022):

- Borge, R., de la Paz, D., Cordero J.M., Sarwar, G., Napelenok, S.: Comparison of Source Apportionment Methods to attribute summer tropospheric O3 and NO2 levels in Madrid (Spain) 21st International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes. HARMO21, Aveiro, Portugal, 27-30 September 33-37, 2022.

Reference removed:

- ~~• Borge, R., Jung, D., Lejaraga, I., de la Paz, D., and Cordero, J. M.: Assessment of the Madrid region air quality zoning based on mesoscale modelling and k-means clustering, Atmospheric Environment, 287, 119258, <https://doi.org/10.1016/j.atmosenv.2022.119258>, 2022.~~

Some minor comments:

- Introduction: I am missing a discussion of similar source attribution studies (globally, for Europe) and a discussion of comparable source attribution methods.

We included a brief discussion on source apportionment techniques and recent applications in the introductory section (lines 75-87) (see response to Question #1). In addition, we believe that other additions to the description of our methodology the results previously discussed would help the reader to frame our work and better understand our findings.

- Fig 2: COVs instead of VOC

The legend in Figure 2 has been corrected (see response to Question #4 -second part-)

-p5183 I wonder why the contribution of biogenic emissions is so small (see also major comments above).

We include a more detailed analysis of the contribution of biogenic emissions that would definitively contribute to better understand the role of biogenic emissions in this study and potential differences with previous works (see response to Question #2 -last part-)

- P31109 What is the temporal resolution of the boundary conditions?

We clarify that the temporal resolution of boundary conditions from hemispheric CMAQ is 1 hour (line123 of the revised manuscript)

“...the mother domain receives **1 hour-resolution**, dynamic chemical boundary conditions from hemispheric CMAQ (Mathur et al., 2017) simulations. “

- p2145 You mean STE is projected to increase? Please clarify.

We don't mean that STE is projected to increase in this particular location. According to the global scale simulations of Meul et al., (2018) and Banerjee et al., (2016) (among others) downward transport from O₃ from the Stratosphere to the Troposphere is expected to increase significantly due to dynamic and chemical changes in the atmosphere induced by climate change. We made this clarification (lines 46-47) in the revised version of our manuscript:

“...expected to increase in the future globally (Meul et al., 2018; Banerjee et al., 2016) due to dynamic and chemical changes in the atmosphere induced by climate change.”

To our knowledge our work presents the first explicit apportionment of stratospheric O₃ locally transported to ground level in the region. As illustrated in Figure 11 (and analogous ones in the supplement) of our original submission, the average contribution of stratospheric O₃ (PVO3) is negligible. As shown in Figure AC5 (added in the supplementary material as Figure S4), the maximum 1-hour contribution in the region is less than 0.4 ppb. It should be bear in mind that PVO3 accounts only for stratospheric ozone downward fluxes within the modeling domain, and presumably a significant part of the contribution of BC relates to STE. We have included this discussion in section 3.2 (lines 297-305):

“In addition, we tagged stratospheric ozone (PVO3 in Figure 12) due to the influence of vertical injections on ground level O₃ levels (Hsu et al., 2005) and the potential contribution reported in this region for specific extraordinary ozone levels (San José et al., 2005). Pay et al. (2019) hypothesize that stratosphere-troposphere exchange (STE) may have played a significant role towards the end of July 2016 in the Iberian Peninsula. According to our results, however, the direct transport of O₃ from the stratosphere in our modeling domain was negligible in this period, with 1-hour maximum contributions below 0.4 ppb in the southwest end of the Madrid region (see Figure S4). This contrasts with remarkably higher contributions reported in other areas of Europe (Lupaşcu et al., 2022) and those from global simulations for similar latitudes (Butler et al., 2018). It should be noted that here we account for O₃ STE exclusively within our innermost nested domain and part of the O₃ attributed to BC may be related to contributions from the Stratosphere in other regions.”

References added:

- Butler, T., Lupascu, A., Coates, J., and Zhu, S.: TOAST 1.0: Tropospheric Ozone Attribution of Sources with Tagging for CESM 1.2.2, *Geosci. Model Dev.*, 11, 2825–2840, <https://doi.org/10.5194/gmd-11-2825-2018>, 2018.
- Lupaşcu, A., Otero, N., Minkos, A., and Butler, T.: Attribution of surface ozone to NO_x and volatile organic compound sources during two different high ozone events, *Atmos. Chem. Phys.*, 22, 11675–11699, <https://doi.org/10.5194/acp-22-11675-2022>, 2022.
- San José, R., Stohl, A., Karatzas, K., Bohler, T., James, P., and Pérez, J.L.: A modelling study of an extraordinary night time ozone episode over Madrid domain, *Environmental Modelling & Software*, 20(5), 587-593, <https://doi.org/10.1016/j.envsoft.2004.03.009>, 2005.

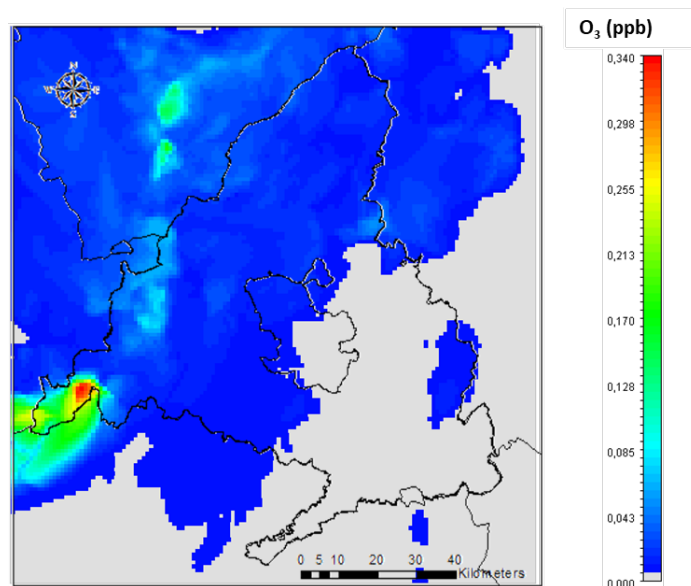


Figure AC5. Maximum 1-hour attribution of stratospheric transport (PVO3) to ground level

- P2147ff I am missing a discussion of the role of the non linearity of the ozone chemistry which lead to an increase of the ozone production efficiency when emissions are reduced. The authors should consider to add this point including a discussion of the relevant literature.

The ozone production efficiency is indeed affected by changes on emissions that induce changes on the oxidation capacity of the atmosphere (Jung et al., 2022; Jung et al., 2023). However, we think that the point raised by Reviewer #1 is particularly relevant for source apportionment studies based on sensitivity approaches (Dunker et al., 2016; Sartelet et al., 2022). Therefore, addressing this question explicitly may be out of the scope of our paper, that presents a diagnosis study based on emission tagging. Nonetheless, we implicitly address this issue in the revised version of our manuscript when we discuss the contribution of VOC emissions, both from SNAP 06 and biogenic sources (please, see response to Question #2 and related additions to the text).

References:

- Dunker, A. M., Koo, B., and Yarwood, G.: Ozone sensitivity to isoprene chemistry and emissions and anthropogenic emissions in central California, *Atmospheric Environment*, 145, 326-337, <https://doi.org/10.1016/j.atmosenv.2016.09.048>, 2016.
- Jung, D., de la Paz, D., Notario, A., and Borge, R.: Analysis of emissions-driven changes in the oxidation capacity of the atmosphere in Europe, *Science of The Total Environment*, 827, 154126, <https://doi.org/10.1016/j.scitotenv.2022.154126>, 2022.
- Jung, D., Soler, R., de la Paz, D., Notario, A., Muñoz, A., Ródenas, M., Vera, T., Borrás, E., and Borge, R.: Oxidation capacity changes in the atmosphere of large urban areas in Europe: Modelling and experimental campaigns in atmospheric simulation chambers, *Chemosphere*, 341, 139919, <https://doi.org/10.1016/j.chemosphere.2023.139919>, 2023.

- Sartelet, K. N., Couvidat, F., Seigneur, C., and Roustan, Y.: Impact of biogenic emissions on air quality over Europe and North America, Atmospheric Environment, 53, 131-141, <https://doi.org/10.1016/j.atmosenv.2011.10.046>, 2012.

- p2158 Please fix, should be Paoletti et. al, 2014

Apparently, the spelling and the cross reference (to <https://doi.org/10.1016/j.envpol.2014.04.040>) were correct.

- p51160 How is soil-NO_x handled?

We rely on MEGAN 2.1 estimates for soil-NO_x emissions (Yienger and Levy, 1995) (see Figure AC6). Although it represents a negligible part of total NO_x emissions in our domain (less than 0,1 t during the simulated period; in comparison with nearly 50 000 t/yr of NO_x from anthropogenic sources only in the Madrid region) we noted this in section 2.4 within the discussion of tagged sources (lines 198-199):

“...(and labeled as BIO in Figure 12). Soil-NO_x emissions provided by MEGAN 2.1 (Yienger and Levy, 1995) are also included in this group although their share to total NO_x emissions in the region is negligible.”

Reference added:

- Yienger, J. J., & Levy, H. (1995). Empirical model of global soil - biogenic NO_x emissions. Journal of Geophysical Research: Atmospheres, 100(D6), 11447-11464. <https://doi.org/10.1029/95JD00370>

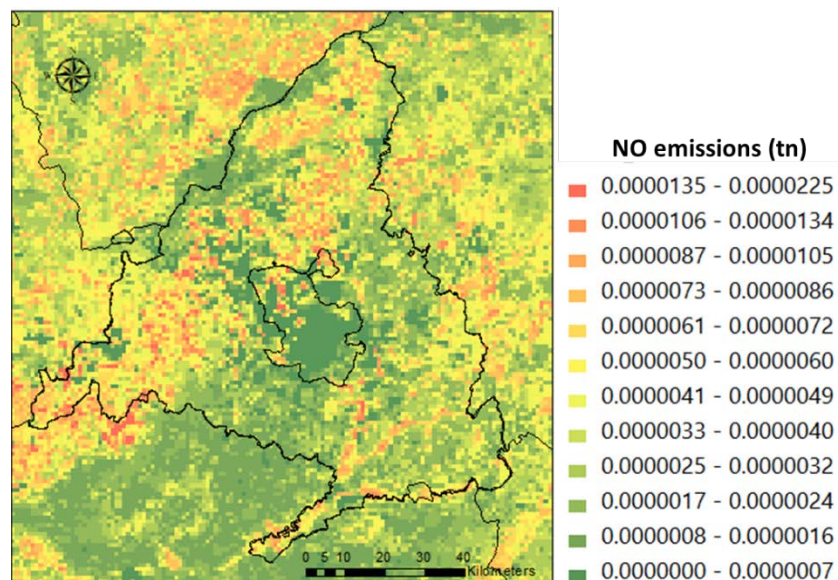


Figure AC6. Soil NO emissions (t) estimated in our modeling domain for July 2016

- p5l185 But Pay et al, 2019 applies the “old” ISAM tagging, right? So I would expect a difference with the new approach? Please discuss.

That is correct (see Table AC1 within the response to Question #3). Nonetheless, the latest version of CMAQ keeps both options (see response to Question #1). We include further discussion of the differences of the different methods. The resulting source attribution may differ in a different degree depending on the pollutant, the scale of analysis and the specific features of each modeling domain. In this particular case, Borge et al., (2022) addresses the comparison of both approaches (along with the single-perturbation method) (Figure AC7). They found significant differences on the attribution of NO₂ but not for O₃. Both methods identified road traffic (SNAP 07) as the major local anthropogenic contributor but CMAQ-ISAM attributes a larger share of ground-level O₃ to this source when the apportionment is based on an equal assignment for all reactants. This version attributes larger contributions to local sources in general (vs BC) (Figure AC8), specially around Madrid metropolitan area. That may be one of the reasons why, for instance, the attribution to biogenic sources in Pay et al., (2019) is apparently smaller than the one obtained in our current study.

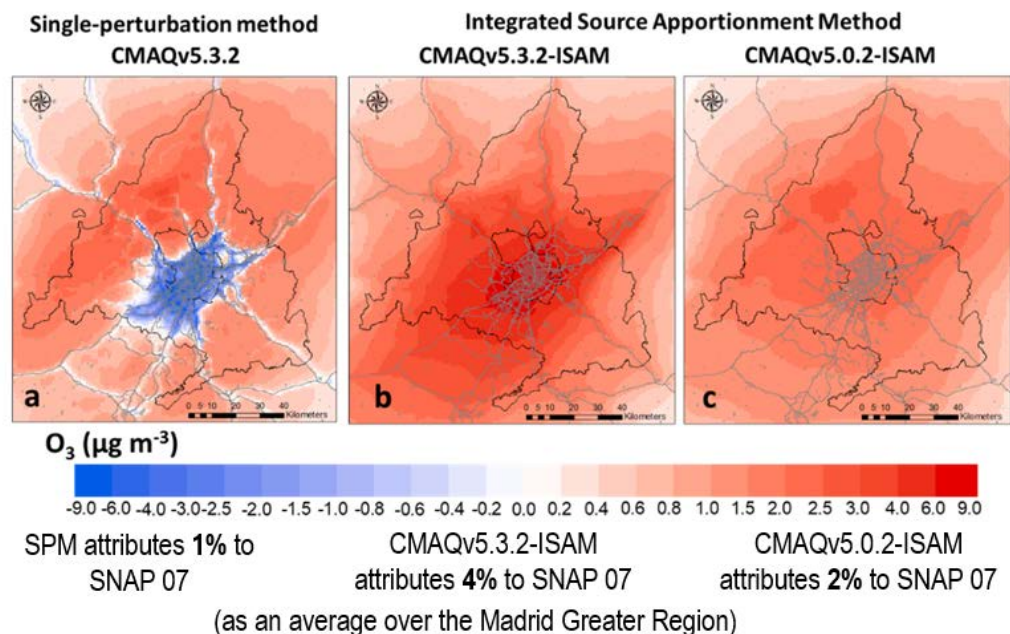


Figure AC7. Comparison of road traffic (SNAP 07) contribution to monthly average O₃ levels depending on the source apportionment methodology. Source: Borge et al., (2022)

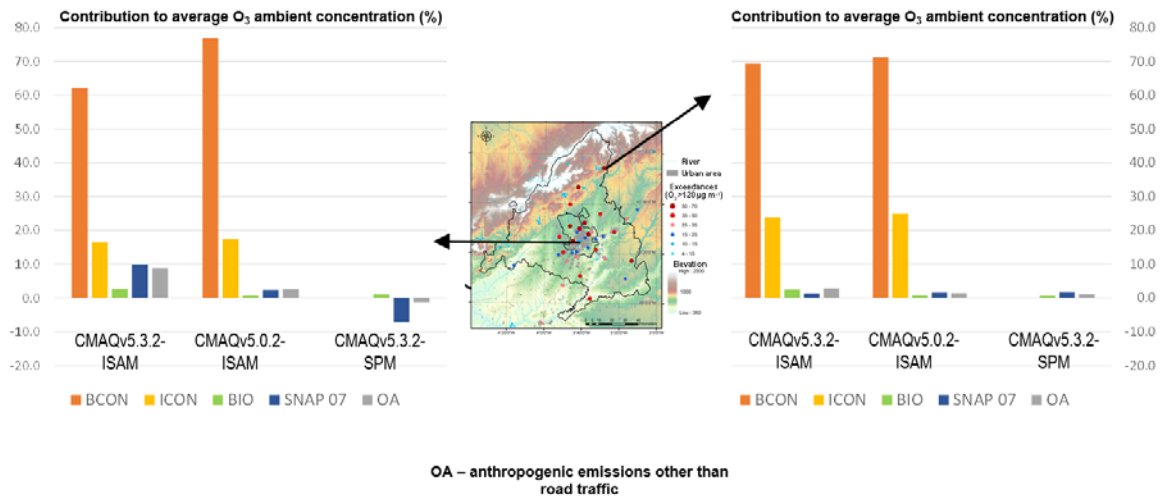


Figure AC8. Comparison average O₃ levels source apportionment in two different locations of the Madrid region (city center -left- and remote rural location -right-) depending on the source apportionment methodology. Source: Borge et al., (2022)

Reference

- Borge, R., de la Paz, D., Cordero J.M., Sarwar, G., Napelenok, S.: Comparison of Source Apportionment Methods to attribute summer tropospheric O₃ and NO₂ levels in Madrid (Spain) 21st International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes. HARMO21, Aveiro, Portugal, 27-30 September 33-37, 2022.

References:

Butler, T., Lupascu, A., Coates, J., and Zhu, S.: TOAST 1.0: Tropospheric Ozone Attribution of Sources with Tagging for CESM 1.2.2, *Geosci. Model Dev.*, 11, 2825–2840, <https://doi.org/10.5194/gmd-11-2825-2018>, 2018

Grewe, V., Tsati, E., Mertens, M., Frömming, C., and Jöckel, P.: Contribution of emissions to concentrations: the TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52), *Geosci. Model Dev.*, 10, 2615–2633, <https://doi.org/10.5194/gmd-10-2615-2017>, 2017.

RC2

Review article: Summertime tropospheric ozone source apportionment study in Madrid (Spain)

The paper describes a modeling study that investigates the source of summertime surface ozone (O₃) in Madrid, Spain, using an integrated source apportionment method within the Community Multiscale Air Quality model (CMAQv5.3.2). The paper highlights the importance of local sources (road traffic) in the build-up of O₃ during peak events, which tends to happen during anticyclonic stagnation conditions in summertime. Suggesting that local measurements aim to reduce O₃ precursors could have a positive effect during such periods. In general, the findings are valuable for the understanding of the O₃ build-up mechanism in the region and, consequently, for policy decision-making.

Thank you for the time devoted to our manuscript, your reassuring remarks and the suggestions to improve our work.

The narrative in the abstract suggests that the study focused on the source contributions to urban O₃ pollution. However, the results include the contribution to O₃ in different chemical environments (urban, suburban, and rural); therefore, I believe that the scope needs to be clearly stated in the document.

Air pollution is a multi-scale problem and urban air quality is affected by emissions from different geographical areas. At the same time, pollutants released in cities have an impact beyond the urban areas. In the case of Madrid, pollution dynamics is strongly determined by emissions from the metropolitan area (Borge et al., 2014) that affects the whole region. That is particularly true when dealing with secondary pollutants such as ozone. While we think this is reflected in the abstract, we agree that the title of our paper may be misleading and, therefore it has been slightly changed to “Summertime tropospheric ozone source apportionment study in **the Madrid region** (Spain)” in the revised version of our manuscript.

We revised the introductory section to clearly define the scope of our research and provide a better context of previous source apportionment studies. The changes made are highlighted in red in the revised version (included in full after the point-to-point responses to RC2) but most of them relate to the passage between lines 75 and 87):

“...perspective. **Furthermore, information on the relative importance of emission sources on ambient levels should be considered when designing plans and measures, especially when they target highly non-linear secondary pollutants such as O₃ (Cohan and Napelenok, 2011).**

There are different source apportionment techniques that may support air pollution research and decision making (Thunis et al., 2019). Approaches based on sensitivities, such as single-perturbation or brute force methods (Borge et al., 2014, Tagaris et al., 2014, Zhang et al., 2022, Qu et al., 2023) may be useful to anticipate the potential effect of a given intervention. However, tagging methods (Grewe et al., 2017, Butler et al., 2018) provide fully mass conservative apportionment at receptors of interest and may be better suited for diagnosis purposes (Borge, 2022). These pollution tracking capabilities have been integrated into modern air quality models to provide attribution information

together with the standard concentration and deposition output fields, can be successfully applied to study pollution dynamics (Simon et al., 2018; Pay et al., 2019, Li et al., 2022). This approach may be particularly interesting to describe how O₃ levels are linked to emission sources under unfavorable meteorological conditions (Cao et al., 2022; Zohdirad et al., 2022) or specific local atmospheric circulation patterns (Zhang et al., 2023) that may lead to high concentration events (Lupaşcu et al., 2022).

This research focuses on the center of the Iberian Peninsula, encompassing the city of Madrid and its surroundings. Consistently with general emission trends in Europe, the emission of the main O₃ precursors in the Madrid region decreased by 47%, for VOCs, and by 44% for NO_x from 1990 to 2018 (CM, 2021). While recent control measures succeeded in reducing NO₂ levels (AM, 2022), such emissions reductions have, at the same time, substantially impacted urban atmospheric chemistry by modifying its oxidative capacity. Recent studies (Saiz-Lopez et al., 2017; Querol et al., 2016) suggest that O₃ ~~concentration~~ levels have increased in Madrid by 30-40% during the 2007-2014. A greater decrease in NO emissions than in NO₂ emissions (with the subsequent reduction of the NO/NO₂ ratio) may be one of the factors responsible for this response (Querol et al., 2016; Querol et al., 2017; Zaveri et al., 2003; Jhun et al., 2015). The exceedances of the target value for the protection of human health in the region mainly occur in summer periods, especially under adverse meteorological conditions that have been extensively characterized in previous studies (Querol et al., 2016; Querol et al., 2017; Millan et al., 2000; Plaza et al., 1997; Querol et al., 2018; Pay et al., 2019; Escudero et al., 2019). Preventing these exceedances in the region requires an understanding of the source attribution of O₃, specially under specific weather patterns that may lead to high pollution levels (Zhang et al., 2023)."

Reference:

- Borge, R., Lumberras, J., Pérez, J., de la Paz, D., Vedrenne, M., de Andrés, J. M., and Rodríguez, M. E.: Emission inventories and modeling requirements for the development of air quality plans. Application to Madrid (Spain), *Science of the Total Environment*, 466-467, 809-819, <https://doi.org/10.1016/j.scitotenv.2013.07.093>, 2014.

References added:

- Butler, T., Lupascu, A., Coates, J., and Zhu, S.: TOAST 1.0: Tropospheric Ozone Attribution of Sources with Tagging for CESM 1.2.2, *Geosci. Model Dev.*, 11, 2825–2840, <https://doi.org/10.5194/gmd-11-2825-2018>, 2018.
- Cao, J., Qiu, X., Liu, Y., Yan, X., Gao, J., and Peng, L.: Identifying the dominant driver of elevated surface ozone concentration in North China plain during summertime 2012–2017, *Environmental Pollution*, 300, 118912, <https://doi.org/10.1016/j.envpol.2022.118912>, 2022.
- Grewe, V., Tsati, E., Mertens, M., Frömming, C., and Jöckel, P.: Contribution of emissions to concentrations: the TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52), *Geosci. Model Dev.*, 10, 2615–2633, <https://doi.org/10.5194/gmd-10-2615-2017>, 2017.

- Lupaşcu, A., Otero, N., Minkos, A., and Butler, T.: Attribution of surface ozone to NO_x and volatile organic compound sources during two different high ozone events, *Atmos. Chem. Phys.*, 22, 11675–11699, <https://doi.org/10.5194/acp-22-11675-2022>, 2022.
- Qu, K., Wang, X., Cai, X., Yan, Y., Jin, X., Vrekoussis, M., Kanakidou, M., Brasseur, G. P., Shen, J., Xiao, T., Zeng, L., and Zhang, Y.: Rethinking the role of transport and photochemistry in regional ozone pollution: insights from ozone concentration and mass budgets, *Atmos. Chem. Phys.*, 23, 7653–7671, <https://doi.org/10.5194/acp-23-7653-2023>, 2023.
- Tagaris, E., Sotiropoulou, R.E.P., Gounaris, N., Andronopoulos, S., and Vlachogiannis, D.: Impact of biogenic emissions on ozone and fine particles over Europe: Comparing effects of temperature increase and a potential anthropogenic NO_x emissions abatement strategy, *Atmospheric Environment*, 98, 214-223, <https://doi.org/10.1016/j.atmosenv.2014.08.056>, 2014.
- Zhang, S., Zhang, Z., Li, Y., Du, X., Qu, L., Tang, W., Xu, J., and Meng, F.: Formation processes and source contributions of ground-level ozone in urban and suburban Beijing using the WRF-CMAQ modelling system, *Journal of Environmental Sciences*, 127, 753-766, <https://doi.org/10.1016/j.jes.2022.06.016>, 2023.
- Zhang, Y., Yu, S., Chen, X., Li, Z., Li, M., Song, Z., Liu, W., Li, P., Zhang, X., Lichtfouse, E., and Rosenfeld, D.: Local production, downward and regional transport aggravated surface ozone pollution during the historical orange-alert large-scale ozone episode in eastern China, *Environ Chem Lett*, 20, 1577–1588, <https://doi.org/10.1007/s10311-022-01421-0>, 2022.
- Zohdirad, H., Jiang, J., Aksoyoglu, S., Namin, M. M., Ashrafi, K., and Prévôt, A. S. H.: Investigating sources of surface ozone in central Europe during the hot summer in 2018: High temperatures, but not so high ozone, *Atmospheric Environment*, 279, 119099, <https://doi.org/10.1016/j.atmosenv.2022.119099>, 2022.

...Also, I feel that the source apportionment method is loosely defined in the methods session. Expanding the description of the method with an example of the mechanics would strengthen the paper.

This point was also raised by Reviewer #1 and expanded the description of the apportionment method to allow a better understanding of our methodology and results. In addition, we refer the reader to a new publication (Shu et al., 2023) that came available during the review process of our work. That paper, published in *Geoscientific Model Development* fully details the latest implementation of CMAQ-ISAM and provides a sample application, and compares results to other apportionment techniques.

The changes made in section 2.1 regarding model description are as follows:

~~Source attribution provides information on the relative importance of emissions sources on ambient concentration levels which can be particularly useful for highly non-linear secondary pollutants such as O₃ (Cohan and Napelenok, 2011). In this study, the Integrated Source Apportionment Method (ISAM) (Kwok et al., 2015; Kwok et al., 2013) implemented in CMAQv5.3.2 (Napelenok, 2020) is used. This mass transfer method tracks the contribution of all the precursors and proportionally attributes the products to the corresponding sources (Shu et al., 2023). While this approach is based on the same conceptual basis, it substantially differs from the~~

~~implementation of previous versions (including CMAQv5.0.2) that attribute the formation of a secondary pollutant to the sector contributing the limiting reactant. While other source apportionment approaches (Thunis et al., 2019) based on sensitivities may be better suited to investigate the potential of abatement measures (Borge et al., 2014), tagging methods such as ISAM can serve better for diagnosis purposes (Borge et al., 2022) and thus, can be successfully applied to study pollution dynamics (Simon et al., 2018; Li et al., 2022; Pay et al., 2019).~~

In this study, the Integrated Source Apportionment Method (ISAM) (Kwok et al., 2013, ~~Kwok et al., 2015~~) implemented in CMAQv5.3.2 (~~Napelenok, 2020b~~, Napelenok, 2020; Shu et al., 2023) is used. ISAM provides apportionment capability of the full concentration and deposition output arrays including the gaseous photochemically active species such as O₃ as well as inorganic and organic particulate matter. The CMAQ-ISAM implementation used in this study attributes source identity to secondary pollutants based strictly on reaction stoichiometry with all reactions playing a role that are relevant to the formation and destruction of any species in the chemical mechanism. ISAM is highly customizable for any number of user-specified combinations of emissions source sector and geographical source areas. For O₃, this implementation differs from the previous ISAM versions (including CMAQv5.0.2) that attribute the formation of secondary pollutants to source sectors based on chemical regime – NO_x- or VOC-limited O₃ formation (Kwok et al., 2015) and from other studies where precursor attribution is directed by the user to either NO_x or VOC emissions, such as Butler et al. (2020). Regime-based methods are useful to attribute secondary species that depend on multiple precursors. However, the regime determination relies on predefined thresholds of different metrics, often the H₂O₂/HNO₃ ratio (Sillman, 1995) that dynamically depend on location and time specific parameters (Li et al., 2022). By strictly following stoichiometry of all chemical reactions in the mechanism, this version of ISAM avoids the necessity to make decisions and assumption regarding ozone formation regimes. Decisions on tagging method selections are highly dependent on specific the specific application and the scientific and/or regulatory aims of each individual study. As the needs of the scientific and regulatory communities evolve, so do the apportionment methodologies. Since the conclusion of this study, CMAQ-ISAM has been expanded to include the regime-based, the stoichiometry-based, as well as other configuration options. More information on ISAM as well sample application and comparison results can be found in Shu et al. (2023).

References added/removed:

- ~~● Napelenok, S., Bill Hutzell, C. Hogrefe, B. Murphy, J. Bash, K. Baker, K. Foley, Q. Shu, AND R. Mathur. CMAQ 5.3.2: Updates to Integrated Source Apportionment Method (ISAM). CMAS Annual Conference 2020, Chapel Hill, NC, October 19 – 21, <https://youtu.be/959IYeSeEf4>, 2020b~~
- Shu, Q., Napelenok, S. L., Hutzell, W. T., Baker, K. R., Henderson, B. H., Murphy, B. N., and Hogrefe, C.: Comparison of ozone formation attribution techniques in the northeastern United States, *Geosci. Model Dev.*, 16, 2303–2322, <https://doi.org/10.5194/gmd-16-2303-2023>, 2023.

- Sillman, S.: The use of NO_y, H₂O₂, and HNO₃ as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, *Journal of Geophysical Research*, 100, 14175-14188, <https://doi.org/10.1029/94JD02953>, 1995.

...It also feels that the discussion of the model evaluation has been skipped, and something is missing in the paper to convince the reader of the model's capabilities to reproduce the meteorology and chemical environment of the period study. It would be helpful to show a time series of O₃ at some representative sites (urban, regional, and suburban) to show the diurnal and day-to-day variability (e.g., hourly ozone) and the model performance. This is important as it gives the reader a general idea of the O₃ evolution and the pollution episodes, which are investigated throughout the study. Once these issues have been addressed, along with the points below, the manuscript will be suitable for publication.

Following the suggestions from both reviewers we included a new section (3.1) to provide a better view of the model performance assessment. We keep the detailed results of model assessment for each air quality monitoring station in the supplementary material (Table S3 in the revised version of our submission) because we think it helps the interpretation of site-specific results and complements the information given by aggregated statistics (Table 1). All statistics have been revised and harmonized. In addition to this, we added two new tables (Table S4 and Table S5) to illustrate the differences on model performance (both CMAQ and WRF) depending on the circulation pattern. Following the suggestion of Reviewer #2 we also show the comparison of observed and modeled O₃ series for 3 representative sites (pinpointed now in the revised version of Figure 1) as Figure 3. Besides illustrating the capabilities of the model and the reason for the statistical results obtained, it serves to present the features of the study period. Although a detail investigation of the causes for model discrepancies with observation is out of the scope of this contribution, we think it helps understanding potential reasons for performance differences found. As discussed in this new section, the difficulty of the meteorological model to reproduce wind fields under very weak forcing conditions (accumulation patterns) may contribute to the larger bias found in CMAQ outputs for that circulation type. We acknowledge this limitation and put our results in context with a critical discussion of our results and those from other relevant studies. We think this new section demonstrates a reasonable performance to study ground-level O₃. Furthermore, the results shown in Figure 8 (Figure 9 now) suggest a robust model performance also to describe O₃ mixing ratios aloft. We think this is enough to build the confidence in the ability of the system to accurately describe ozone typical features and thus, we believe the modeling tool is fit for the purpose of the research at hand.

The new section 3.1 is as follows:

“3.1 Ozone levels during the study period and model evaluation

While this period was hotter and dryer than most of recent summers, July 2016 may be representative of typical summer conditions in the Madrid region and included a concatenation of characteristic local circulation patterns (Plaza et al., 1997) with direct implications on ground-level O₃ (Querol et al., 2018; Escudero et al., 2019). Figure 3 presents both observed and modeled

concentration series at representative points (Figure 1), and shows the venting and accumulation days identified in Querol et al., (2018). The time series demonstrate that O₃ levels are significantly lower under venting conditions, although significant differences are found depending on the location, which supports the need to use high-resolution modeling systems to analyze pollution dynamics in the Madrid region. On the other hand, accumulation patterns tend to produce higher concentrations (up to 175 µg/m³), especially during July 27th.

It can be observed that the model is able to reproduce the temporal patterns, as confirmed by the high correlation coefficients (*r*) and index of agreement (IOA) shown in Table 1. The statistical evaluation demonstrates a reasonable model performance, yielding better statistical results than recent simulation studies in this domain. Pay et al. (2019) reported an aggregated correlation coefficient of = 0.66 and mean bias (MB) of 22.5 ug/m³ for the central region of the Iberian Peninsula. In this study, we obtained an average *r* value of 0.74 and a MB of 6.2 ug/m³. Of note, 95.2% and 66.7% of the *r* values for the locations of the 42 monitoring stations used in this study are larger than 0.6 and 0.7, respectively while the overall normalized mean bias (NMB) is only 9 %. The results for a series of common statistics (Borge et al., 2010) for each of the monitoring sites in our modeling domain can be found in Table S3. The model, however, may have some difficulties capturing the amplitude of observed O₃ series and fails to accurately reproduce concentration peaks some days. This is evidenced by the relatively large error in comparison with the bias (23% and 9%, respectively as an average over the 42 monitoring stations in the modeling domain). In the supplementary material (Table S4), we present a separate model performance assessment for accumulation and advective patterns showing that the main differences among them relate to errors, both MGE and RMSE that are systematically higher for accumulation periods. This may be related to the limitations of the meteorological model to depict atmospheric circulation during stagnant conditions suggested by Pay et al., (2019). Even when WRF was found to outperform other models for this particular episode (Escudero et al., 2019), the ability to reproduce wind direction and wind speed clearly deteriorates for accumulation periods, as shown in Table S5.,

As expected, results are poorer for urban background and traffic locations, since the typical spatio-temporal representativeness of the measurements in such locations is not comparable with that of a mesoscale modeling system, even with 1 km² spatial resolution.”

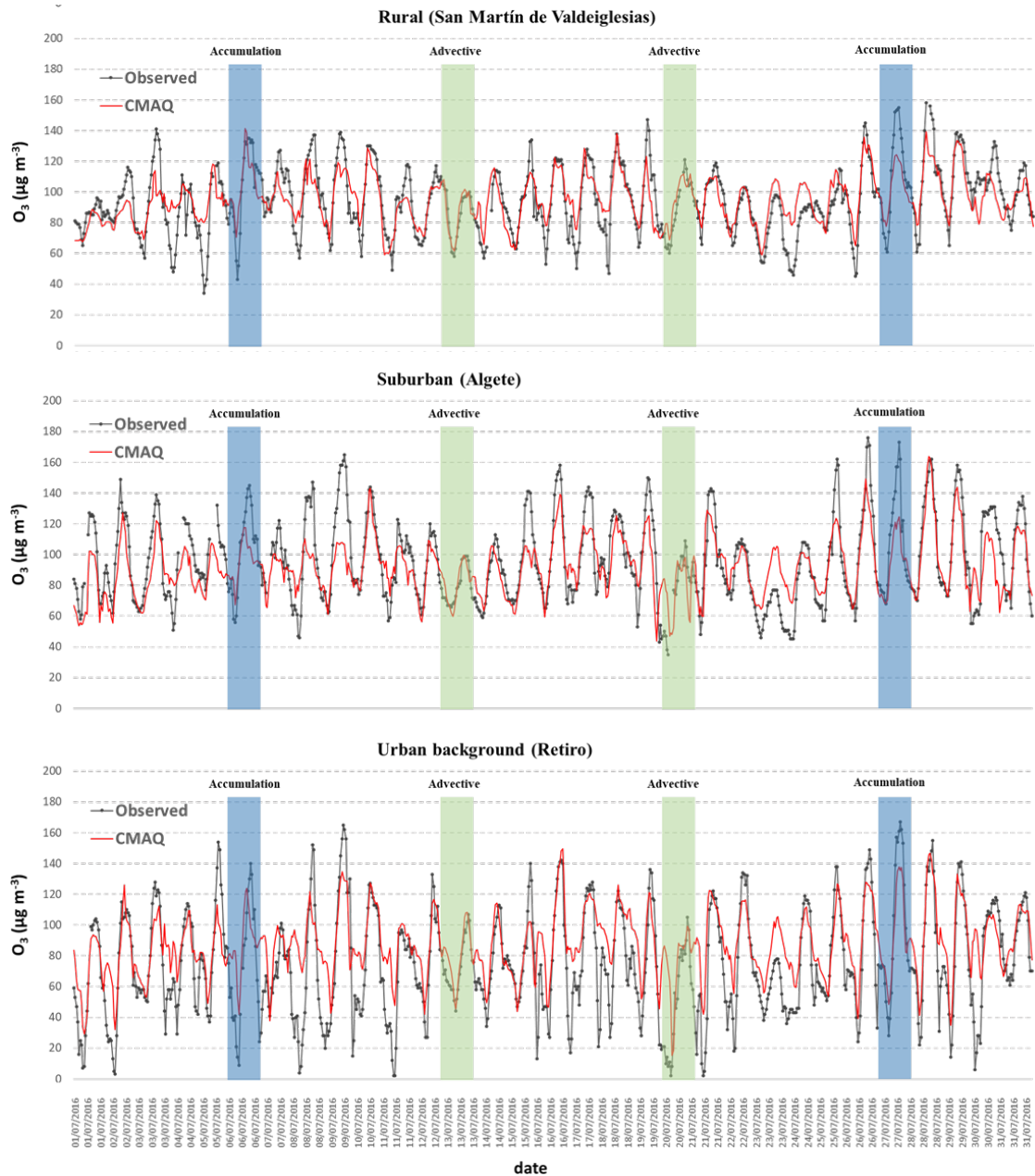


Figure 3. Observed and predicted concentration series for selected locations (1-SMV: a rural location in the southwestern area of Madrid region, 2-ALG: a suburban location in the northeastern area of Madrid region and 3-RET: an urban background site in Madrid city center).

And the new tables included in the supplementary material are:

Table S4. Model performance statistics (dimensionless unless noted otherwise) by station type and circulation pattern for ground-level O₃ concentration.

Station	Pattern	n	FAC2	MB (µgm ⁻³)	MGE (µgm ⁻³)	NMB	NMGE	RMSE (µgm ⁻³)	r	IOA
Rural	Accumulation	240	0.98	-6.7	15.29	-0.06	0.14	18.83	0.83	0.66
	Advection	232	0.98	3.1	9.31	0.04	0.11	12.97	0.83	0.73
	Other	3211	0.98	-3.0	14.01	-0.03	0.15	18.30	0.75	0.67
Suburban	Accumulation	474	0.96	-4.8	20.24	-0.05	0.20	26.69	0.76	0.68
	Advection	468	0.92	7.3	13.59	0.10	0.19	19.69	0.75	0.68
	Other	6412	0.94	2.6	17.18	0.03	0.20	23.22	0.73	0.68
Urban background	Accumulation	669	0.89	2.4	23.46	0.03	0.26	31.04	0.69	0.66
	Advection	670	0.89	11.4	16.95	0.17	0.25	22.34	0.72	0.60
	Other	9014	0.89	8.5	20.41	0.11	0.25	27.08	0.68	0.65
Industrial	Accumulation	96	0.95	4.7	16.40	0.05	0.18	20.15	0.86	0.73
	Advection	96	0.97	9.1	12.55	0.13	0.18	15.26	0.82	0.65
	Other	1278	0.95	7.9	14.54	0.10	0.18	18.79	0.83	0.71
Urban traffic	Accumulation	510	0.91	3.5	20.09	0.04	0.22	25.81	0.79	0.69
	Advection	522	0.87	15.8	18.22	0.25	0.28	24.55	0.69	0.55
	Other	7086	0.87	11.0	19.98	0.14	0.25	26.72	0.73	0.65

Table S5. Model (WRF) performance statistics by circulation pattern for basic meteorological variables

Variable	Pattern	FAC2	MB	MGE	NMB	NMGE	r	IOA
Temperature (T2)	Accumulation	1.00	-1.4 K	2.0 K	-0.05	0.07	0.92	0.81
	Advection	1.00	-0.5 K	1.5 K	-0.02	0.06	0.96	0.86
	Other	1.00	-0.8 K	1.6 K	-0.03	0.06	0.96	0.85
Wind speed (WS10)	Accumulation	0.63	0.9 m/s	1.7 m/s	0.31	0.63	0.30	0.33
	Advection	0.78	0.7 m/s	1.5 m/s	0.17	0.37	0.59	0.55
	Other	0.71	0.5 m/s	1.3 m/s	0.18	0.46	0.58	0.55
Wind direction	Accumulation	0.61	-34.3 °	90.7 °	-0.24	0.63	0.26	0.55
	Advection	0.87	6.5 °	34.5 °	0.05	0.25	0.79	0.81
	Other	0.77	-9.2 °	60.8 °	-0.06	0.38	0.53	0.68

General Comments

When you say that the contribution from biogenic emissions is relatively small and therefore excluded from the analysis, are you referring to the contribution to regional scale O₃? Could you consider including an evaluation of biogenic VOCs, e.g., a time series comparison of isoprene or a statement regarding the performance of the MEGAN model? Biogenic VOCs, in particular isoprene, are important contributors to O₃ formation during photochemical O₃ episodes, particularly in rural areas but also in urban environments (Dunker et al., 2016), due to their reactivity and abundance. You concluded that biogenic sources are responsible for 42.4% of the total VOCs domain-wide, so an important impact from this source should be expected.

We reformulated the narrative not to underestimate the influence of biogenic VOCs (BVOC) and compare our results with the findings of previous studies in the literature. We make clear that direct

comparison is not possible since the interpretation depends on the specific source apportionment methodology used and the specific model domain and scale of application.

Considering that caveat, we found that global and continental studies usually attribute a more important role to biogenic volatile organic compounds (BVOC) in the explanation of O₃ budgets. Nonetheless, our results seem consistent for other studies in the Iberian Peninsula or the Madrid region specifically. Nonetheless, we highlight the need to use caution comparing results from different studies, so the reader is not misled by methodological differences. We connect this discussion with the reactivity of specific VOCs for better understanding of the impact of VOCs on ground-level O₃. Following Reviewer #2's suggestion, we focus on isoprene to illustrate the question. Unfortunately, there are no routine measurements of isoprene in the Madrid region, but some measurements were performed during the experimental campaign of Querol et al., (2018) that are compared with our model predictions in Figure AC2 below (included in the supplementary material of our revised submission as Figure S3).

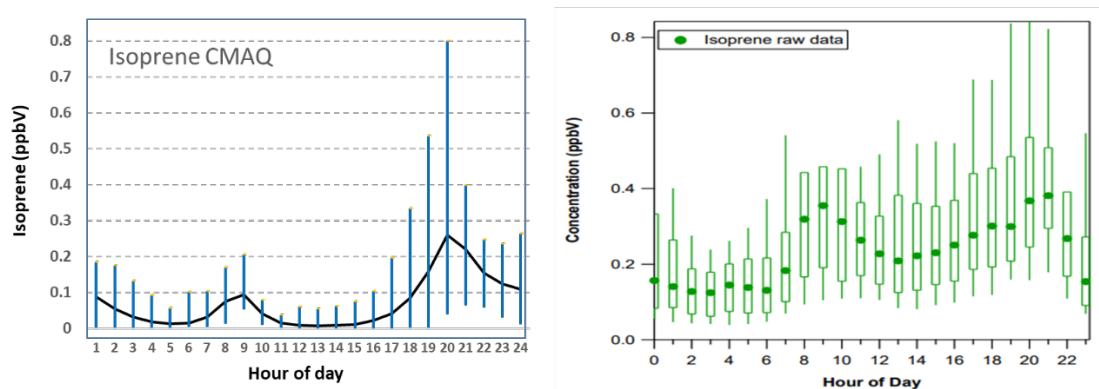


Figure AC2. Comparison of isoprene ground-level mixing ratios predicted by CMAQ (left) and measurements made in Majadahonda (suburban site) by Querol et al., (2018) (right). Both graphs present the hourly values during the day averaged over the period July 5th and July 19th. The source of the right-hand panel is Pérez et al., (2016).

Reference (added to the supplementary material):

- Pérez, N., A. Alastuey, C. Reche, M. Ealo, G. Titos, A. Ripoll, M.C. Minguillón, F. J. Gómez-Moreno, E. Alonso-Blanco, E. Coz, E. Díaz, B. Artíñano, S. García dos Santos, R. Fernández-Patier, A. Saiz-López, F. Serranía, M. Anguas-Ballesteros, B. TemimeRoussel, N. Marchand, D. C. S. Beddows, R. M. Harrison y X. Querol. Campaña intensiva de medidas de UFP, O₃ y sus precursores en el área de Madrid: medidas en superficie., https://www.miteco.gob.es/content/dam/miteco/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/anexo_informea33_madrid_tcm30-561368.pdf (last access: [January 22, 2004]), 2016.

Although the temporal pattern of isoprene was acceptably reproduced by CMAQ, the mixing ratio of this specie was underestimated by nearly a factor of 2 during the period where measurements were available. While this may be a potential factor to explain the relatively low impact, the literature suggests that other anthropogenic VOC may have a larger ozone formation potential

(OFP). More importantly, our results suggest that the contribution of all anthropogenic local emissions are more relevant than those of BVOC because O₃ formation in this study was mainly driven by NO_x emissions. The discussion about biogenics is included at the beginning of the revised section 3.2 (lines 297-305) and it reads as it follows:

“Figure 4 shows the contribution to ground-level O₃ concentration of the BC and that of all local anthropogenic emissions combined for both, monthly average and high values (illustrated by the 90th percentile, hereinafter P90). O₃ apportionment to biogenic emissions is not considered in Figure 4 because i) they have less interest from the point of view of possible abatement measures (Oliveira et al., 2023) and ii) their contribution is relatively small (below 4% to total O₃ levels in this period). However, it is not a negligible apportionment since biogenic emissions account for 27% (monthly mean) and 22% (P90) of total O₃ averaged over the Madrid region when BC and IC are not considered (Figure S1). In other words, their contribution represents around 21% and 28% of that of local anthropogenic emissions. This is a similar relative importance to that reported by Sartelet et al. (2012) at European scale. As well as Collet et al., (2018), they argue that the influence of BVOC becomes stronger on VOC-limited areas which is consistent with our findings (Figure S2), since the Madrid region is predominantly NO_x-limited in summer, except for the metropolitan area of Madrid city and surroundings, that remains VOC-limited all year round (Jung et al., 2022, Jung et al., 2023). Pay et al. (2019) did not quantify explicitly the contribution of biogenic emissions to ozone in the Iberian Peninsula. However, the contribution of “other”, that included emissions from SNAP 11 along with other sectors was around 5% in the center of the Iberian Peninsula, even though biogenic emissions represent a large fraction of total VOCs.

The contribution of BVOC to ozone levels in Europe reported by Tagaris et al. (2014), Karamchandani et al. (2017) or Zohdirad et al. (2022) are slightly larger (below 6%) and are even more according to some source apportionment at global scale for this latitude (Grewe et al. 2017; Butler et al., 2020). It should be noted that different experimental design and apportionment algorithms would lead to significant differences (Zhang et al., 2017; Borge et al., 2022) preventing the direct comparison of the results from different studies. Nonetheless, the contribution of biogenic emissions found in our work is not remarkably different than those previously reported, especially for this same geographical area.

Previous studies suggested that relatively low contributions of biogenic VOCs to O₃ levels may relate to underestimations of isoprene levels (Lupaşcu et al., 2022), a very relevant specie for O₃ chemistry (Dunker et al., 2016) that constitutes more than 25% of global biogenic VOC emissions Guenther et al. (2012). Nonetheless, it is widely recognized that BVOC emission estimates involve large uncertainties (Poupkou et al., 2010; Wang et al., 2017; Zhang et al., 2017) and the MEGAN model used in this study has been found to overestimate isoprene emissions (Wang et al. 2017 and references within). According to our inventory, isoprene represents 48% of total BVOC. While isoprene ambient measurements are not made routinely, Querol et al., (2018) recorded an average level of isoprene around 0.2 ppb in Majadahonda, a suburban site some 15 km away from downtown Madrid (in the west, northwest direction) between July 5th and July 19th, 2016. That is in relatively good agreement with the results of CMAQ in our simulation, that predicted slightly less than 0.1 ppb for that location and period and reproduced quite accurately the average daily pattern (see Figure S3).

Arguably, the relatively low contribution of BVOC in our and previous studies in this area (Valverde et al., 2016; Pay et al., 2019) may be a consequence of the underestimation of isoprene mixing ratios. However, that is compatible with the stronger influence of other anthropogenic VOC species reported elsewhere. Querol et al., (2018) estimated the total ozone formation potential (OFM) applying the maximum incremental reactivity (MIR) proposed by Carter (2009) to the VOC measurements made in their campaign for the same period and location than our study. Based on this methodology, they identified formaldehyde as the single most important compound (35.5% of total OFP) while isoprene was ranked 7th with an OFP below 5%. By family, primary BVOCs represented 6% of total OFP as an average during the experimental campaigns in this period. Similar studies elsewhere (e.g. Meng et al., 2022 in the Pearl River Delta region) conclude as well that the ozone formation potential of BVOCs is lower than that of anthropogenic VOCs applying a similar reactivity scale (Carter and Atkinson, 1989). That may be consistent with the apparent insensitivity of O₃ to isoprene emissions reported in other studies (Simpson, 1995; Jing et al., 2019; Ciccioli et al., 2023). “

References added:

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- Jung, D., Soler, R., de la Paz, D., Notario, A., Muñoz, A., Ródenas, M., Vera, T., Borrás, E., and Borge, R.: Oxidation capacity changes in the atmosphere of large urban areas in Europe: Modelling and experimental campaigns in atmospheric simulation chambers, *Chemosphere*, 341, 139919, <https://doi.org/10.1016/j.chemosphere.2023.139919>, 2023.

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Evaluation of the model is reported in the supplemental material and loosely mentioned in the manuscript. Please adjust section 3 and provide a quantitative statement of the model performance for meteorology and chemistry (especially O3) for the model domains, along with some plots. This could be a spatial contour plot showing the model and observed mean or P95 of O3 or time series of O3 at some representative sites.

Following the suggestion from Reviewer #2, we included a new subsection (3.1) to provide a better view of model performance. Please, see the response to a previous question related to this and the changes made.

Specific Comments

Line 32:33: ‘These measures, however, have failed to significantly improve ozone (O3) ambient concentration levels’. I feel this is a strong affirmation that needs to be re-phrased, taking into account the nonlinearity nature of O3 formation and the different aspects related to the concentrations observed in different chemical environments (e.g., urban, rural, and suburban) as well as the effects of emissions reductions such as the urban decrement.

Considering the point raised, we revised the sentence that now reads: “These measures, however, have **not reported comparable reductions of ozone (O₃) ambient concentration levels.**”

We don’t further elaborate on this because we feel it would be redundant with the following discussion in the introduction (lines 58-69 of the revised manuscript) about recent ozone trends.

Line 140: It would be helpful to have a paragraph describing how experiments were designed, for instance, how the chemical cycling is performed and how often the meteorology is restarted.

We provided additional information on the initialization of the meteorological model (WRF) in the supplementary material to complement the information about model setup and modeling spatial and temporal domains. Additionally, we amended Table S1 since it didn’t reflect the actual setup used in this experiment. Now the material in the supplement regarding WRF is as follows:

Table S1. WRF model physics options and parametrizations.

Option	Setup
Initialization	GFS
Shortwave radiation	Dudhia scheme
Longwave radiation	GFDL
Land-surface model	Noah LSM
Microphysics scheme	WSM 6-class Graupel scheme
PBL Scheme	YSU scheme
Surface Layer option	Monin-Obukhov
Cumulus Parametrization	No
Urban Physics	BEP (Building Environment Parameterization)
Nudging	Yes

The WRF model was initialized from global reanalysis made available by NCEP (National Centers for Environmental Prediction) from outputs of the GFS (Global Forecast System) (ds083.0). They have a spatial resolution of 1° x 1° and a temporal resolution of 6 hours ((00Z, 06Z, 12Z, 18Z). Data assimilation was applied (via nudging excluding the planetary boundary layer) for a more realistic representation of meteorological fields using both, surface observations from NCEP ADP Global Surface Observational Weather Data (ds461.0) and vertical soundings from NCEP ADP Global Upper Air Observational Weather Data (ds351.0).

References:

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Atmospheric Research, Computational and Information Systems Laboratory. <https://doi.org/10.5065/4F4P-E398>. Accessed 27 January 2016

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In addition, we clarified the interpretation of initial conditions, related to 24-h runs of the CMAQ model. We think this helps clarifying our experimental design and the interpretation of the results. For that we added an explicit discussion at the end of section 2 (lines 209-217) to make it clear before discussing the results:

“In addition to the attribution of O₃ **ambient levels** to the emissions within the modeling domain, hereinafter referred to as local sources, the contribution of boundary conditions (BC) and initial conditions (IC) are also estimated in this **study (labeled as BCO and ICO in Figure 12)**. Considering the typical O₃ daily patterns and the variability of circulation patterns, the latter refer to the **initial mixing ratios** on a daily (24 hour) basis, i.e., each day is run separately using the **outputs** from the previous day as IC. **This is a difference with most previous source apportionment studies that analyze shorter periods (Pay et al., 2019) or specific high concentration events (Lupaşcu et al., 2022; Zhang et al., 2022)**. While this may hinder the comparability of our results, this methodological option may be appropriate considering the temporal span of the period analyzed (a whole month), the typical diurnal cycle of O₃ and the goal of characterizing this attribution under specific meteorological conditions. This helps understanding differences on O₃ source apportionment depending on regional circulation patterns (Zhang et al., 2023) and explicitly considering the influence of vertical transport of O₃ from residual layers from previous days that may lead to rapid increases of O₃ concentrations near the surface (Qu et al., 2023 and references within). Therefore, this approach may be better suited to provide useful information for decision making, especially for the design of short-term action plans intended to control ozone peaks.”

References added:

- Lupaşcu, A., Otero, N., Minkos, A., and Butler, T.: Attribution of surface ozone to NO_x and volatile organic compound sources during two different high ozone events, *Atmos. Chem. Phys.*, 22, 11675–11699, <https://doi.org/10.5194/acp-22-11675-2022>, 2022.
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Line 249: The link provided does not work

Line 360: The link provided does not work

Thanks for letting us know. We have revised all links, including those of the references both new and those already included in the original manuscript.