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. NOx 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., (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 O_3 (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 O_3 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., 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 NOx 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 NOx 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 O_3 (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 O_3 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 O_3, 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 – NOx- or VOC-limited O_3 formation (Kwok et al., 2015) and from other studies where precursor attribution is directed by the user to either NOx 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 H_2O_2/HNO_3 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/959lYeSeEf4, 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 NOy, H_2O_2, and HNO_3 as indicators for ozone-NOx-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 O_3 P90 (close to 20% in some points), but this refers to the anthropogenic contribution, so it is in the range of 2% of total O_3 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.

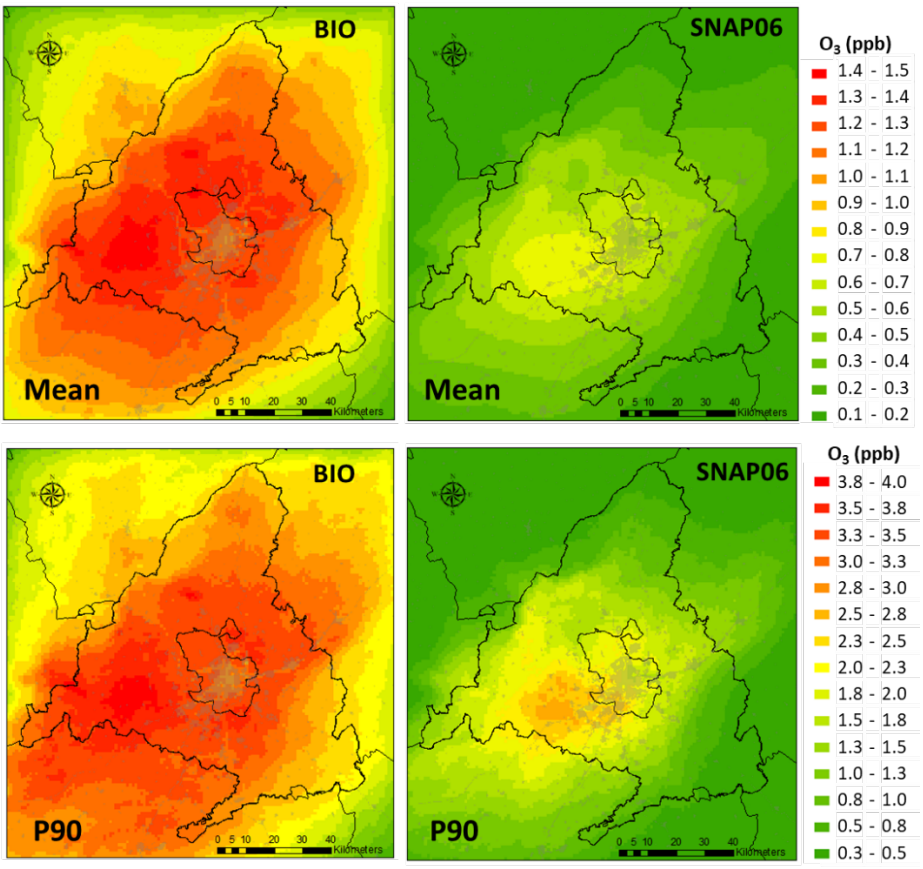

Figure AC1. Absolute contribution (ppb) to the monthly mean 1-hour 90th O_3 percentile of the SNAP 06 sector (use of solvents and other products) and biogenic emissions.

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 O_3 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 O_3 levels during July 2016 in the Madrid region. While the spatially-averaged attribution of O_3 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 O_3 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 O_3 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 O_3 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 O_3 levels in VOC-limited areas. On the contrary, the production of O_3 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 O_3 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.

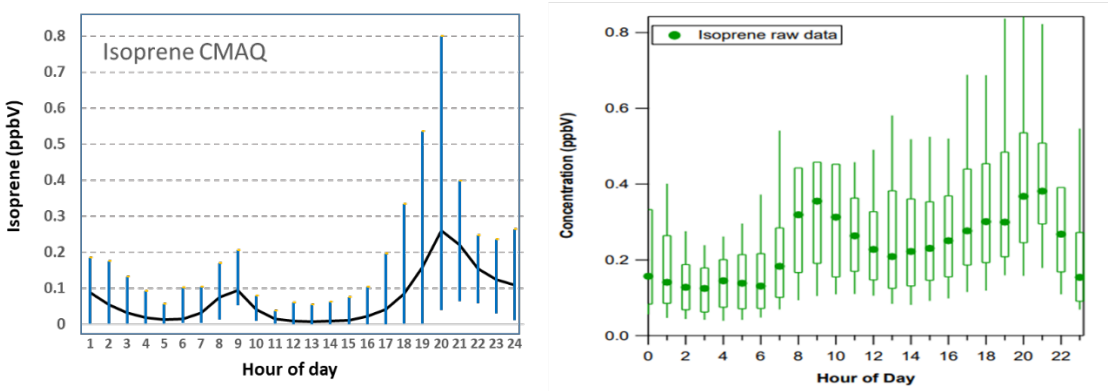

Figure AC2. Comparison of isoprene ground-level mixing ratios predicted by CMAQ (left) and measurements made in Majadahonda (suburban site) by Querol et al., (2018) (right). Both graphs present the hourly values during the day averaged over the period July 5th and July 19th. The source of the right-hand 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 O_3 ~~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). O_3 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 O_3 levels in this period). However, it is not a negligible apportionment since biogenic emissions account for 27% (monthly mean) and 22% (P90) of total O_3 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 O_3 levels may relate to underestimations of isoprene levels (Lupaşcu et al., 2022), a very relevant specie for O_3 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 (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 O_3 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
- Ciccioli, P., Silibello, C., Finardi, S., Pepe, N., Ciccioli, 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 O_3 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 O_3 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) group~~s~~ 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 O_3 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 O_3 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 O_3 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 O_3 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 O_3 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-O_3 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 O_3 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 O_3, 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 O_3 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 O_3 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-O_3 episodes. In addition, we think our

methodology may be illustrative for other regions worldwide to perform local source apportionment studies that may support subsequent O_3 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 patters identified in previous studies (Querol et al., 2018, Escudero et al., 2019) for O_3 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 O_3 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 O_3 levels
- Considering these new findings, we propose some options for future research that may further improve our understanding of complex O_3 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 O_3 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 O_3 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 O_3 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 O_3 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 O_3 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 O_3 ~~concentration~~ peaks than average values. This is particularly true under unfavorable, stagnation conditions associated with accumulation patterns when the highest O_3 values occur. According to our results, up to 35% of total O_3 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 O_3 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 O_3 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 O_3 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 O_3 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 NOx 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 $\mu g/m^3$ 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 $\mu g/m^3$, 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, NOx emissions account for both NO and NO_2 emissions collectively expressed as NO_2 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-termporally 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:

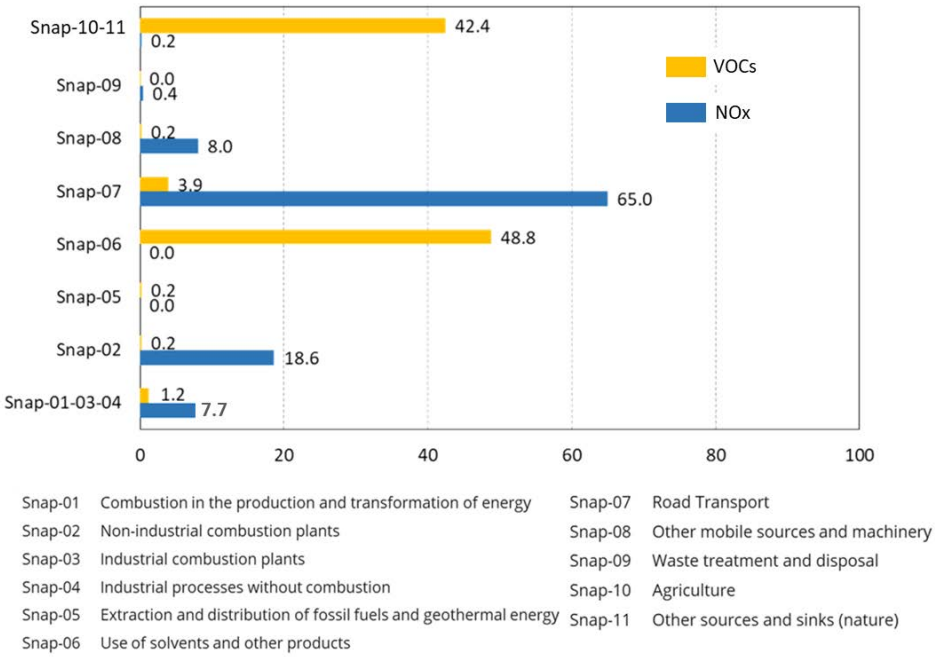

Figure. 2. NO_X and VOCs emissions of tagged sectors (percentage on an annual basis) for the source apportionment analysis.

5) Parts of the manuscript are confusing and missing a proper proof-reading. As example, on P5l197 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 O_3 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 O_3 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 O_3 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 O_3. Furthermore, the results shown in Figure 8 (Figure 9 now) suggest a robust model performance also to describe O_3 mixing rations 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 O_3 (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 O_3 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 $\mu g/m^3$), 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/m^3 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/m^3. 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 O_3 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 (Escuedero 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 km^2 spatial resolution."

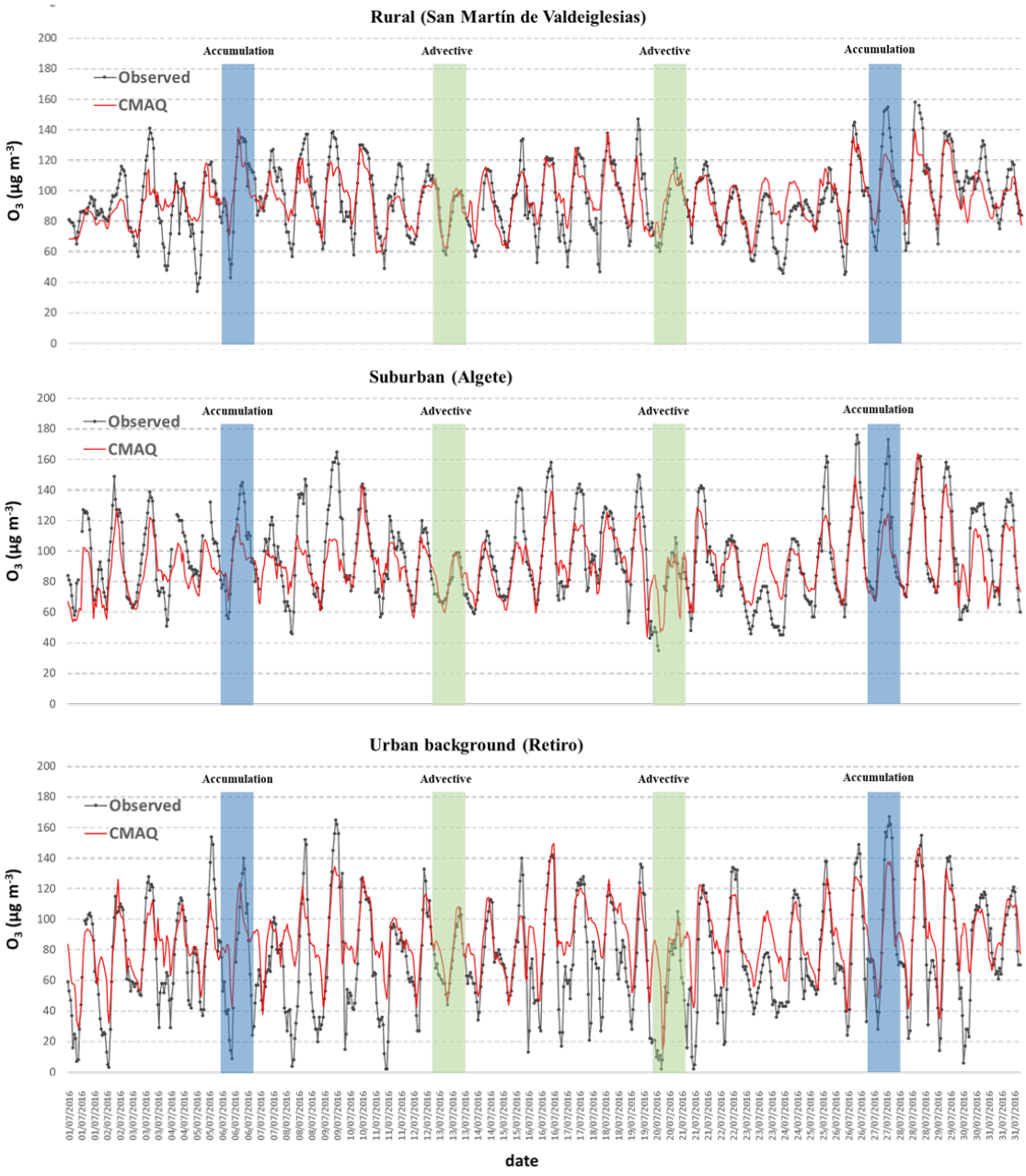

Figure. 3. Observed and predicted concentration series for selected locations (1-SMV: a rural location in the southwestern area of Madrid region, 2-ALG: a suburban location in the northeastern area of Madrid region and 3-RET: an urban background site in Madrid city center).

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 O_3 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
	Advective	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
	Advective	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
	Advective	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
	Advective	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
	Advective	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 º	90.7 º	-0.24	0.63	0.26	0.55
	Advection	0.87	6.5 º	34.5 º	0.05	0.25	0.79	0.81
	Other	0.77	-9.2 º	60.8 º	-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 O_3 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 O_3 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 O_3 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 O_3 and the goal of characterizing this attribution under specific meteorological conditions. This helps understanding differences on O_3 source apportionment depending on regional circulation patterns (Zhang et al., 2023) and explicitly considering the influence of vertical transport of O_3 from residual layers form previous days that may lead to rapid increases of O_3 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 NOx 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 O_3 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).

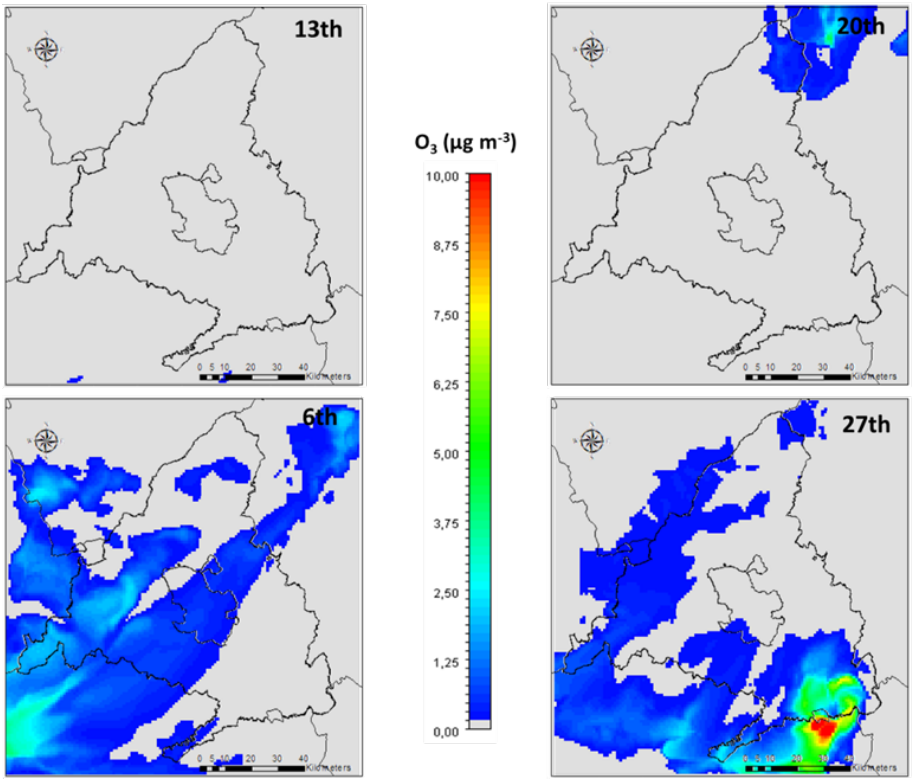

Figure AC3. Contribution of anthropogenic sources at the end of the day (23:59 PM) for advective conditions (July 13th and July 20th) and accumulation conditions (July 6th and July 27th)

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 O_3 from previous days, but it does not distort the sectoral analysis.

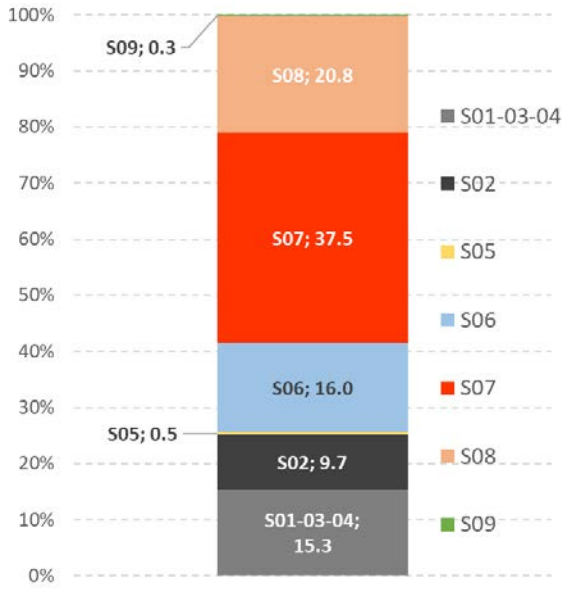

Figure AC4. Sectoral breakdown of the contribution of IC (BC excluded)

8) Some of the reference seems to be not adequate. As an example, P3l118 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., Lejarraga, 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-)

-p5l183 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-)

- P3l109 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. "

- p2l45 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 form O_3 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 O_3 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 O_3 (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 O_3 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 O_3 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 O_3 STE exclusively within our innermost nested domain and part of the O_3 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 NOx 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.

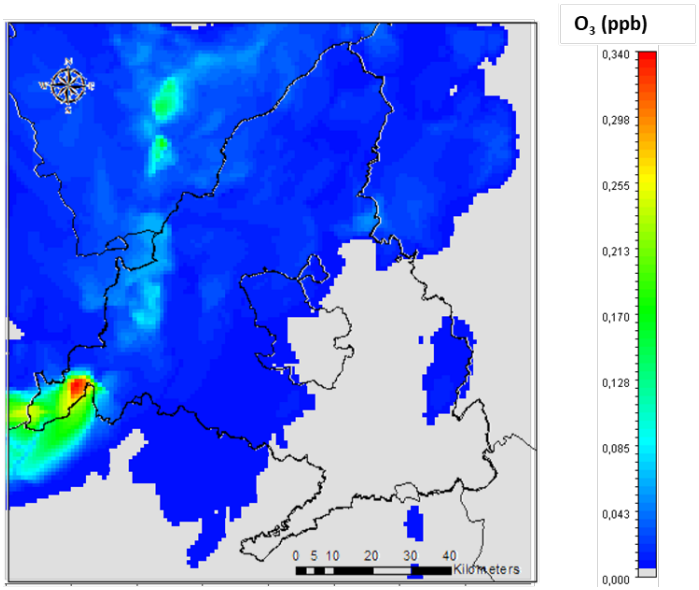

Figure AC5. Maximum 1-hour attribution of stratospheric transport (PVO3) to ground level

- P2l47ff 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.

- p2l58 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.

- p5l160 How is soil-NOx 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-NOX 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 χ emissions. Journal of Geophysical Research: Atmospheres, 100(D6), 11447-11464. https://doi.org/10.1029/95JD00370

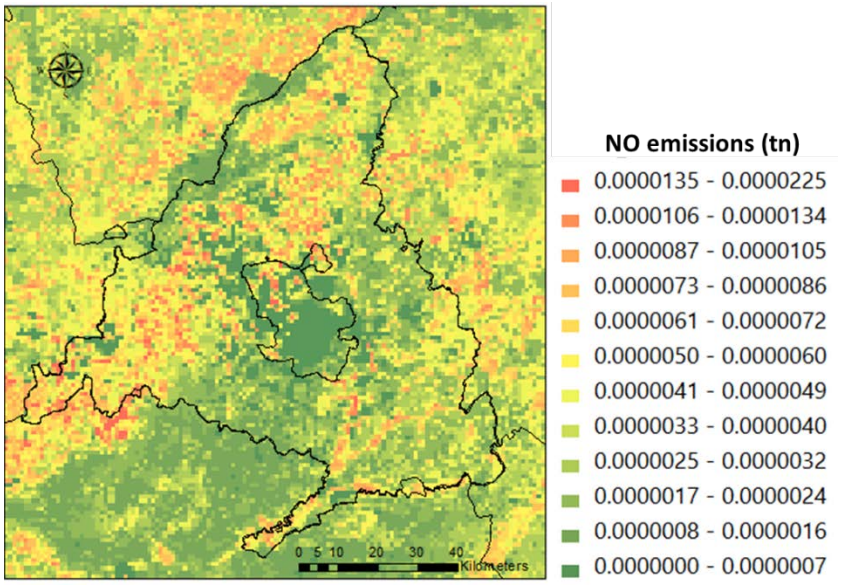

Figure AC6. Soil NO emissions (t) estimated in our modeling domain for July 2016

- 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 NO_2 but not for O_3. Both methods identified road traffic (SNAP 07) as the major local anthropogenic contributor but CMAQ-ISAM attributes a larger share of ground-level O_3 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.

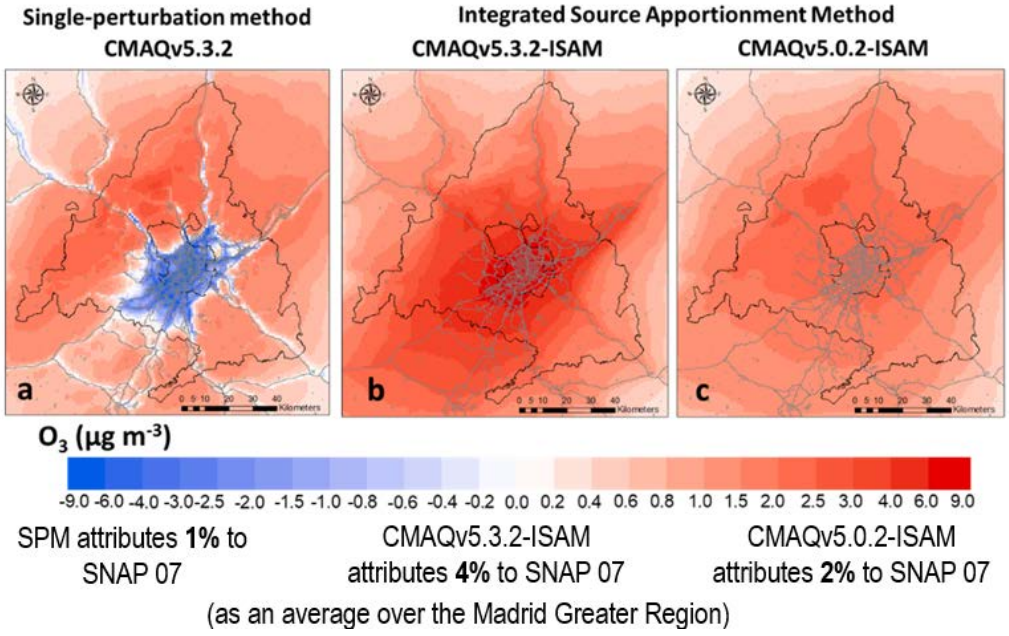

Figure AC7. Comparison of road traffic (SNAP 07) contribution to monthly average O_3 levels depending on the source apportionment methodology. Source: Borge et al., (2022)

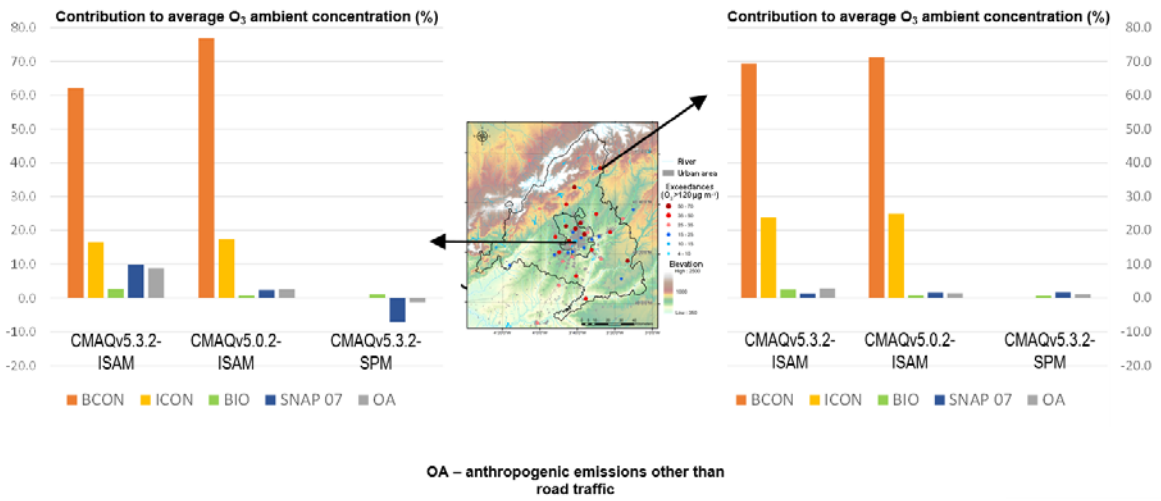

Figure AC8. Comparison average O_3 levels source apportionment in two different locations of the Madrid region (city center -left- and remote rural location -right-) depending on the source apportionment methodology. Source: Borge et al., (2022)

Reference

- Borge, R., de la Paz, D., Cordero J.M., Sarwar, G., Napelenok, S.: Comparison of Source Apportionment Methods to attribute summer tropospheric O_3 and NO_2 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 O_3 (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 O_3 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 O_3 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 NO_2 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 O_3 ~~concentration~~ levels have increased in Madrid by 30-40% during the 2007-2014. A greater decrease in NO emissions than in NO_2 emissions (with the subsequent reduction of the NO/NO_2 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 O_3, specially under specific weather patterns that may lead to high pollution levels (Zhang et al., 2023).”

Reference:

- Borge, R., Lumbreras, 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 NOx 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 NOx 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 O_3 (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 O_3 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 O_3, 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 – NOx- or VOC-limited O_3 formation (Kwok et al., 2015) and from other studies where precursor attribution is directed by the user to either NOx 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 H_2O_2/HNO_3 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/959lYeSeEf4, 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 NOy, H_2O_2, and HNO_3 as indicators for ozone-NOx-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 O_3 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 O_3. Furthermore, the results shown in Figure 8 (Figure 9 now) suggest a robust model performance also to describe O_3 mixing rations 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 O_3 (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 O_3 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/m^3), 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/m^3 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/m^3. 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 O_3 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 (Escuedero 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 km^2 spatial resolution.”

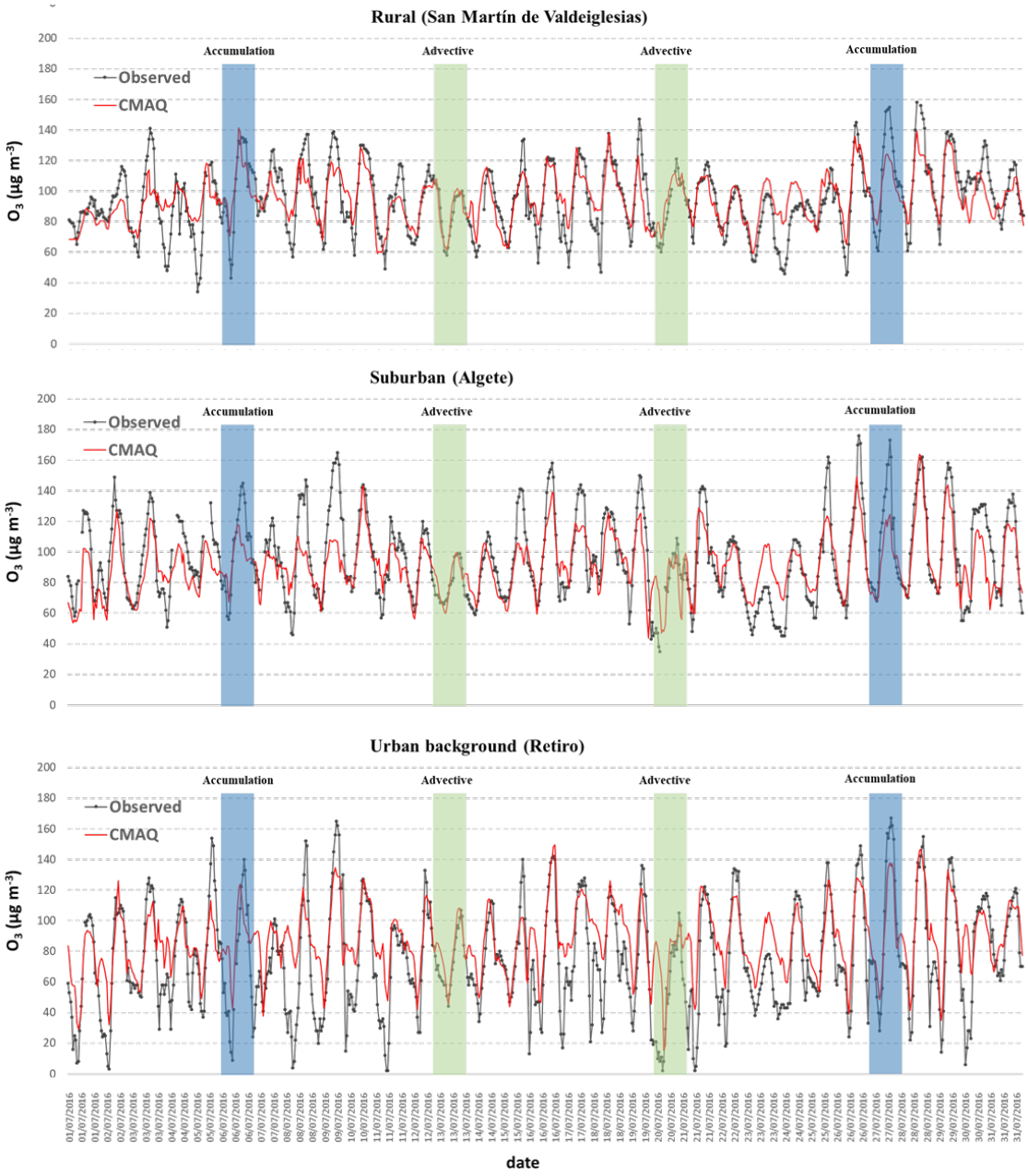

Figure. 3. Observed and predicted concentration series for selected locations (1-SMV: a rural location in the southwestern area of Madrid region, 2-ALG: a suburban location in the northeastern area of Madrid region and 3-RET: an urban background site in Madrid city center).

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 O_3 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
	Advective	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
	Advective	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
	Advective	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
	Advective	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
	Advective	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 º	90.7 º	-0.24	0.63	0.26	0.55
	Advection	0.87	6.5 º	34.5 º	0.05	0.25	0.79	0.81
	Other	0.77	-9.2 º	60.8 º	-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 O_3 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 O_3. 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).

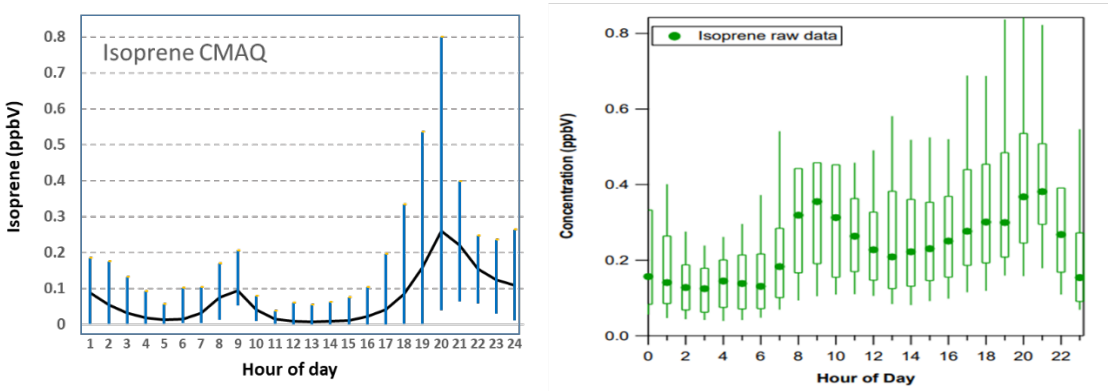

Figure AC2. Comparison of isoprene ground-level mixing ratios predicted by CMAQ (left) and measurements made in Majadahonda (suburban site) by Querol et al., (2018) (right). Both graphs present the hourly values during the day averaged over the period July 5th and July 19th. The source of the right-hand 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 NOX 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 O_3 ~~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). O_3 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 O_3 levels in this period). However, it is not a negligible apportionment since biogenic emissions account for 27% (monthly mean) and 22% (P90) of total O_3 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 al 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 O_3 levels may relate to underestimations of isoprene levels (Lupaşcu et al., 2022), a very relevant specie for O_3 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 O_3 to isoprene emissions reported in other studies (Simpson, 1995; Jing et al., 2019; Ciccioli et al., 2023). "

References added:

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- 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.
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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 (O_3) 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 1º x 1º 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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- Satellite Services Division/Office of Satellite Data Processing and Distribution/NESDIS/NOAA/U.S. Department of Commerce, and National Centers for Environmental Prediction/National Weather Service/NOAA/U.S. Department of Commerce. 2004, updated daily. NCEP ADP Global Upper Air Observational Weather Data, October 1999 - continuing. Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory. https://doi.org/10.5065/39C5-Z211. Accessed 25 January 2016.

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 O_3 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 O_3 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 O_3 and the goal of characterizing this attribution under specific meteorological conditions. This helps understanding differences on O_3 source apportionment depending on regional circulation patterns (Zhang et al., 2023) and explicitly considering the influence of vertical transport of O_3 from residual layers form previous days that may lead to rapid increases of O_3 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:

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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.

Summertime tropospheric ozone source apportionment study in the Madrid region (Spain)

David de la Paz[1], Rafael Borge[1], Juan Manuel de Andrés[1], Luis Tovar[1], Golam Sarwar[2], Sergey L. Napelenok[2]

[1]Laboratory of Environmental Modelling, Department of Chemical & Environmental Engineering, Universidad Politécnica de Madrid, (UPM), c/ José Gutiérrez Abascal 2, 28006, Madrid, Spain

[2]Center for Environmental Measurement & Modeling, U.S. Environmental Protection Agency, Research Triangle Park, NC, USA

Correspondence to: Rafael Borge (rafael.borge@upm.es)

Abstract. The design of emission abatement measures to effectivly reduce high ground-level ozone (O_3) concentrations in urban areas is very complex. In addition to the strongly non-linear chemistry of this secondary pollutant, precursors can be released by a variety of sources in different regions and locally produced O_3 is mixed with that transported from the regional or continental scales. All of these processes depend also on the specific meteorological conditons and topography of the study area. Consequently, high-resolution comprehensive modeling tools are needed to understand the drivers of photochemical pollution and to assess the potential of local strategies to reduce adverse impacts from high tropospheric O_3 levels. In this study, we apply the Integrated Source Apportionment Method (ISAM) implemented in the Community Multiscale Air Quality (CMAQv5.3.2) model to investigate the origin of summertime O_3 in the Madrid region (Spain). Consistent with previous studies, our results confirm that O_3 levels are dominated by non-local contributions, representing around 70% of mean values across the region. Nonetheless, precursors emitted by local sources, mainly road traffic, play a more important role during O_3 peaks, with contributions as high as 25 ppb. The potential impact of local measures is higher under unfavorable meteorological conditions associated with regional accumulation patterns. These findings suggest that this modeling system may be used in the future to simulate the potential outcomes of specific emission abatement measures to prevent high-O_3 episodes in the Madrid metropolitan area.

1. Introduction

Air pollution is one of the main environmental problems and is recognized as a global threat to public health. In 2019, 4.2 million people died prematurely worldwide as a result of a poor air quality (WHO, 2021). Even in regions that have taken decisive actions to curb emissions, such as Europe, over 300,000 premature deaths (EU27) are currently associated to air pollution, most of them related to high levels of $PM_{2.5}$ (particles with aerodynamic diameter of ≤ 2.5 microns) (238,000) and NO_2 (nitrogen dioxide) (49,000) (EEA, 2022). In recent years, concentrations of many of the regulated pollutants in Europe have decreased as a result of a general reduction of emissions. From 2009 to 2018, the concentration of PM_{10} (particles with aerodynamic diameter of ≤ 10 microns), $PM_{2.5}$ and NO_2 diminished on average by 19%, 22% and 18-23% (depending on the air quality monitoring station type), respectively (EEA, 2020). These measures, however, have not reported comparable reductions of ozone (O_3) ambient concentration levels.

Tropospheric O_3 is a secondary pollutant formed from photochemical reactions between many different precursors, mainly nitrogen oxides (NO_x = NO (nitric oxide) + NO_2) and non-methane volatile organic compounds (VOCs) (Seinfeld and Pandis, 2016; Jenkin and Clemitshaw, 2000; Monks et al., 2015). According to the last European Union (EU) emission inventory

report (EEA, 2022), the most important activity sectors regarding O_3 precursors emissions are the "Road transport" sector (7% and 37% of total VOCs and NO_X emissions, respectively), the "Commercial, institutional and households" sector (15% and 14%, respectively) and the "Solvent and product use" sector, representing 42% of total VOCs emissions. Once emitted from urban and industrial areas, these precursors are subsequently transported by the prevailing wind regime (Xu et al., 2011). Atmospheric life-time of O_3 depends on numerous variables. In the boundary layer, atmospheric life-time of O_3 is short, roughly 1 or 2 days, depending on the abundance of precursors (Young et al., 2013). In the free troposphere, its lifetime can be of up to 2 weeks, time enough to be transported long distances, from the local to the global scale (Monks et al., 2015; Stevenson et al., 2006). In addition to in-situ formation, transport of O_3 from the stratosphere is also relevant to explain the tropospheric ozone levels (IPCC, 2007; Hsu et al., 2005). Furthermore, this gas exchange between layers of the atmosphere is 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.

Due to these complex dynamics, tropospheric O_3 levels have not decreased (Jung et al., 2022; Sicard et al., 2023) in accordance to significant NO_X and VOCs emissions reduction (45% and 41%, respectively in the 2009- 2018 period). As a result, 12% of the urban population in Europe is still exposed to high O_3 concentrations according to EU regulations, with a toll of 24,000 premature annual deaths (EEA, 2022), especially in the Mediterranean basin (Amann, 2008; EEA, 2018, EEA, 2020). The share of urban population that suffers from excessive exposure to O_3 rises to 95% (EEA, 2022) when the World Health Organization (WHO) guidelines are considered (WHO, 2021). Of note, tropospheric O_3 produces both short-term (Bates et al., 1972; Bell et al., 2004; Goodman et al., 2018) and long-term health effects (Jerrett et al., 2009; Seltzer et al., 2018), impacting the population living in large urban agglomerations as well as their surroundings. Moreover, it also may have relevant effects on ecosystems (De Andrés et al., 2012; Mills et al., 2011; Harmens et al., 2011) and climate (Sitch et al., 2007; Stocker et al., 2013; IPCC, 2015).

Globally, the latest studies using satellite data suggest that tropospheric O_3 average ~~concentration~~ levels increased over the last four decades (Ziemke et al., 2019; Gaudel et al., 2018). (Paoletti et al., 2014) evaluated observations from monitoring stations in the United States (US) and Europe from 1990 to 2010 and concluded that the O_3 annual average increased by 7%/year in rural stations and around 12-17%/year (US and EU, respectively) in urban stations. However, O_3 formation is highly non-linear and trends may change depending on the evaluated time period and region, the metric used, and other local factors such as topography or the proximity to the precursor's emission sources (Reche et al., 2018; Massagué et al., 2023). According to specific studies for the Iberian Peninsula, the trend of the annual average of O_3 for rural stations in the 2004-2012 period was not clear (Querol et al., 2014). In contrast, an increasing trend around 1 – 3%/year was observed in all seasons in urban, traffic and industrial stations. (Borge et al., 2019) reported an average increase of 10 $\mu g \cdot m^{-3}$ of daily 8-hour maximum O_3 moving average concentrations (MDA8) for the 1993-2017 period. However, they detected that the highest increase related to fall and winter months (up to 19 $\mu g \cdot m^{-3}$), in agreement with general increases of the oxidation capacity in the atmosphere of the largest urban areas in Europe modeled by Jung et al. (2022).

Nonetheless, the O_3-forming photochemical activity is largely regulated by weather conditions, especially temperature and solar radiation. For this reason, tropospheric O_3 formation has a marked seasonal character, with the highest O_3 ~~concentration~~ values typically recorded in spring and summer (Logan, 1985; Granados-Muñoz and Leblanc, 2016), especially in those locations that are highly influenced by nearby urban areas (Brodin et al., 2010; Carnero et al., 2010) where large amounts of precursors are emitted. Therefore, understanding summertime O_3 dynamics is more 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 O_3 (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 O_3 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 (Lupașcu 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 O_3 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 NO_2 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 O_3 ~~concentration~~ levels have increased in Madrid by 30-40% during the 2007-2014. A greater decrease in NO emissions than in NO_2 emissions (with the subsequent reduction of the NO/NO_2 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 O_3, specially under specific weather patterns that may lead to high pollution levels (Zhang et al., 2023).

In this research, we apply a state-of-the-science air quality model to provide insights into the emission sources and transport patterns which are involved in the formation of tropospheric O_3 during typical summertime conditions in the Madrid region. In addition to contributing to the scientific understanding of photochemical pollution, the final purpose of this work is to inform the decision-making process needed to design further emission reduction measures in the study area.

2. Methodology

2.1. Modeling system

The research is supported by a mesoscale modeling system with three main components. Meteorological fields are generated by WRFv3.7.1 (Weather Research and Forecasting) (Skamarock and Klemp, 2008). Physics options and parameterizations (Table S1 in the supplement) are based on previous studies (Borge et al., 2008a; de la Paz et al., 2016) and WRF outputs were postprocessed with MCIP v5.1 (Meteorology - Chemistry Interface Processor) (Otte and Pleim, 2010). Emission processing

relies on the US EPA SMOKEv3.6.5 (Sparse Matrix Operator Kernel System) model (Institute and Environment, 2015; Baek and Seppanen, 2018) that has been specifically adapted for the Iberian Peninsula (Borge et al., 2008b; Borge et al., 2014). Biogenic emissions are generated by MEGAN v2.1 (Model Emissions Gases and Aerosols from Nature) (Guenther, 2006; Guenther et al., 2012). The third component is the CMAQv5.3.2 (Community Multiscale Air Quality) modeling system (Byun and Schere, 2006; Ching and Byun, 1999). This 3D chemical-transport model (CTM) simultaneously predicts the concentration of all relevant substances considering transport (advection and diffusion), chemical transformation and deposition. Gas-phase atmospheric chemistry is represented by the Carbon Bond 6 (CB06) (Yarwood et al., 2010) chemical mechanism with chlorine chemistry (CB06r3) (Sarwar et al., 2012; Whitten et al., 2010, Emery et al., 2015) according to SPECIATE 4.0 (Hsu et al., 2006) while the module AERO6 (Appel et al., 2013) is used to describe aerosol dynamics and chemistry. Considering the influence of different scales, from the continental to the regional-urban, on O_3 levels (Valverde et al., 2016; Pay et al., 2019; Baker et al., 2016; Han et al., 2018), boundary conditions are of particular interest. Previous studies in the Iberian Peninsula have demonstrated that O_3 is particularly sensitive to boundary conditions (Borge et al., 2010). For a more realistic representation of the boundary influence, the mother domain receives 1 hour-resolution, dynamic chemical boundary conditions from hemispheric CMAQ (Mathur et al., 2017) simulations.

~~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 O_3 (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 O_3 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 O_3, 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 – NOx- or VOC-limited O_3 formation (Kwok et al., 2015) and from other studies where precursor attribution is directed by the user to either NOx 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 H_2O_2/HNO_3 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).

2.2. Modeling domains

The three nested domains shown in Figure 1 were used to perform ~~the~~ numerical simulations in this study. This layout is intended to capture medium (Millán et al., 1991) and long-range influences of O_3 transport (Zhang et al., 2020; Qu et al., 2021; Brook et al., 2013) and to provide enough resolution over the area of interest to depict local dynamics (Plaza et al., 1997; Borge et al., 2022). The mother domain (D1) includes Europe and Northern Africa with a 12 km x 12 km spatial resolution while D2 is centered over the Iberian Peninsula and has a 4 km x 4 km spatial resolution (Table S2 in supplement). The innermost domain (D3) used in this study covers Madrid and surrounding areas with 1 km^2 spatial resolution (136 km in the east-west direction and 144 km in the north-south direction). All three domains have a common 35-level vertical structure covering the whole Troposphere with 18 layers within the first kilometer to accurately represent atmospheric processes within the planetary boundary layer (Borge et al., 2010).

The region has a continental Mediterranean climate with an annual mean temperature of 14.6 ºC and 367 mm of accumulated precipitation with a typical summer drought (https://www.madrid.org/iestadis/fijas/coyuntu/otros/cltempe.htm). The Central Range (Sierra de Guadarrama), with maximum elevations of 2500 meters above sea level (m.a.s.l.), crosses the D3 modeling domain in the NE-SW direction and divides it into two main regions; the northern and southern plateaus of the Iberian Peninsula. The southern half of the domain, where the city of Madrid (with an average elevation of 657 m) is located, features the Tajo river basin. This topography configures a dominant wind circulation along the NE-SW direction and enhances anticyclonic stagnation conditions (Plaza et al., 1997; Querol et al., 2018) usually induced by the semi-permanent Azores High (García et al., 2002). O_3 formation typically peaks with high temperature and solar radiation under stagnation conditions (Querol et al., 2018; Reche et al., 2018; Garrido-Pérez et al., 2020) that often occur at summertime.

2.3. Temporal domain

Model simulations were completed for July 2016, using a previous 3-day period as model spin-up. According to the Spanish Meteorological Agency (AEMET, 2017) it was an unusually warm month (with an average temperature of 25.5 ºC), being the 4th hottest month of July since 1961 in the Iberian Peninsula. It was also a dry month, with 13% less precipitation than the average of the month in the 1981-2010 reference period. Considering the meteorological trends in this region (Borge et al., 2019), it may be considered as a representative summer period for modern weather conditions. More importantly, this period was selected because of an intensive experimental campaign carried out to characterize ozone episodes in Madrid and surroundings (Reche et al., 2018). This period was thoroughly analyzed by (Querol et al., 2018) that identified two typical circulation patterns associated to venting and accumulation episodes. The later are characterized by weak wind forcing (wind speed <4-5 m s^{-1}), stable conditions and air stagnation that favor O_3 local formation. Oppositely, stronger winds (> 7 m s^{-1}) promote advection and prevents from reaching O_3 peaks under venting conditions.

During this period (2016), 26 out of the 42 air quality monitoring stations in the innermost (D3) modeling domain (Figure 1), recorded exceedances of the concentration threshold related to the O_3 target value for the protection of human health (MDA8 > 120 $\mu g \cdot m^{-3}$). The highest number of exceedances (up to 359 in the month, 47% of total annual exceedances) were found around the Madrid metropolitan area, in the city outskirts. Of note, no exceedances of the MDA8 were recorded downtown Madrid.

2.4. Emission sources for the apportionment analysis

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, 2021). These inventories are compiled according to the EMEP/EEA standardized methodology (EEA, 2019) and are conveniently adapted, spatio-termporally resolved for modeling purposes (Borge et al., 2008b; Borge et al., 2018) and consistently combined for the different modeling domains (Borge et al., 2014).

The share of NO_X and VOCs emissions of each SNAP (Selected Nomenclature for Air Pollution) group~~s~~ 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). 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.

Consequently, 8 emission sources were tagged for the source apportionment analysis of ambient O_3 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 O_3 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 O_3 daily patterns and the variability of circulation patterns, the latter refers 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 O_3 and the goal of characterizing this attribution under specific meteorological conditions. This helps understanding differences on O_3 source apportionment depending on regional circulation patterns (Zhang et al., 2023) and explicitly considering the influence of vertical transport of O_3 from residual layers form previous days that may lead to rapid increases of O_3 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.

3. Results

The results are presented in four subsections. Firstly, the main features of the simulated period and model performance are presented. Then, an overview of the source apportionment analysis carried out in the study area for the whole month is discussed. Finally, this same analysis is performed for two specific days representative of different circulation patterns defined by Querol et al. (2018): advective pattern (July 13th) and accumulation pattern (July 27th). Additional information for July 20th and July 6th, identified by Querol et al. (2018) as advective and accumulation days, respectively, is provided in the supplement. Finally, the temporal patterns of the O_3 apportionment are examined at the location of the air quality monitoring stations within ~~in~~ the simulation domain. Aggregated results by station type are discussed in 3.4 while the results for different geographical areas relative to the location of Madrid city (quadrants) are presented in the supplement.

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 O_3 (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 O_3 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/m^3), 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/m^3 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/m^3. 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 O_3 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 km^2 spatial resolution.

3.2. Spatial analysis of the source apportionment assessment

Figure 4 shows the contribution to ground-level O_3 ~~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). O_3 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 O_3 levels in this period). However, it is not a negligible apportionment since biogenic emissions account for 27% (monthly mean) and 22% (P90) of total O_3 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 O_3 levels may relate to underestimations of isoprene levels (Lupaşcu et al., 2022), a very relevant specie for O_3 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 in the supplementary material).

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 O_3 to isoprene emissions reported in other studies (Simpson, 1995; Jiang et al., 2019; Ciccioli et al., 2023).

In addition, we tagged stratospheric ozone (PVO3 in Figure 12) due to the influence of vertical injections on ground level O_3 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 O_3 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 O_3 STE exclusively within our innermost nested domain and part of the O_3 attributed to BC may be related to contributions from the Stratosphere in other regions.

Both monthly average and high ~~concentration~~ O_3 values (illustrated by the 90th percentile, hereinafter P90) come mostly from BC. This is consistent with previous studies that have identified boundary conditions as the dominant contribution to ground-level O_3, i.a. Pay et al. (2019) for the Iberian Peninsula, ~~(~~Collet et al.~~,~~ (2018) for the USA or ~~(~~de la Paz et al.~~,~~ (2020) for Madrid specifically. However, the weight of each of the sources on both metrics is different. As an average, 70% of the mean O_3 ~~concentration~~ levels in the Madrid region comes from BC (Figure 4a), while for P90, the contribution from BC is considerably smaller, around 50% (Figure 4b).

The maximum anthropogenic contribution for the monthly average (Figure 4c) reaches 17% (7.5 ppb in absolute terms), with a mean contribution of 8.7% over the whole Madrid Region (Figure S1). Regarding P90 (Figure 4d), the maximum contribution of local anthropogenic emissions is 28% (in the center and southwest of the Madrid municipality), around 22 ppb in absolute terms. This corresponds to a spatially averaged contribution of 12.2% over the Madrid (Figure S1), which corresponds to an absolute value around 11 ppb. Despite the general dominance of BC on O_3 levels, these results point out the relevance of local emissions (Figure 2) is higher for O_3 peaks, a consistent finding with those of previous studies (Valverde et al., 2016; Qu et al., 2023).

Figure 5 shows the apportionment to P90 of each emission sector for local sources. Consistently with Valverde et al. (2016) and Pay et al., (2019) our results clearly identify road transport (SNAP07) as 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). In absolute terms, this means an average contribution of 5 ppb and a maximum one of 11 ppb (Figure S5). The next sector with the highest contribution relates to off-road mobile sources (SNAP08), with an average contribution in the Madrid region of 17% (1.8 ppb) and a maximum of 8 ppb in the vicinity of the Adolfo S)uárez 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 O_3 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 O_3 levels during July 2016 in the Madrid region (see Figure S2). While the spatially-averaged attribution of SNAP 06 to P90 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 O_3 P90 (Figure 5c). 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 O_3 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).

If the analysis is done on a daily basis, it is worth noting the significance of the initial conditions (IC) as well, with a spatially-averaged contribution of 19% and of 34% to monthly average and P90 O_3 levels, respectively (Figure S1). However, the role of IC is more relevant to analyze how meteorological conditions may affect the source apportionment. Of note, in this study IC refers to O_3 from the previous 24-hour period. Consequently, the effect of IC on O_3 does not necessarily diminish throughout the month. Instead, we found that the influence of IC relates mainly to regional circulation patterns. We elaborate on this in the following sections.

3.3. Source apportionment assessment under characteristic circulation patterns

The study of the influence of meteorology on the O_3 ambient levels is carried out by analyzing the results for specific days representative of the two circulation patterns. Querol et al., (2018) identified an advective pattern for 13th and 20th July and an accumulation pattern for 6th and 27th July. In this section, we examine the source apportionment for those dates (13th and 27th in more detail) to test the hypothesis that local atmospheric conditions may induce a significant difference on O_3 attributions, as reported elsewhere (Zhang et al., 2023).

Figure 6 shows the daily average and the P90 of hourly O_3 levels during the accumulation and advective episodes. It is observed that during accumulation days (6th and 27th), mixing rations averaged over the Madrid region were 13 - 20% higher than those of advective periods (days 13th and 20th) and, although not shown, around 4 - 8% higher than the monthly average. Regarding the maxima, the average P90 (3rd highest hourly mixing ratio for a given day) during the accumulation periods in the Madrid region may be 25% higher than that of the ventilation periods.

3.3.1. Accumulation pattern

Consistent with previous studies that highlight the role of meteorology on O_3 (Nguyen et al., 2022), modeling results show that accumulation days are especially relevant regarding the potential impacts on health and vegetation and a deeper analysis of pollution dynamics under those conditions is of interest. Figure 7 shows the hourly evolution (3:00, 9:00; 15:00, 21:00 UTC) of surface O_3 mixing ratios during the day 27th (day 6th is shown in Figure S7), along with O_3, NOx and VOCs vertical levels up to 5 km height for a NE-SW cross section, related to the dominant wind directions (the same results for a perpendicular SE-NW cross section are shown in Figure S8 in the supplement).

A low O_3 mixing ratio surface layer (around 40 ppb) can be clearly seen for early hours of the day (03:00 UTC, 05:00 local time). This relates to a shallow Planetary Boundary Layer (PBL) (a few hundred meters high) and weak winds from the NE (between 1-2 m s^{-1}). Around 6:00 UTC (08:00 local time), the main emitting sectors (such as road transport) begin to emit O_3 precursors (see ~~(~~Quaassdorff et al.~~,~~ ~~(~~2016) for characteristic emission temporal profiles). The prevailing surface wind directs the urban plume towards the SW and the southern slope of the Sierra de Guadarrama (Figure S6). Of note, the wind direction aloft is the opposite, in accordance with recirculation processes reported for this domain (Plaza et al., 1997). As the day progresses (09:00 UTC, 11:00 local time), the PBL height grows (up to 1.5 km) as radiation and temperature increase, mixing O_3 vertically. At the same time, the emissions of precursors (concentrated in the Madrid city, MD) lead to an increase in the local production of O_3 in the plume, more evidently in the rural areas (NOx limited regions) in the leeward side of the city. On the contrary, in the vicinity of high NO_X emission intensity areas, O_3 is consumed by NO through the reaction $NO+O_3 \rightarrow NO_2 + O_2$, a titration effect documented in previous studies (Saiz-Lopez et at., 2017).

Over the following mid-day hours (09:00-15:00 UTC, 11:00-17:00 local time) the PBL further develops and a vertical homogenization process occurs. There is a deep vertical mixing of newly formed ozone with O_3-enriched upper layers generated in previous days (Querol et al., 2018; Escudero et al., 2019). As illustrated in Figure 8, there is a first O_3 reservoir located around 1500 m altitude (at 00:00 UTC, 02:00 local time) that relates mainly to local sources and contributes with 2-8 ppb, while higher O_3 reservoirs (around 4000 meters a.s.l) relate to BC and have a considerably higher contribution (50-75 ppb). Around 15:00 UTC (17:00 local time) the PBL reaches 3000 - 4000 m in accumulation periods and O_3 levels up to 75 - 80 ppb are found (Figure 7). This dynamics is compatible with the ozone sounding (~~http://www.woudc.org/data/metadata/query_results_platform_e.html?Platform=308~~ https://woudc.org/data/explore.php) included in Figure 9, that shows a very constant O_3 value around 65 to 70 ppb from the surface to 4000 m a.s.l.

Later, around 17:00 UTC, the local O_3 production from anthropogenic local emissions released earlier is maximum (Figure 8), with ground-level contributions that can reach 30 ppb SE in the municipality of Madrid. However, the greatest contribution during these hours continues to be from the BC (up to 50 - 60 ppb at surface level). From 21:00 UTC, the PBL has already decreased to a few hundred meters, the turbulence dwindles, the surface flow towards the SW is re-established and the formation of enriched levels of precursors (Figure 7) and ozone (Figure 8) in the 1000-2000 meters a.s.l. occurs again, in accordance with the regional recirculation processes reported in the literature for this area (Querol et al., 2018; Escudero et al., 2019).

3.3.2. Advective pattern

As an example of an advective pattern, Figure 10 shows the plan view and the NE-SW cross section of O_3, NOx and VOCs levels during July 13th (Figure S9 shows the SE-NW cross section for day 13th and Figure S10 and Figure S11 represent the NE-SW cross section and the SE-NW cross section for day 20th, respectively in the Supplement). It can be seen that surface O_3 levels at 3:00 UTC are around 8% lower than those of July 27th (accumulation), (average in the Madrid region of 39 ppb and 42 ppb, respectively) with maximum values along the Sierra de Guadarrama, where elevated terrain reaches layers rich in O_3 and precursors from the lower troposphere and from the residual layers formed the day before (Figure S11). This occurs (also under accumulation conditions) when the PBL height is lower than the maximum height of the Sierra de Guadarrama. However, during advective periods, a stronger stratification of ~~the~~ O_3 ~~concentration~~ is observed during the early hours (3:00 –

9:00 UTC) due to the existence of more intense wind direction speed vertical gradients (relative to accumulation conditions), perfectly captured by the modeling system (Figure 11).

At 09:00 UTC, the local O_3 production downwind of the city is lower than during the accumulation periods (Figure S12), not only quantitatively but also in terms of the total area affected. This can be explained by the weather conditions (promoting dispersion) and the corresponding lower surface levels of the main precursors (5-8 ppb NOx and 15-20 ppb of VOCs on the day 13th, compared to 10-15 ppb NOx and 30-40 ppb of VOCs during accumulation day 27th). At 15:00 UTC (Figure 10), the PBL height increases reaching 2,500-2,800 m altitude (compared to 4,000 m on day 27th). As the PBL grows, the vertical mixing dominates the wind-driven pollution displacement in the SW direction. Similarly to the dynamics described for accumulation conditions, this allows precursors and fresh O_3 to ascend and mix existing ozone in higher layers (Figure 10 and Figure 11). Nonetheless, the vertical mixing is lower during advective patterns, as observed in the ozone soundings (Figure 9), with the consequent difficulty of the boundary layer to incorporate O_3 from higher strata (beyond 4000 meters a.s.l.) in the central hours of the day. This results in lower O_3 mixing ratios at surface level under advective conditions, up to 60 ppb SW of Madrid City (Figure 10). As for the relative importance of local sources, Figure 11 shows that their contribution can reach nearly 30 ppb, similar to that under accumulation conditions. However, the area affected is clearly associated with the city plume and their contribution averaged over the region is smaller. In fact, our results point out that precursors advected can produce hourly peaks above 30 ppb outside the Madrid region.

3.4. Source apportionment assessment at the location of monitoring stations

A source apportionment assessment has also been carried out at the location of the air quality monitoring stations distributed throughout the simulation domain (Figure 1) to inform on the contributions of different sources in those points where air quality is routinely monitored. Differences are found depending on the type of station (urban, suburban and rural) and, consistently with the results discussed in the previous subsection, the type of circulation pattern (advective or accumulation). 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 O_3 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 O_3 to any of the other sources.

Urban and suburban monitoring stations have a similar aggregated behavior. During the first hours of the morning, the initial and boundary conditions make up the totality of O_3 levels until 06:00 UTC approximately. After that time, O_3 generated from precursors emitted by local sources appears, reaching contributions up to 15 and 12 ppb for urban and suburban locations (28 and 22% of the total ozone, respectively) around 12:00 UTC. The road transport (14-10%) and the residential (2-4%) sectors are those with the highest contributions. The signal of anthropogenic sources is lower in rural monitoring stations. As an average, road traffic contributes a maximum of 5% (5 ppb), the residential sector 2% (2 ppb) and the use of solvents (VOC emissions) also around 2% in rural locations.

The results in Figure 12 demonstrate the persistent relevance of IC in all locations, but especially in rural locations. Even though the initial conditions contribute to O_3 levels throughout the day, the maximums values are found in the first hours (0:00 -5:00 UTC). As the day evolves, the influence of IC progressively decreases until they disappear at 21:00 UTC approximately. However, clear differences are found depending on the circulation pattern as illustrated for July 27th (accumulation) and July,

13th (advection). According to the model predictions, O_3 levels are greater during the accumulation period (and are reached slightly earlier), with maxima up to 68 ppb (17:00 UTC) in contrast with 52 ppb under advective conditions. Of note, the model is ~~able to~~ reproduces observed O_3 temporal patterns quite consistently, but it misses the peak values during accumulation periods, as discussed in section 3.1.

It may be highlighted that the influence of residual layers of the previous day, tracked through the ICO tag, is observed again at the central hours of the day is very significant under accumulation conditions (IC contribution of up to 12 ppb, around 18% of total O_3) while is practically missing for advective days. This relates to the enhancement of O_3 levels from reservoirs aloft discussed in section 3.3.1. that does not occur under advective conditions. Of note, and consistently with the analysis in section 3.3, we observe that the average contribution from local anthropogenic sources to O_3 peaks (around 16 hours local time) in urban locations in accumulation periods is higher than that of advective periods. That is true both, for absolute levels (18 ppb and 11 ppb, respectively) and relatively contributions (32% and 22%, respectively). These results point out that the source apportionment under unfavorable circulation patterns significantly differs from that for average or advective conditions and, consistently with previous studies (Lupaşcu et al., 2022: Qu et al., 2023) demonstrate that the influence of local sources is larger for high O_3 levels associated to stagnation conditions.

Nonetheless, clear differences are found for individual stations depending on their location relative to the city center and prevailing winds. In the supplement (Figure S14 to Figure S16) a stratification of the same results by station type and geographical quadrant (Figure S13) and distance to Madrid is shown. For instance, urban locations within Madrid municipality in the NE direction for the 27th July (accumulation) present much higher contributions from local sources that those of urban stations in the NW direction and further away from the metropolitan area (Figure S15). This variability suggests that the outcome of local measures may differ throughout the region and should be modeled under specific meteorological conditions and assesses specifically for each location of interest.

4. Conclusions

A high-resolution chemical-transport model has been used to investigate O_3 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 O_3 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 O_3 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 O_3 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 O_3 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 O_3 ~~concentration~~ peaks than average values. This is particularly true under unfavorable, stagnation conditions associated with

accumulation patterns when the highest O_3 values occur. According to our results, up to 35% of total O_3 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 O_3 originated from local anthropogenic emissions in some locations. At the same time, our results point out that the contribution of biogenic emissions is lower than that of anthropogenic sources (below 4% to total O_3 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 O_3 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 O_3 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.

Author contributions

RB and DP designed the research. DP and LT conducted the CMAQ modeling and data postprocessing. DP, JMA, LT, and RB analyzed the results. DP, RB and JMA wrote the paper with contributions from all authors. GS and SN provided support for the CMAQ model and reviewed the article.

Competing interests

The authors declare that they have no conflict of interest.

Disclaimer

The views expressed in this paper are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

Financial support

This study was carried out within AIRTEC-CM (urban air quality and climate change integral assessment) scientific program funded by the Directorate General for Universities and Research of the Greater Madrid Region (S2018/EMT-4329).

Acknowledgements

The authors gratefully acknowledge the Universidad Politécnica de Madrid (www.upm.es) for providing computing resources on Magerit Supercomputer.

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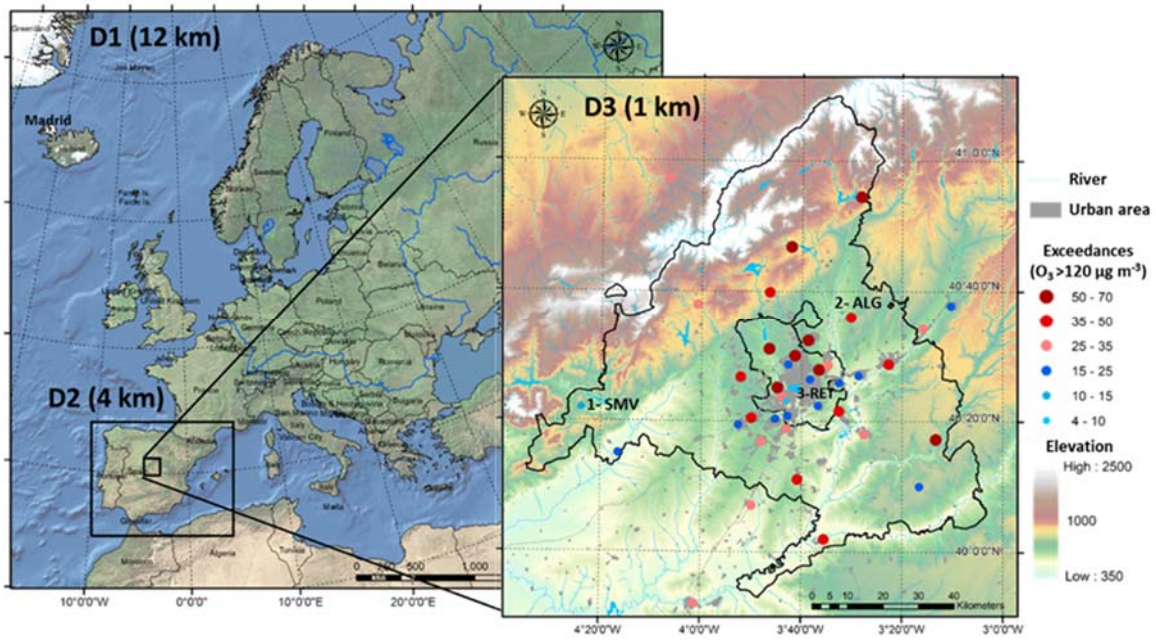
Table 1. Model performance statistics (dimensionless unless noted otherwise) by station type for ground-level O_3 concentration

Station type	FAC2	MB ($\mu g \cdot m^{-3}$)	MGE ($\mu g \cdot m^{-3}$)	NMB	NMGE	RMSE ($\mu g \cdot m^{-3}$)	r	IOA
Industrial	0.95	7.8	14.5	0.10	0.18	18.7	0.84	0.71
Rural	0.98	-2.9	13.8	-0.03	0.14	18.1	0.76	0.68
Suburban	0.94	2.4	17.15	0.03	0.20	23.3	0.74	0.69
Urban background	0.89	8.3	20.4	0.10	0.25	27.1	0.69	0.65
Urban traffic	0.88	10.8	19.9	0.14	0.25	26.5	0.73	0.65



860 **Figure. 1. Modeling domains including the location of the air quality monitoring stations within the innermost domain and number of exceedances of the O_3 target value for protection of human health (MDA8 > 120 µg·m^{-3}) in 2016.**

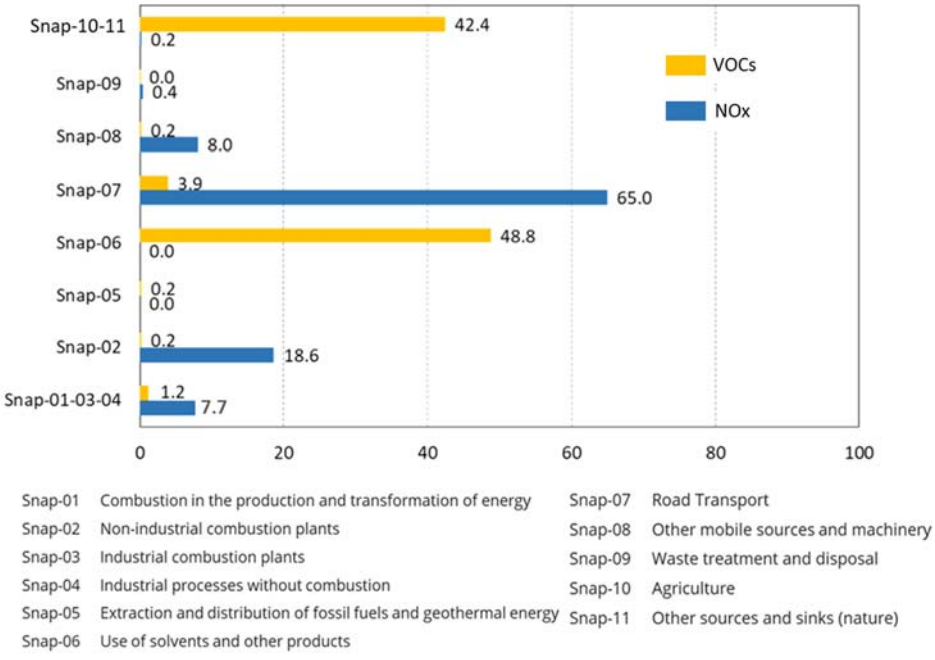


Figure. 2. NO_X and VOCs emissions of tagged sectors (percentage on an annual basis) for the source apportionment analysis.

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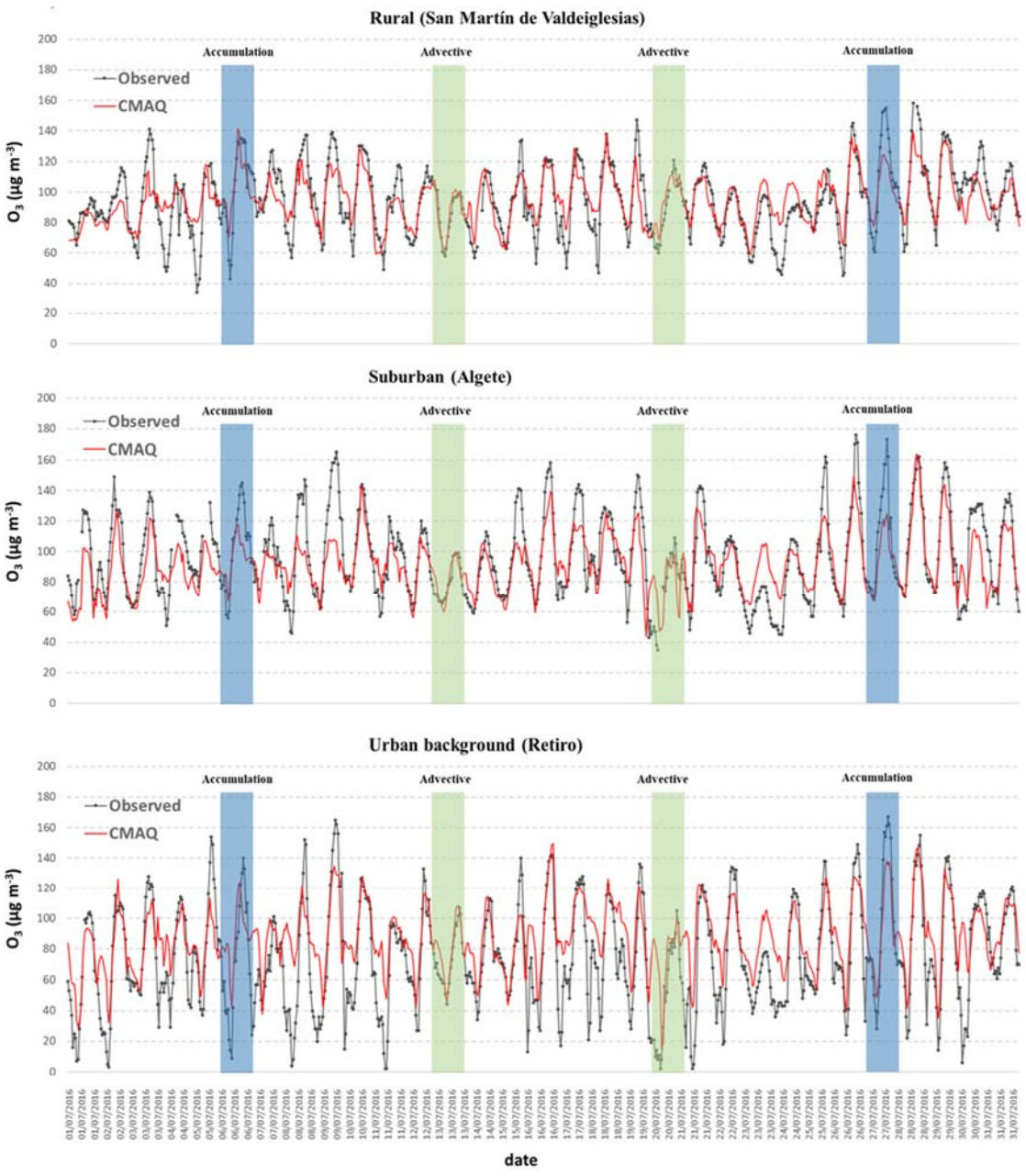

Figure. 3. Observed and predicted concentration series for selected locations (1-SMV: a rural location in the southwestern area of Madrid region, 2-ALG: a suburban location in the northeastern area of Madrid region and 3-RET: an urban background site in Madrid city center).

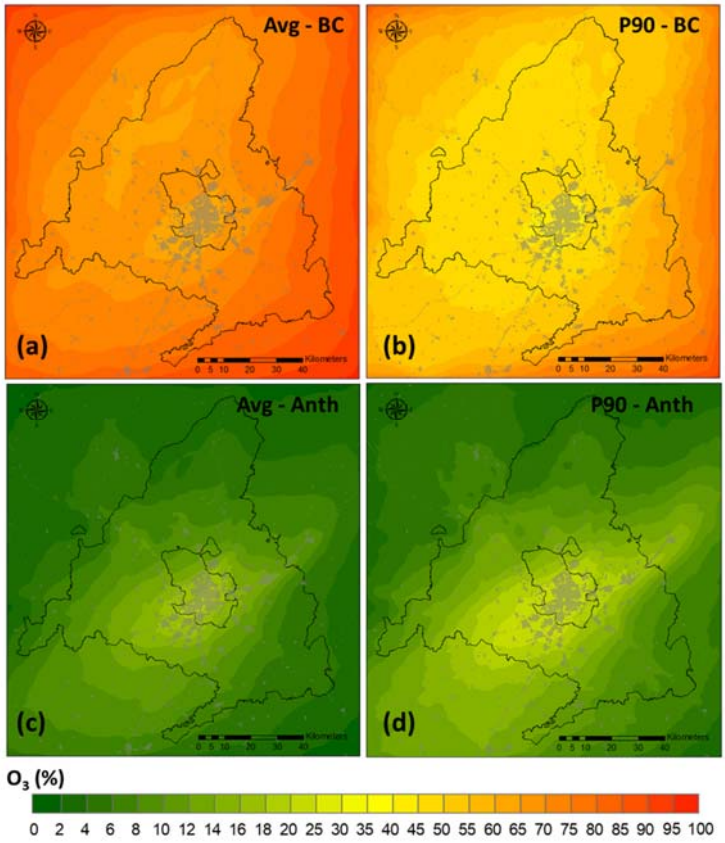

Figure 4. Contribution (%) of BC to O_3 concentration: (a) monthly average and (b) 90th percentile. Contribution (%) of local anthropogenic emissions to (c) monthly average and (d) 90th percentile.

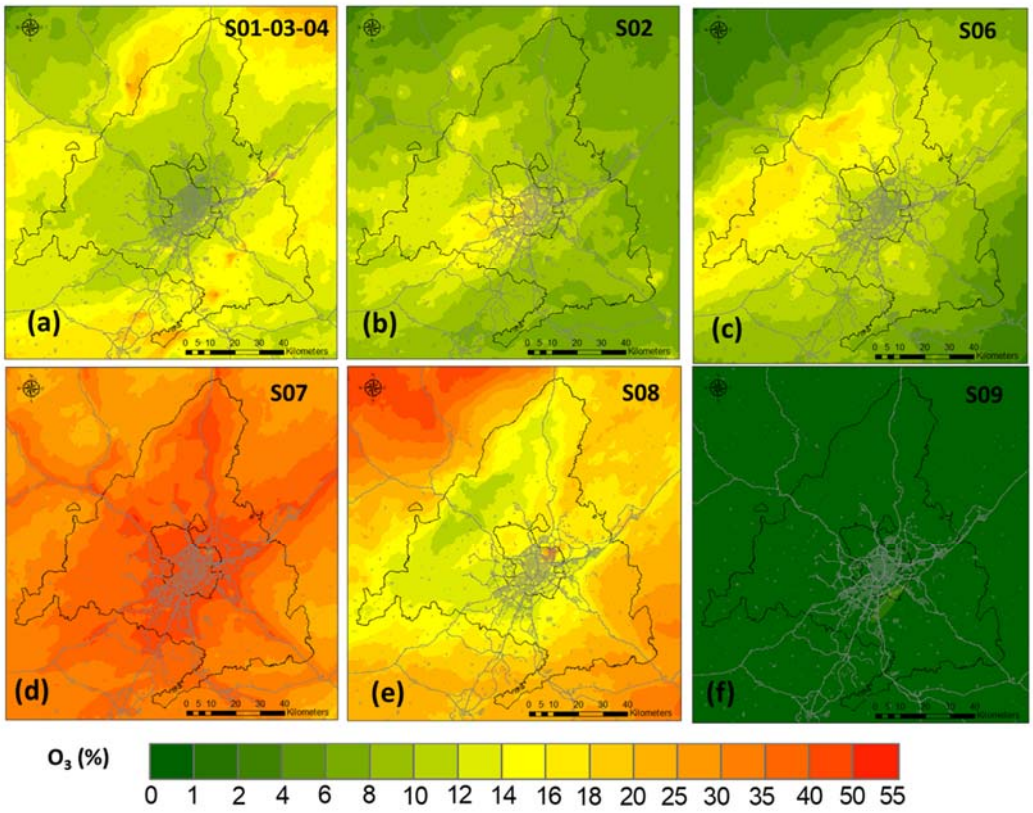

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Figure 5. Percentage contribution to the 1-hour 90th O_3 percentile of the main emitting sectors with respect to the total anthropogenic contribution.

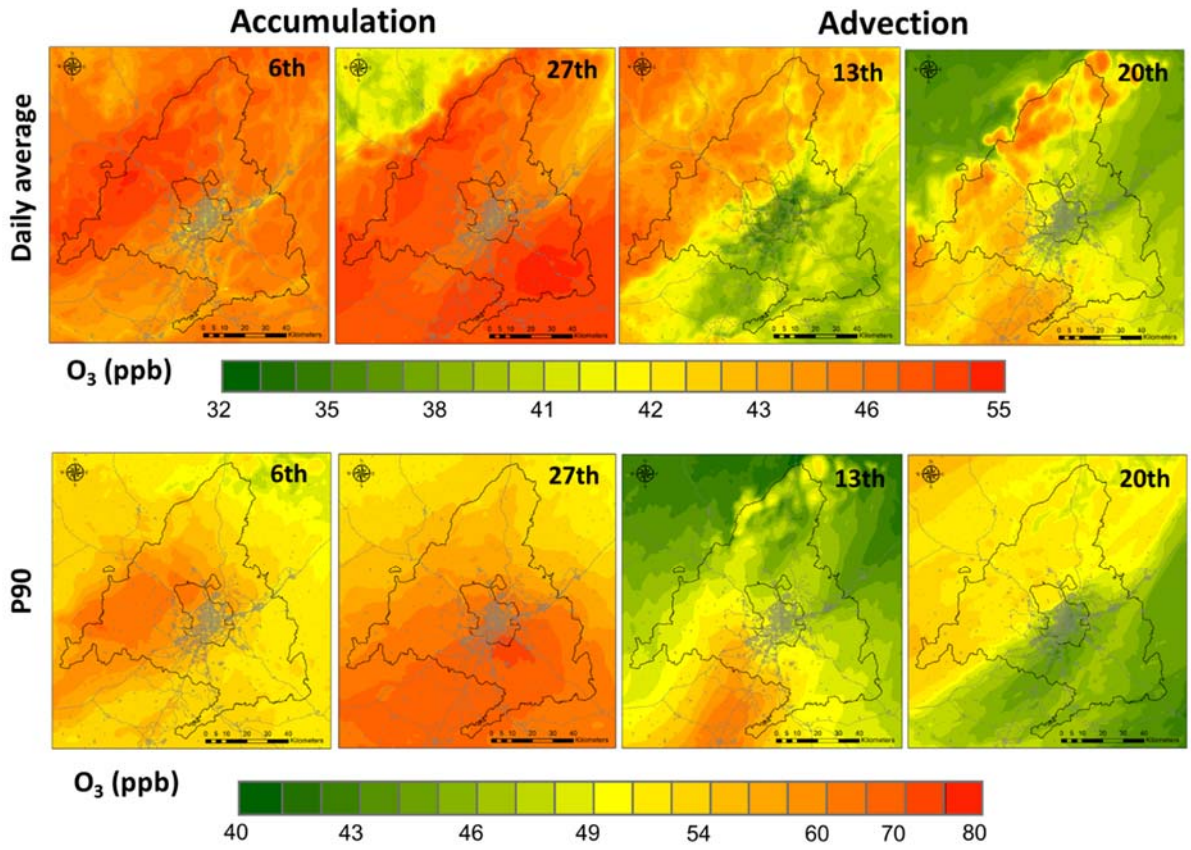


Figure 6. Daily mean (top) and 90th percentile (bottom) of O_3 levels (ppb) during accumulation (6th and 27th July, 2016) and advective (13th and 20th July, 2016) periods

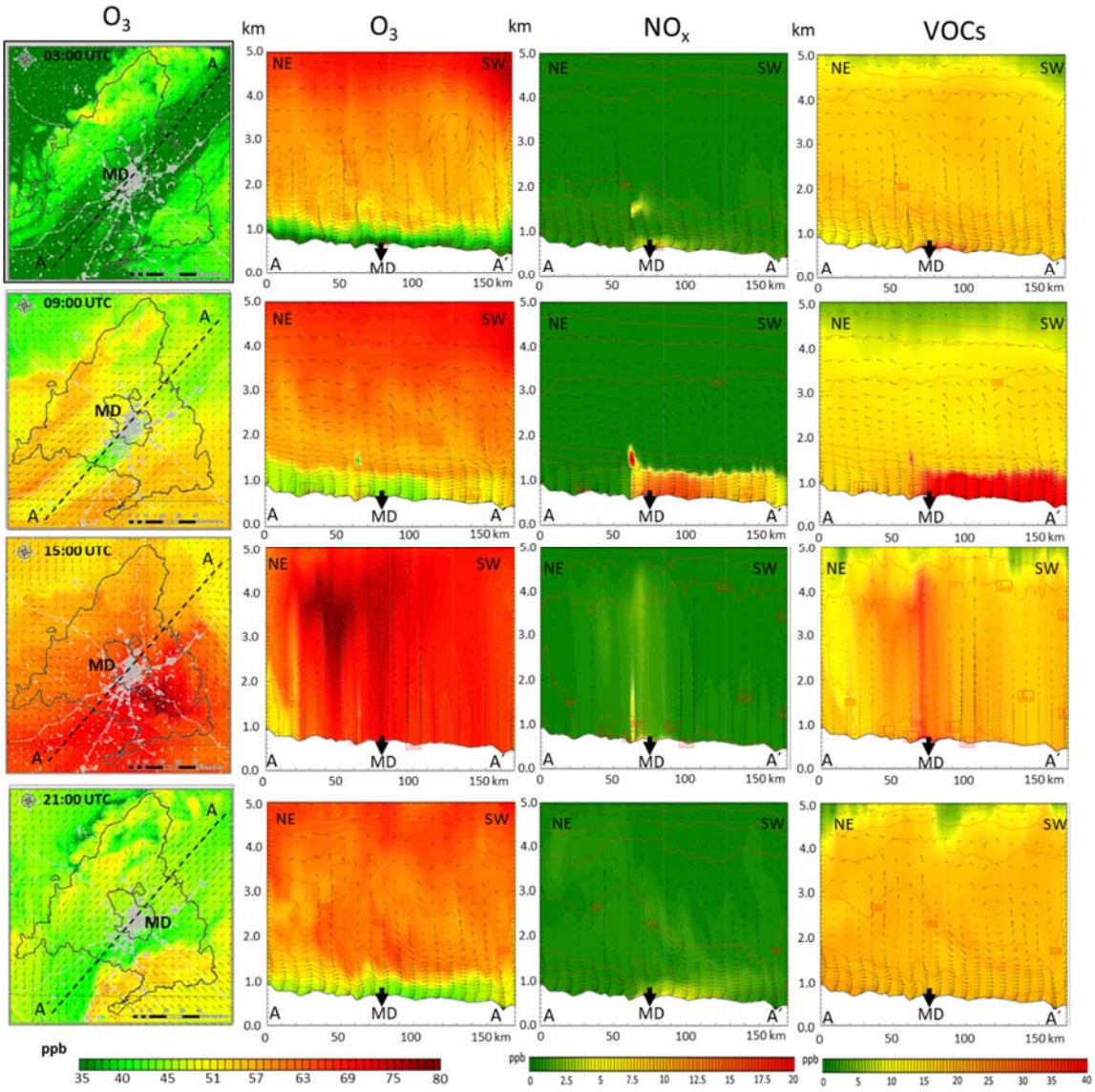
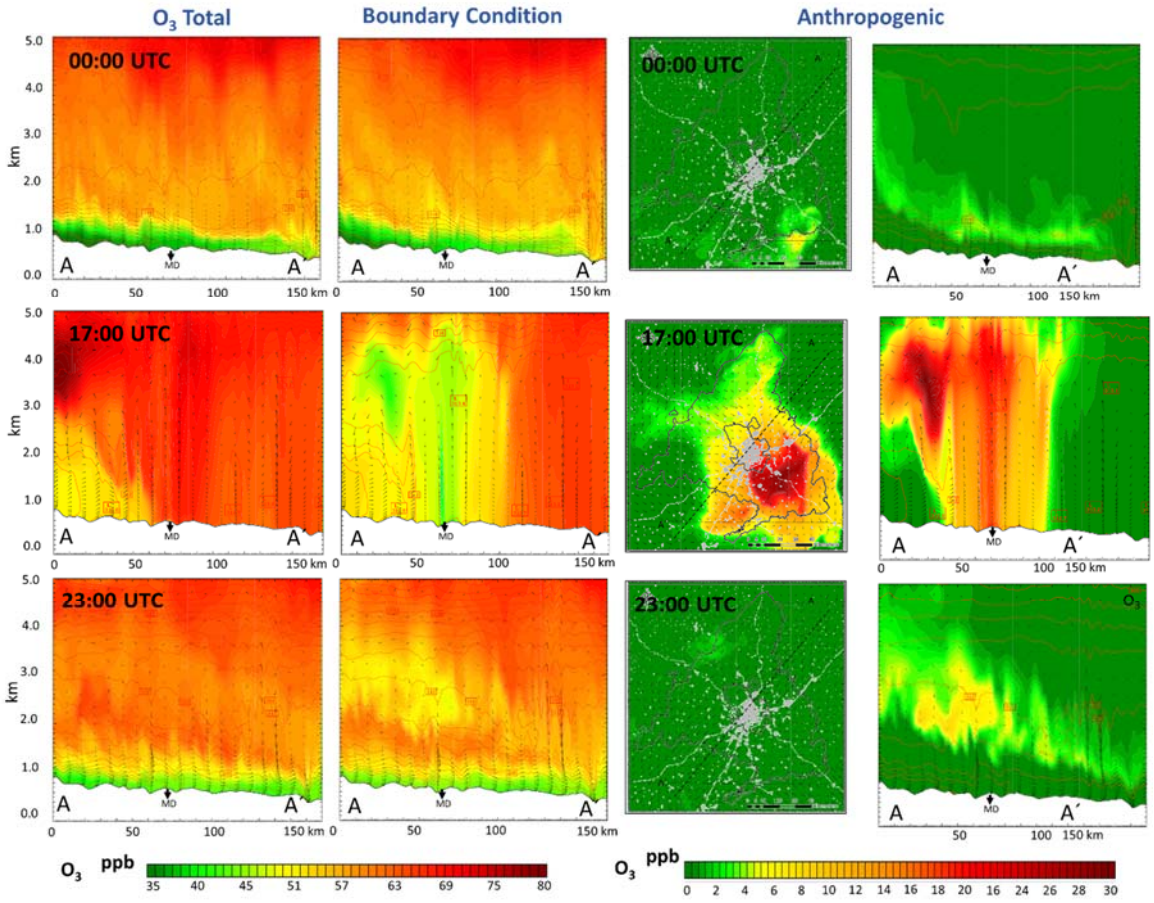


Figure 7. Accumulation period: evolution during July 27th, 2016. From left to right, plan view and NE-SW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at the 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.



885 **Figure 8. Hourly O_3 mixing ratios profiles (at 0:00, 17:00; 23:00 UTC) for the NE-SW cross section and contribution of BC and anthropogenic local emissions on July 27th, 2016 (accumulation). MD = Madrid City.**

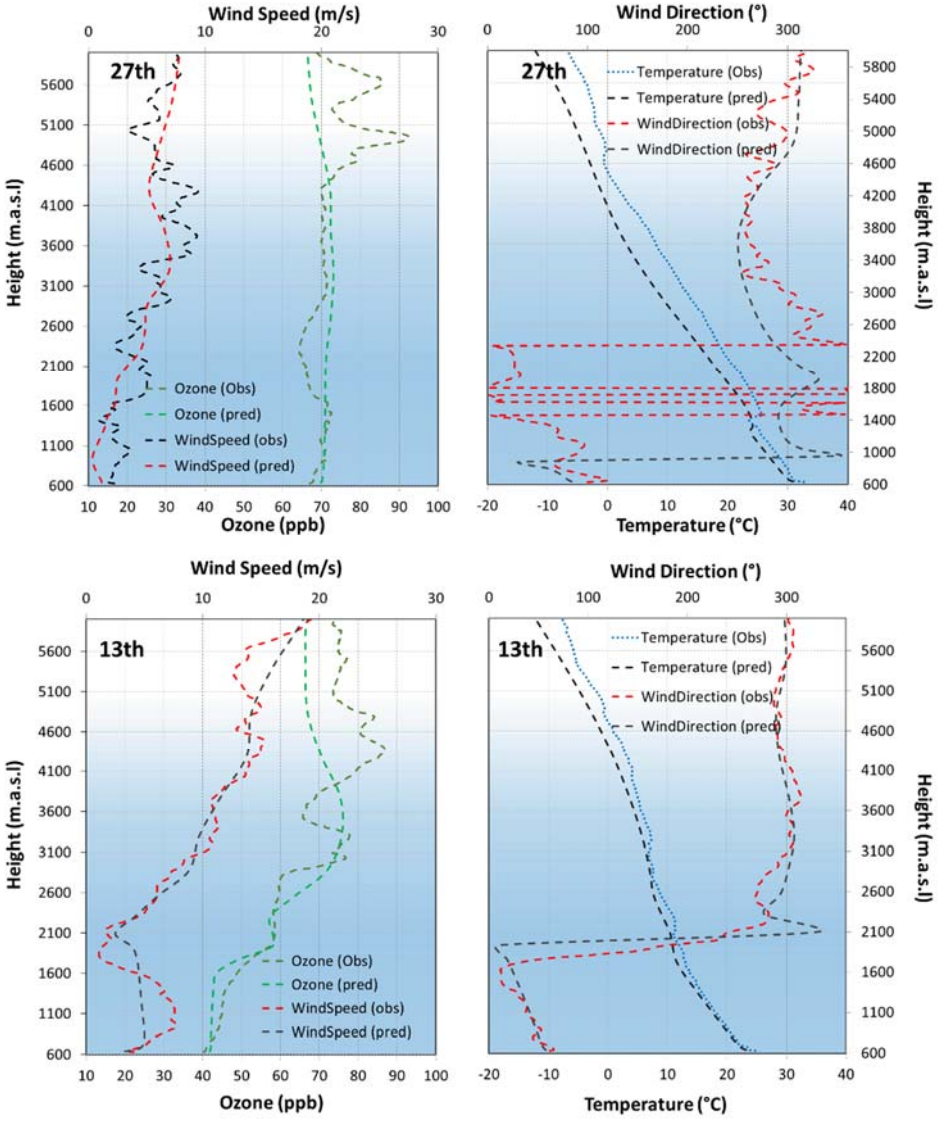


Figure 9. Vertical profiles (noon UTC) of O_3 mixing ratios, temperature, wind speed and wind direction for July 27th (accumulation, up) and the July13th (advective, down).

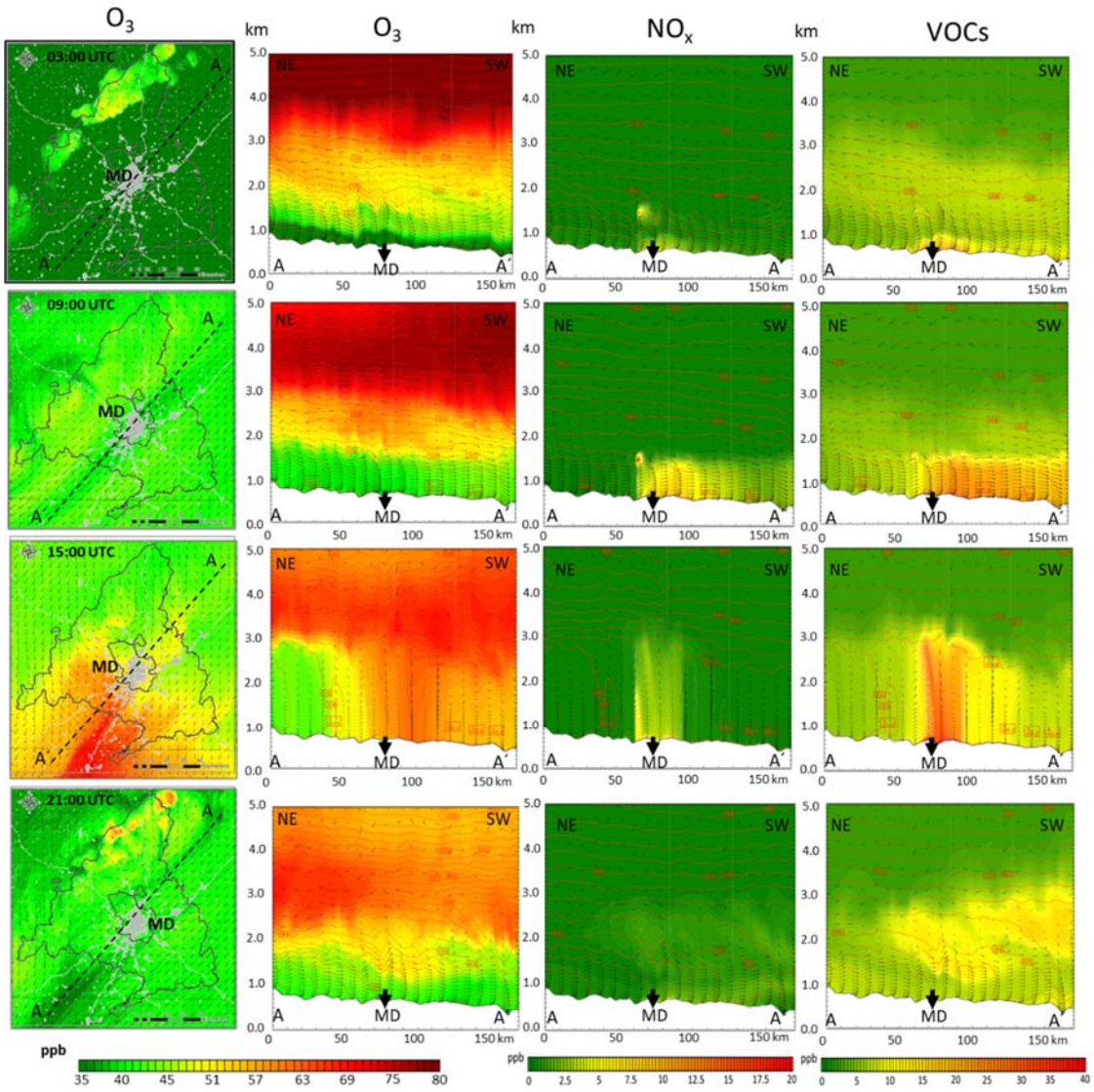


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Figure 10. Advective period: hourly evolution during July 13th, 2016. From left to right, plan view and NE-SW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at the 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

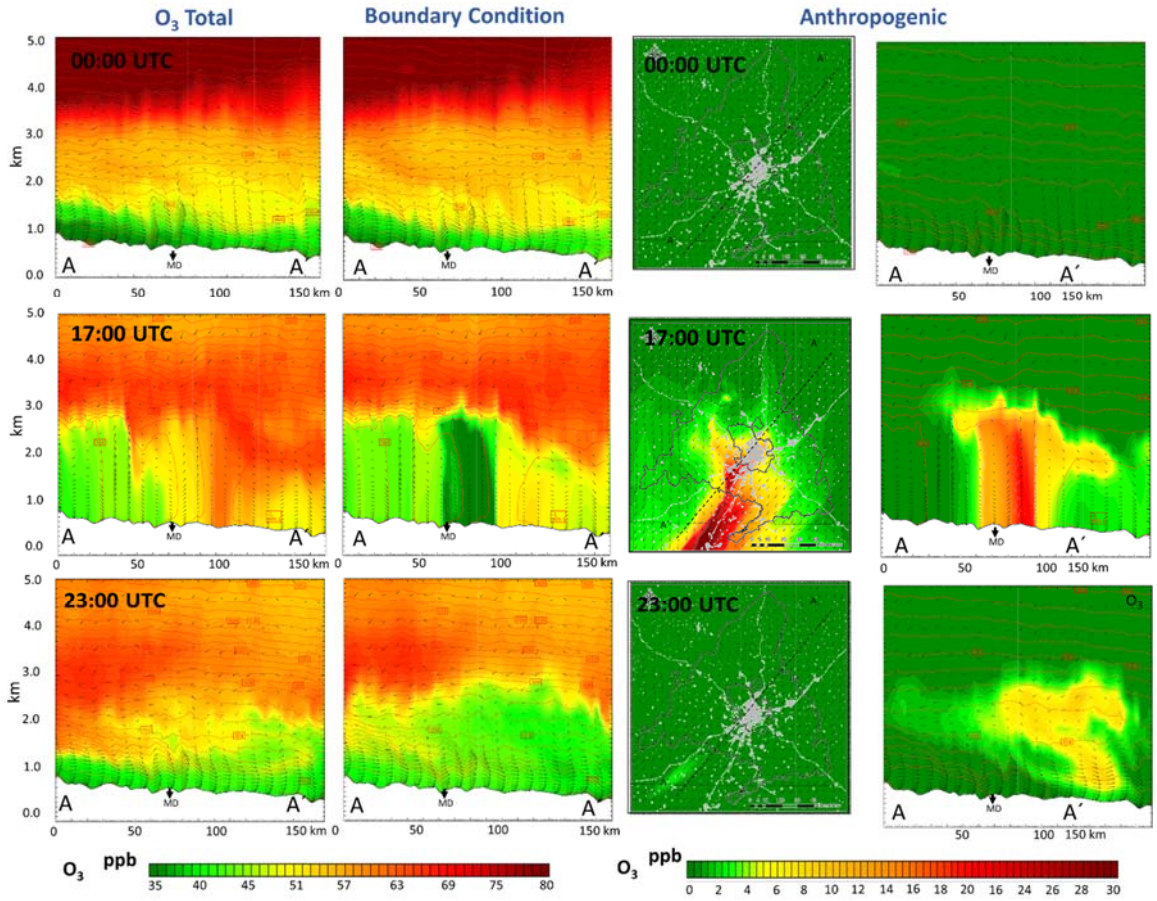

Figure 11. Hourly O_3 mixing ratios (at 0:00, 17:00; 23:00 UTC) for the NE-SW cross section and contribution of BC and anthropogenic local emissions on July 13th, 2016 (advection). MD = Madrid City.

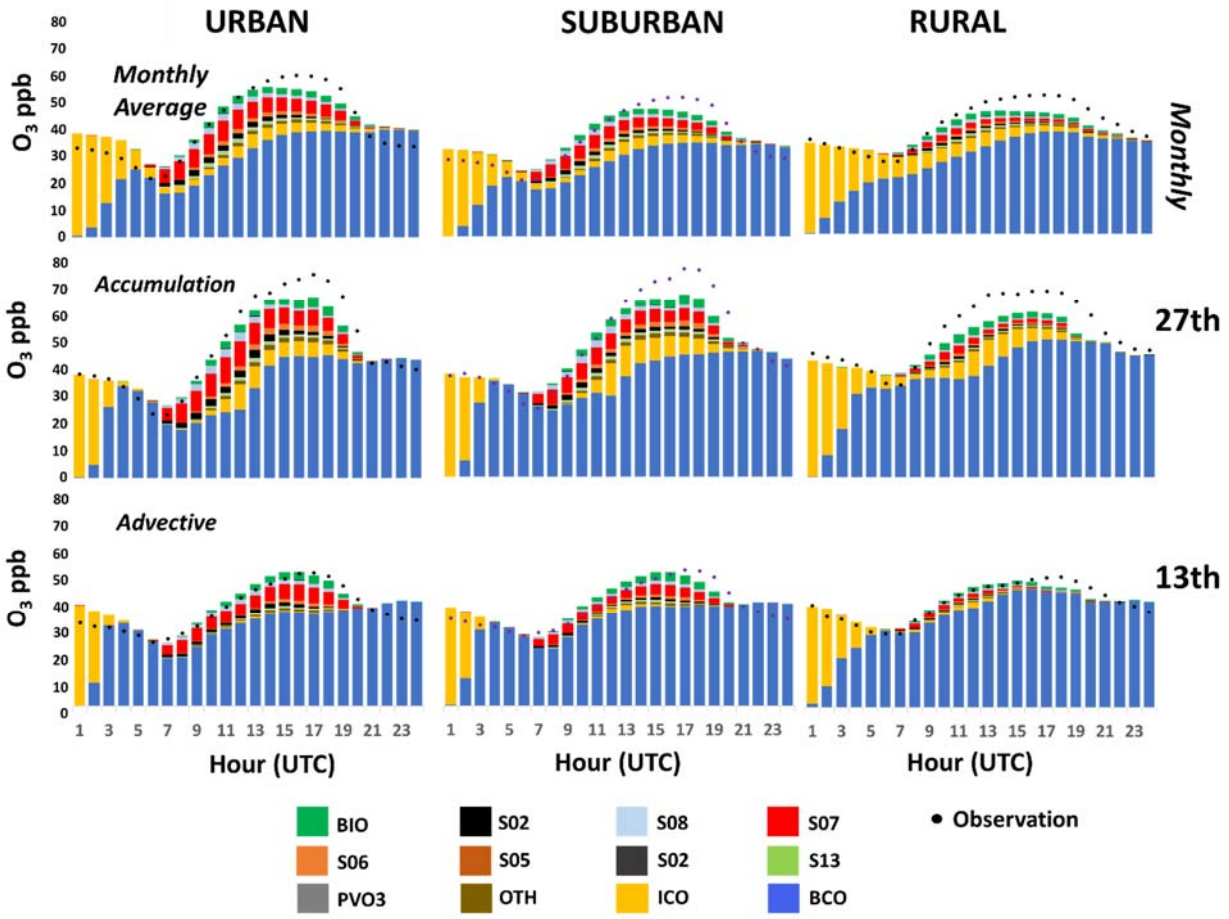

Figure 12. Hourly contribution for the monthly average (top) and specifically for accumulation (27th July, 2016) and advective (13th July, 2016) days (middle and bottom, respectively).

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 1º x 1º 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).

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National Centers for Environmental Prediction/National Weather Service/NOAA/U.S. Department of Commerce. 2004, updated daily. NCEP ADP Global Surface Observational Weather Data, October 1999 - continuing. Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory. https://doi.org/10.5065/4F4P-E398. Accessed 27 January 2016

Satellite Services Division/Office of Satellite Data Processing and Distribution/NESDIS/NOAA/U.S. Department of Commerce, and National Centers for Environmental Prediction/National Weather Service/NOAA/U.S. Department of Commerce. 2004, updated daily. NCEP ADP Global Upper Air Observational Weather Data, October 1999 - continuing. Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory. https://doi.org/10.5065/39C5-Z211. Accessed 25 January 2016.

Table S2. Horizontal dimensions and resolution of WRF and CMAQ modeling domains.

Domains	Geographic area	WRF X-Y dimensions (grid cells)	CMAQ X-Y dimensions (grid cells)	Horizontal resolution (km)
D1	Europe	560 x 496	459 x 406	12
D2	Iberian Peninsula	384 x 312	300 x 240	4
D3	Greater Madrid area	256 x 256	136 x 144	1

~~**Table S3. Compliance objectives of Directive 2008/50/EC and those defined by the World Health Organization (WHO) in relation to the pollutant analyzed.**~~

~~Average time~~	~~O_3 ($\mu g\ m^{-3}$)~~	
	~~R.D 102/2011~~	~~OMS~~
~~Maximum daily eight-hour mean~~	~~120 $\mu g\ m^{-3}$ not to be exceeded on more than 25 days per calendar year averaged over three years~~	~~100 $\mu g\ m^{-3}$ 3-4 exceedance days per year~~

Table S3. Model performance statistics (dimensionless unless noted otherwise) by station for ground-level O_3 concentration.

STATION	TYPE	FAC2	MB (μgm^{-3})	MGE (μgm^{-3})	NMB	NMGE	RMSE (μgm^{-3})	r	IOA
Arganda del Rey	Industrial	0.96	5.8	14.6	0.07	0.17	18.6	0.84	0.72
Fuenlabrada	Industrial	0.95	9.8	14.4	0.13	0.19	18.7	0.84	0.69
Villa del Prado	Rural	0.99	-0.8	11.8	-0.01	0.13	15.3	0.82	0.72
S.Mde Valdeiglesias	Rural	1.00	0.0	10.5	0.00	0.11	13.7	0.80	0.71
Orusco de Tajuña	Rural	1.00	-10.0	12.7	-0.10	0.12	16.1	0.84	0.66
Guadalix de la sierra	Rural	0.92	7.6	17.9	0.09	0.21	22.7	0.79	0.67
El Atazar	Rural	0.99	-11.2	16.1	-0.11	0.15	20.7	0.69	0.58
Algete	Suburban	1.00	-4.4	13.1	-0.05	0.14	17.1	0.81	0.72
La Sagra	Suburban	0.94	7.3	14.5	0.09	0.18	20.0	0.81	0.71
Mostoles	Suburban	0.94	8.0	15.5	0.10	0.19	20.6	0.83	0.71
Majadahonda	Suburban	0.96	-2.7	15.7	-0.03	0.17	21.4	0.81	0.71
Valdemoro	Suburban	0.91	6.7	16.0	0.08	0.19	22.1	0.80	0.71
Rivas Vaciamadrid	Suburban	0.91	7.0	17.3	0.09	0.21	23.0	0.81	0.70
Torrejon de Ardoz	Suburban	0.90	10.1	17.6	0.13	0.22	23.7	0.82	0.70
Azuqu. de Henares	Suburban	0.95	3.6	16.8	0.04	0.20	21.6	0.78	0.70
Toledo2	Suburban	0.95	-0.9	16.3	-0.01	0.18	22.0	0.72	0.68
Aranjuez	Suburban	0.91	9.3	16.7	0.11	0.20	22.5	0.77	0.67
El Pardo	Suburban	0.92	-0.2	22.2	0.00	0.24	28.0	0.74	0.65
Casa de campo	Suburban	0.94	1.7	20.1	0.02	0.23	26.7	0.61	0.63
Juan Carlos I	Suburban	0.90	-4.6	24.2	-0.05	0.27	31.0	0.61	0.63
Alcorcón	Urb.Background	0.96	4.8	14.6	0.06	0.18	19.7	0.83	0.73
Guadalajara	Urb.Background	0.94	7.4	15.6	0.09	0.19	21.4	0.77	0.70
Tres olivos	Urb.Background	0.92	-4.0	22.8	-0.04	0.25	29.2	0.66	0.63
Villaverde	Urb.Background	0.86	13.1	22.2	0.17	0.29	29.4	0.66	0.61
Farolillo	Urb.Background	0.88	5.8	22.4	0.07	0.27	29.7	0.62	0.62
Retiro	Urb.Background	0.86	11.9	23.0	0.16	0.31	29.3	0.64	0.60
Barajas pueblo	Urb.Background	0.81	11.2	25.1	0.15	0.33	32.2	0.65	0.62
Arturo Soria	Urb.Background	0.84	15.4	23.2	0.22	0.32	29.8	0.63	0.57
Ench de Vallecas	Urb.Background	0.88	6.2	21.1	0.07	0.25	27.9	0.66	0.64
Plaza del Carmen	Urb.Background	0.72	23.9	29.9	0.39	0.48	37.0	0.59	0.47
Segovia 2	Traffic	0.97	3.5	13.6	0.04	0.16	17.0	0.84	0.71
Vill.de Salvanés	Traffic	0.99	3.1	10.6	0.04	0.12	14.6	0.78	0.71
Colmenar Viejo	Traffic	0.99	-0.7	13.0	-0.01	0.14	17.3	0.78	0.69
Alcobendas	Traffic	0.93	-0.8	17.8	-0.01	0.20	23.6	0.80	0.70
Getafe	Traffic	0.92	8.8	16.8	0.11	0.21	23.1	0.80	0.70
Alcala de Henares	Traffic	0.87	10.0	19.3	0.13	0.24	25.0	0.83	0.69
Leganes	Traffic	0.87	12.4	18.4	0.16	0.24	25.7	0.79	0.67
Barrio del Pilar	Traffic	0.88	9.0	20.8	0.11	0.27	28.2	0.64	0.62
Coslada	Traffic	0.79	18.9	24.7	0.27	0.35	31.2	0.80	0.61
Collado Villalba	Traffic	0.78	19.3	23.6	0.26	0.32	31.7	0.73	0.59
Escuelas Aguirre	Traffic	0.83	16.5	23.7	0.24	0.35	29.9	0.63	0.54
Pzs. Fedz Ladreda	Traffic	0.80	22.1	26.7	0.34	0.41	33.4	0.6	0.5

Table S4. Model performance statistics (dimensionless unless noted otherwise) by station type and circulation pattern for ground-level O_3 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
	Advective	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
	Advective	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
	Advective	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
	Advective	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
	Advective	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 º	90.7 º	-0.24	0.63	0.26	0.55
	Advection	0.87	6.5 º	34.5 º	0.05	0.25	0.79	0.81
	Other	0.77	-9.2 º	60.8 º	-0.06	0.38	0.53	0.68

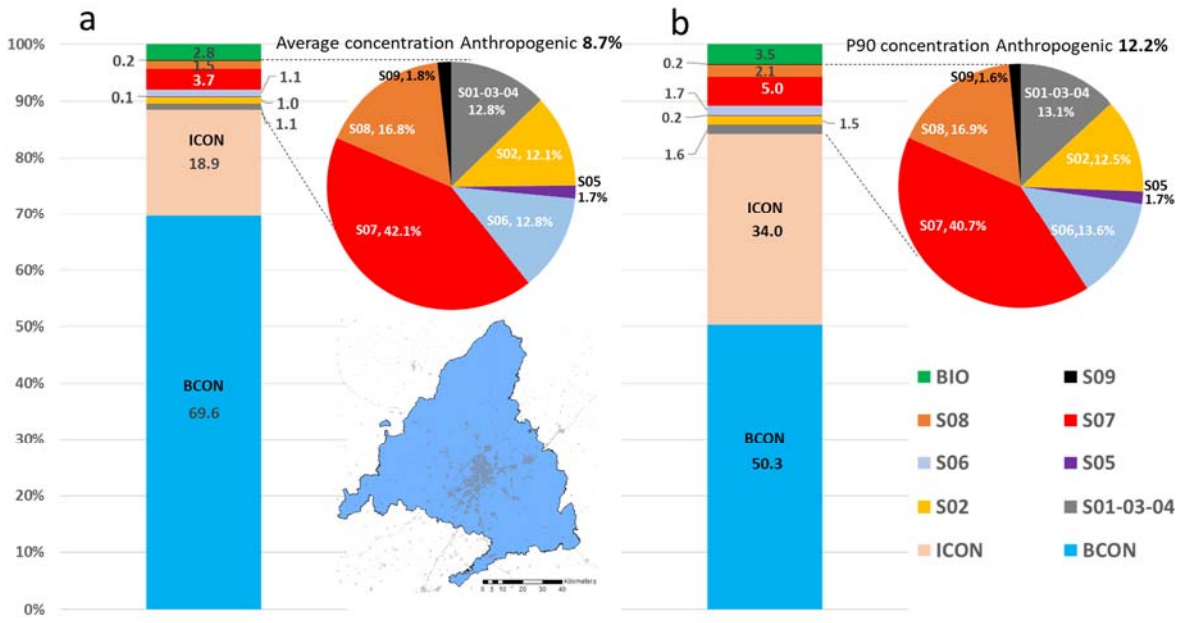

Figure S1. Spatially-averaged source apportionment (%) over the whole Madrid Region for (a) O_3 monthly mean and (b) 90th 1-hour percentile, including the sectoral breakdown within anthropogenic contributions.

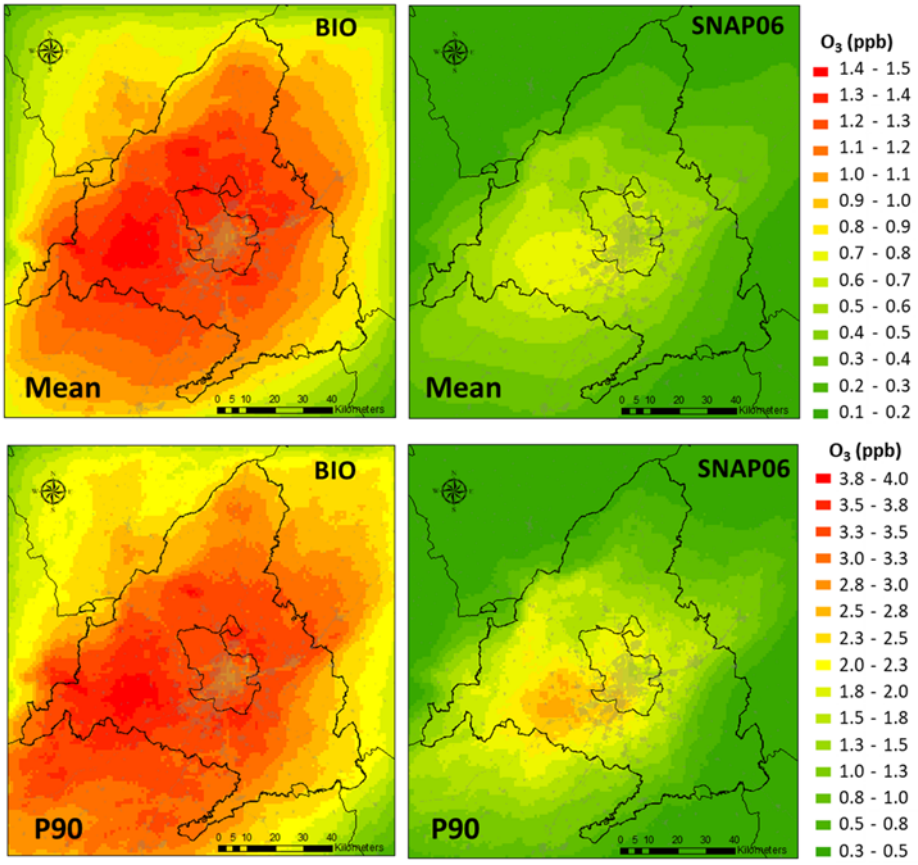

Figure S2. Absolute contribution (ppb) to the monthly mean 1-hour 90th O_3 percentile of the SNAP 06 sector (use of solvents and other products) and biogenic emissions.

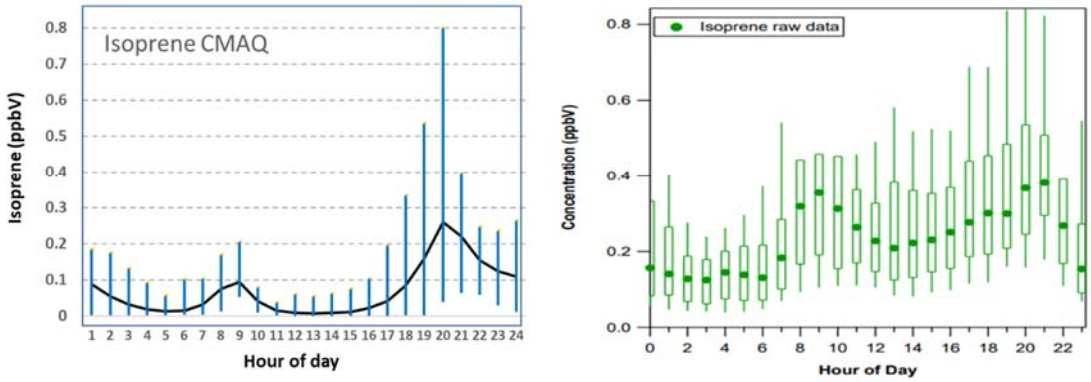

Figure S3. Comparison of isoprene ground-level mixing ratios predicted by CMAQ (left) and measurements made in Majadahonda (suburban site) by Querol et al., (2018) (right). Both graphs present the hourly values during the day averaged over the period July 5th and July 19th. The source of the right-hand panel is Pérez et al., (2016).

Reference:

- 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.

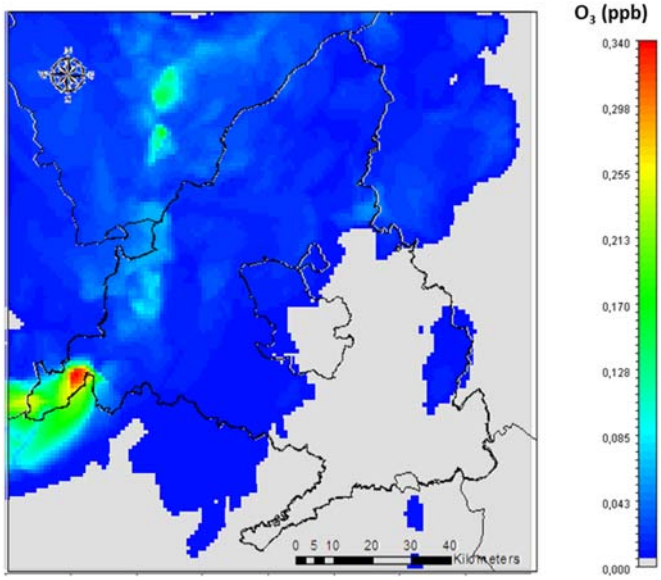

Figure S4. Maximum 1-hour attribution of stratospheric transport (PVO3) to ground level

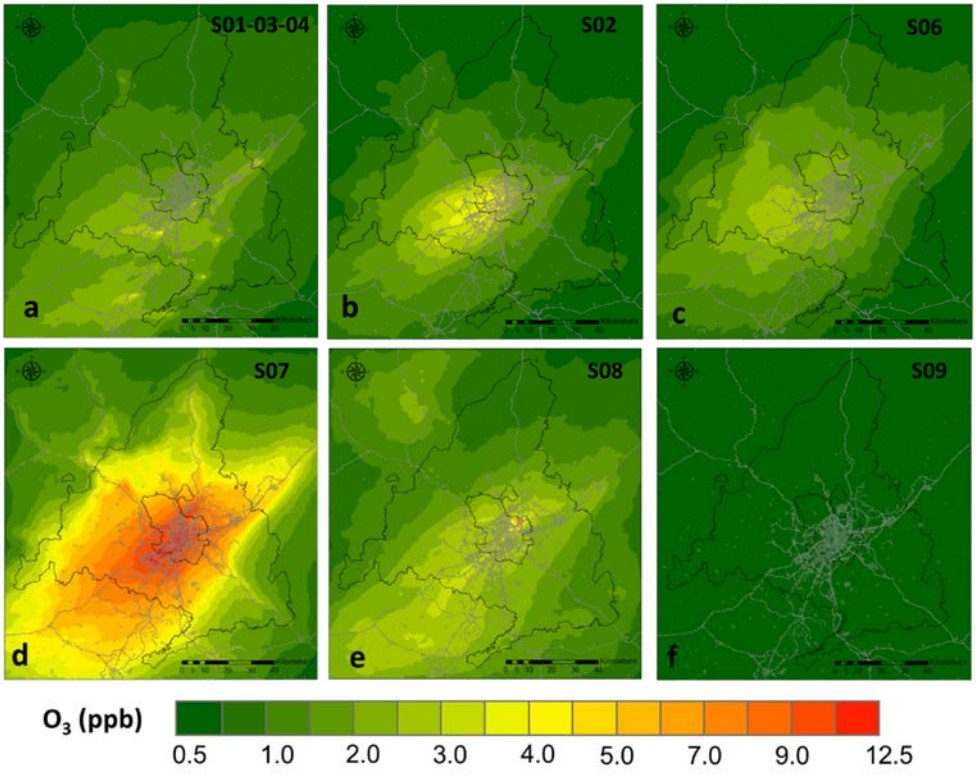

Figure S5. Absolute contribution to the 1-hour 90th O_3 percentile of the main emitting sectors.

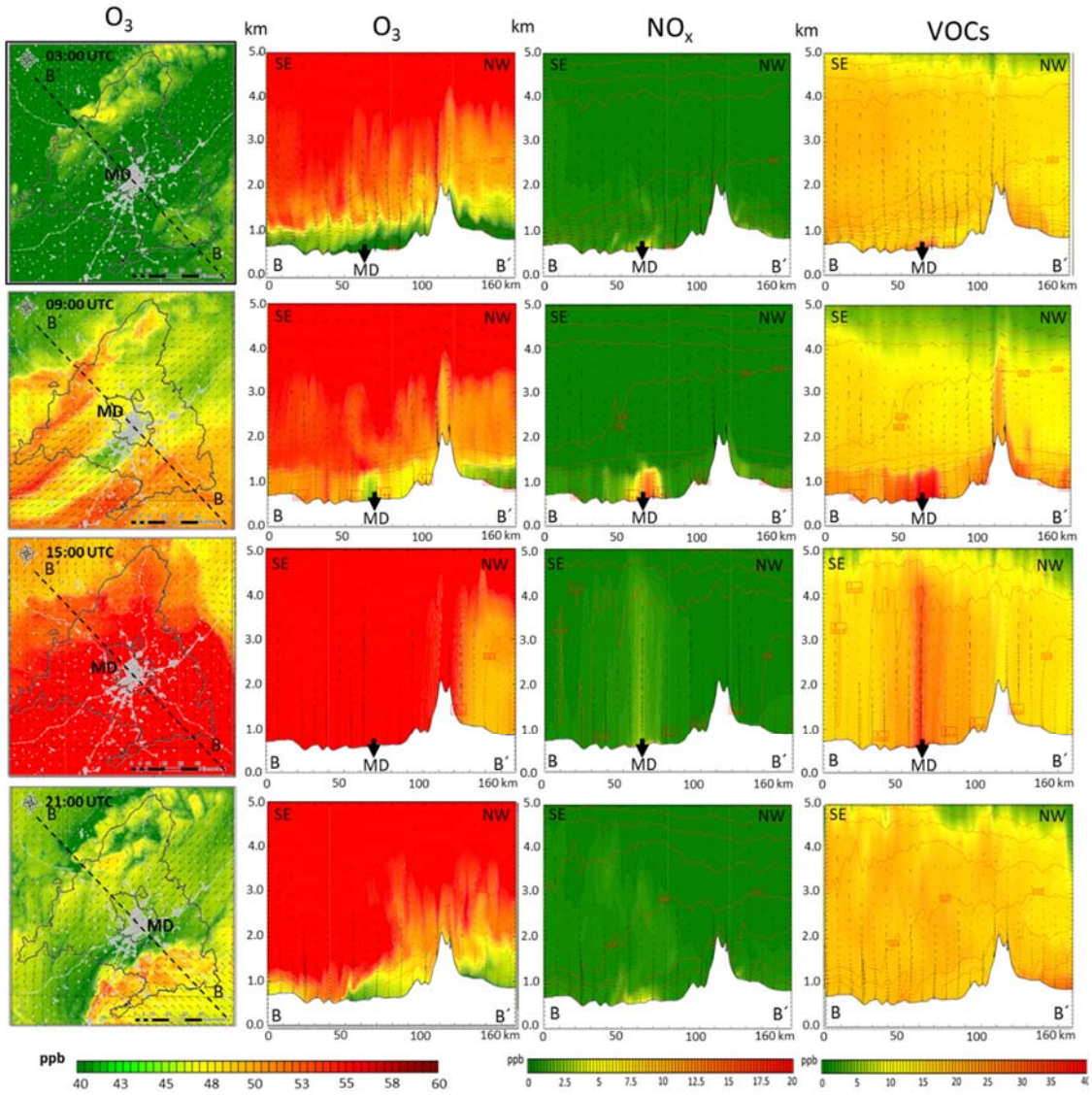

Figure S6. Accumulation period: evolution during July 27th. From left to right, plan view and SE-NW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

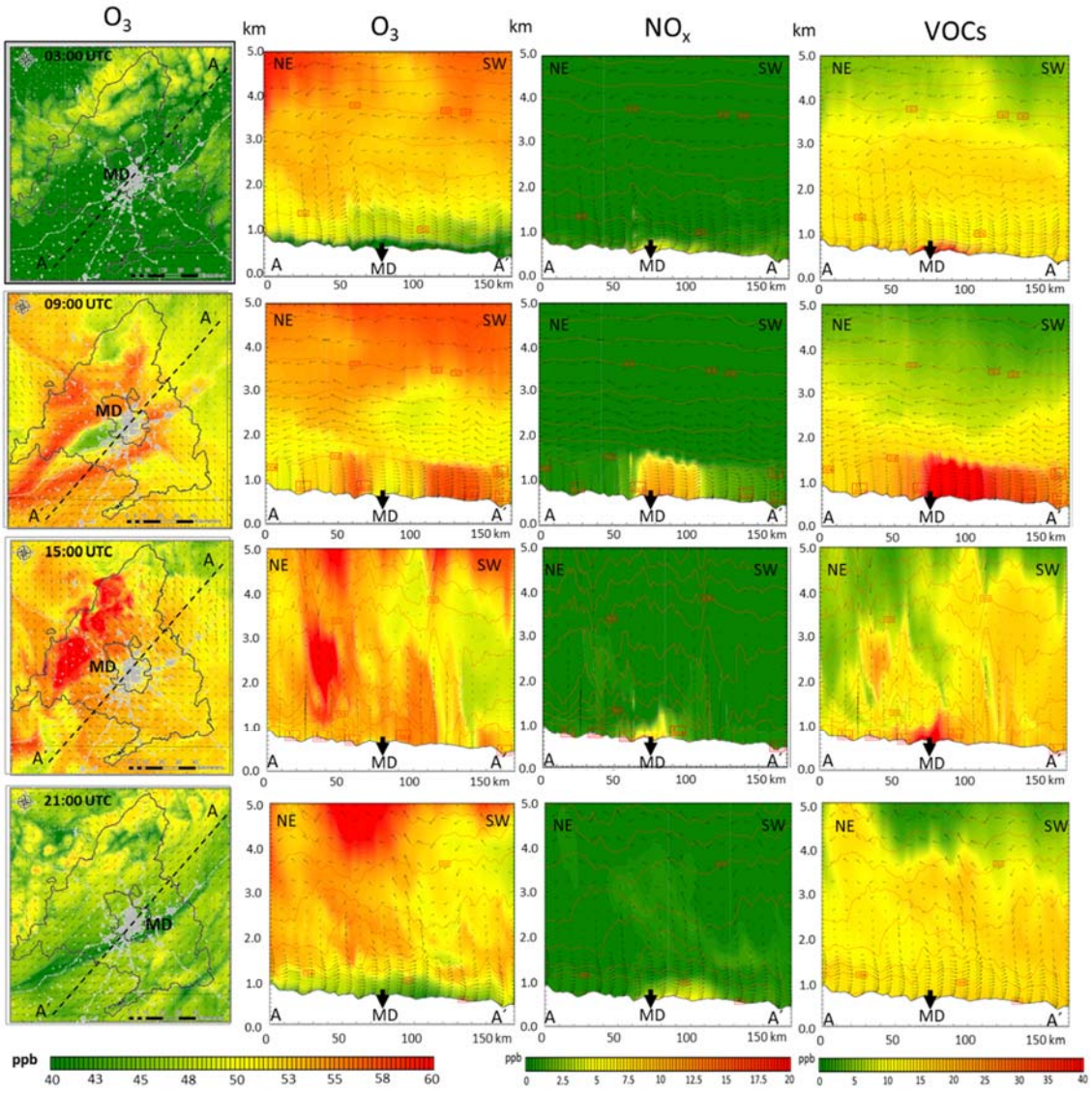

Figure S7. Accumulation period: evolution during July 6th. From left to right, plan view and NE-SW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

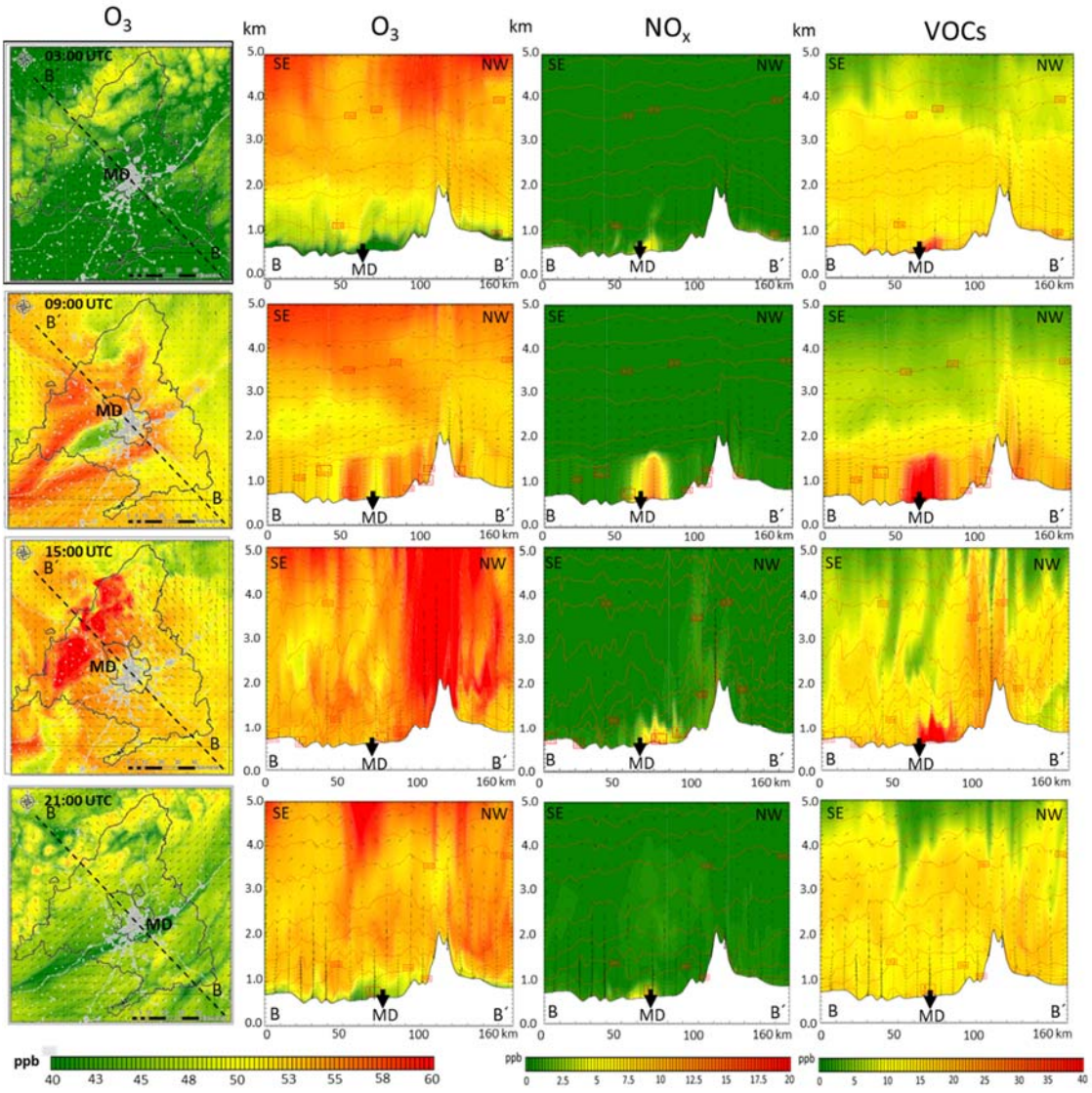

Figure S8. Accumulation period: evolution during July 6th. From left to right, plan view and SE-NW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

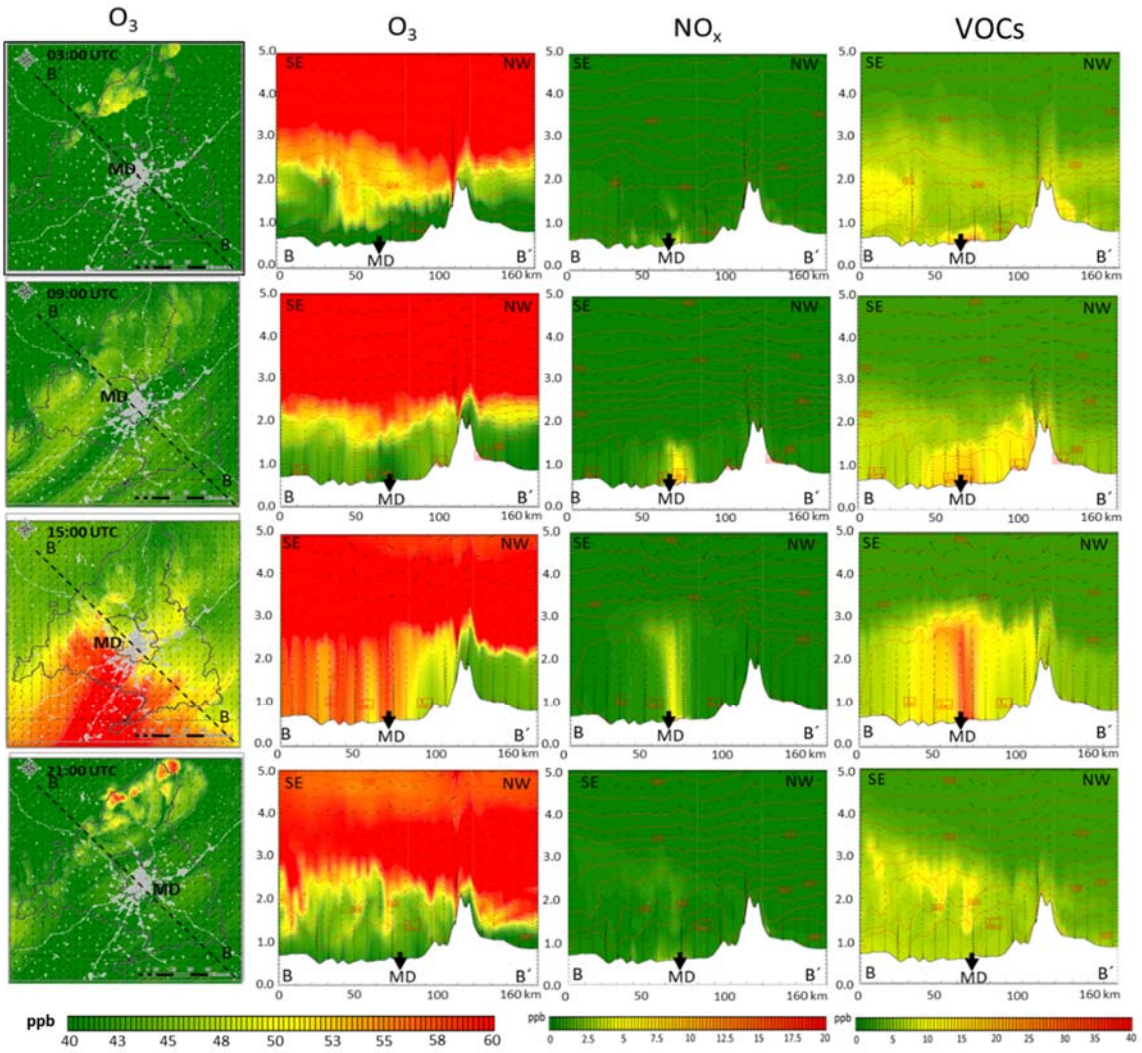

Figure S9. Advection period: evolution during July 13th. From left to right, plan view and SE-NW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

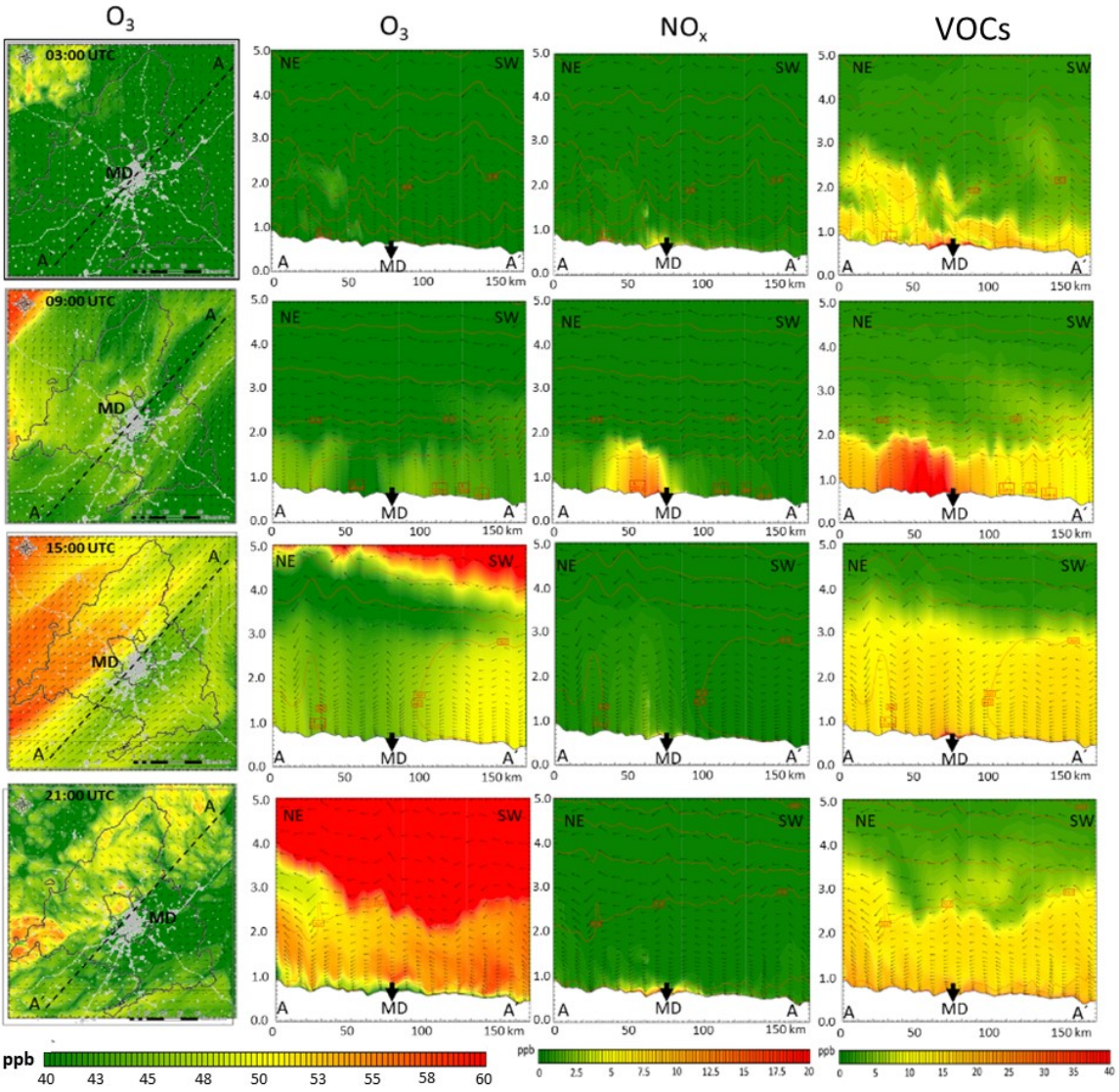

Figure S10. Advection period: evolution during July 20th. From left to right, plan view and NE-SW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

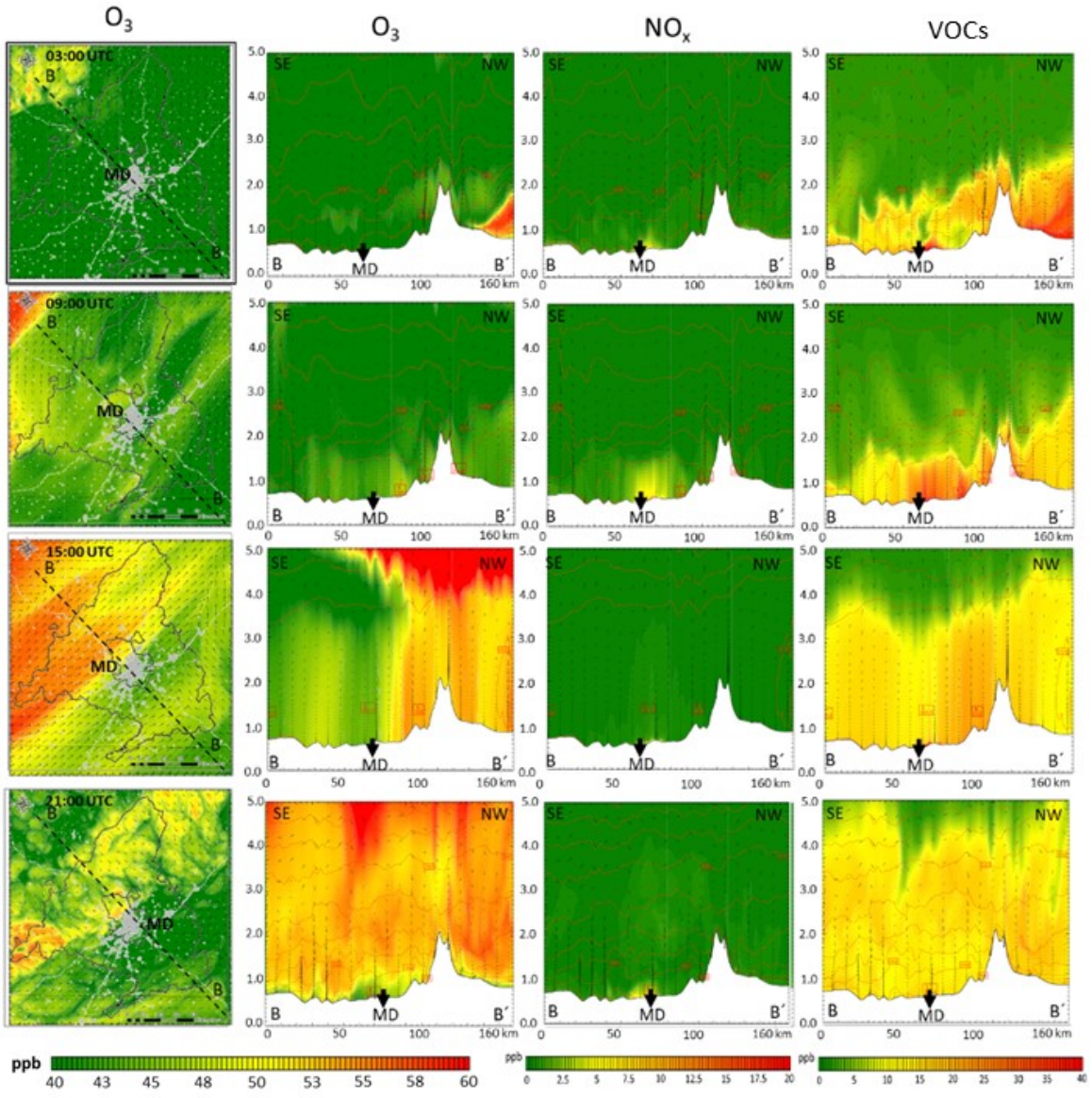

Figure S11. Advection period: evolution during July 20th. From left to right, plan view and SE-NW cross section (up to 5 km height) O_3 mixing ratios (ppb), NOx (ppb) and VOCs (ppb) at 3:00, 9:00; 15:00, 21: 00 UTC hours. MD = Madrid City.

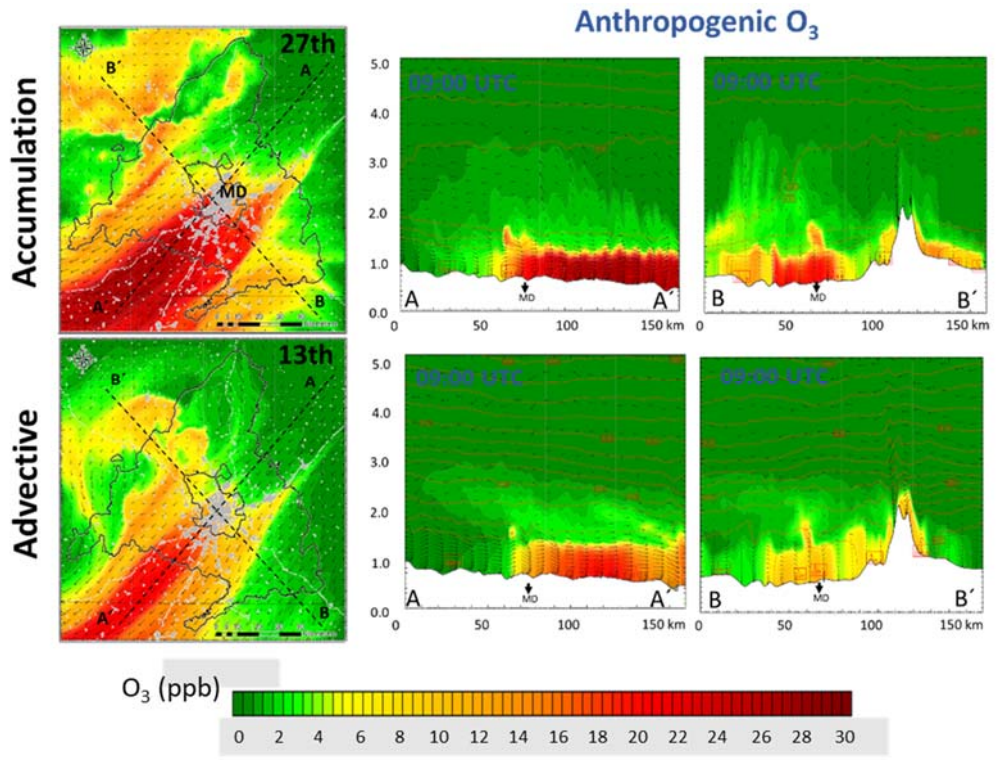

Figure S12. O_3 mixing ratios (ppb) at 09:00 UTC for July 27th (accumulation period) and July 13th (advective period). From left to right, plan view, NE-SW and SE-NW cross sections (up to 5 km height). MD = Madrid City.

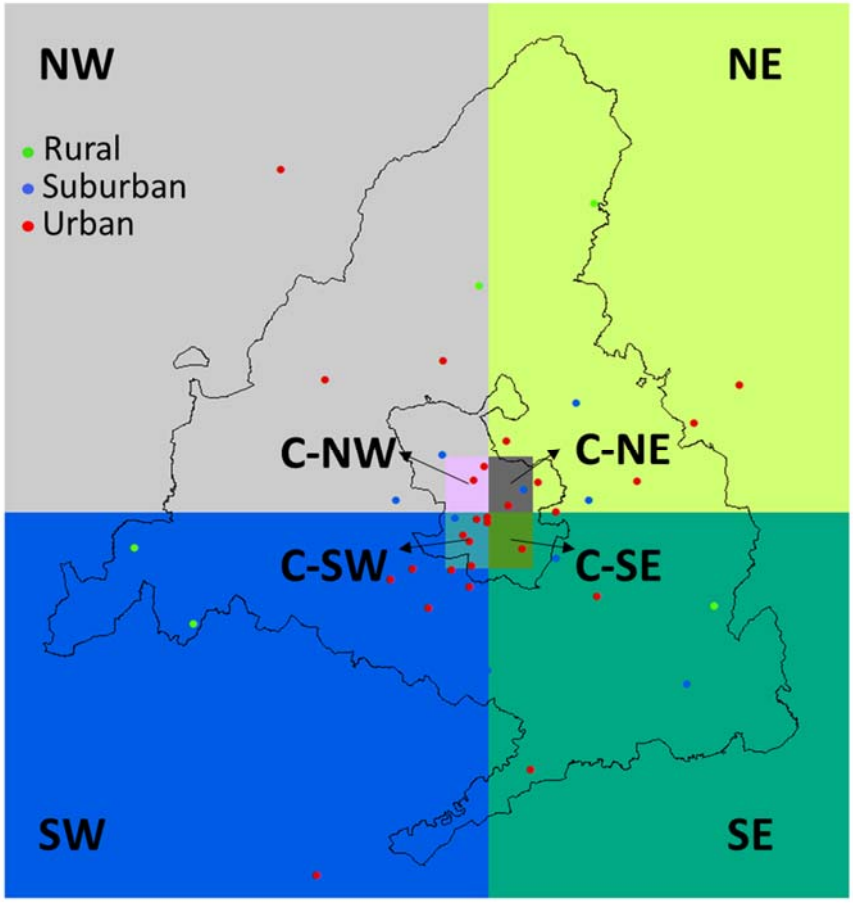

Figure S13. Geographical division (quadrants) of the study area for the analysis of individual monitoring station locations

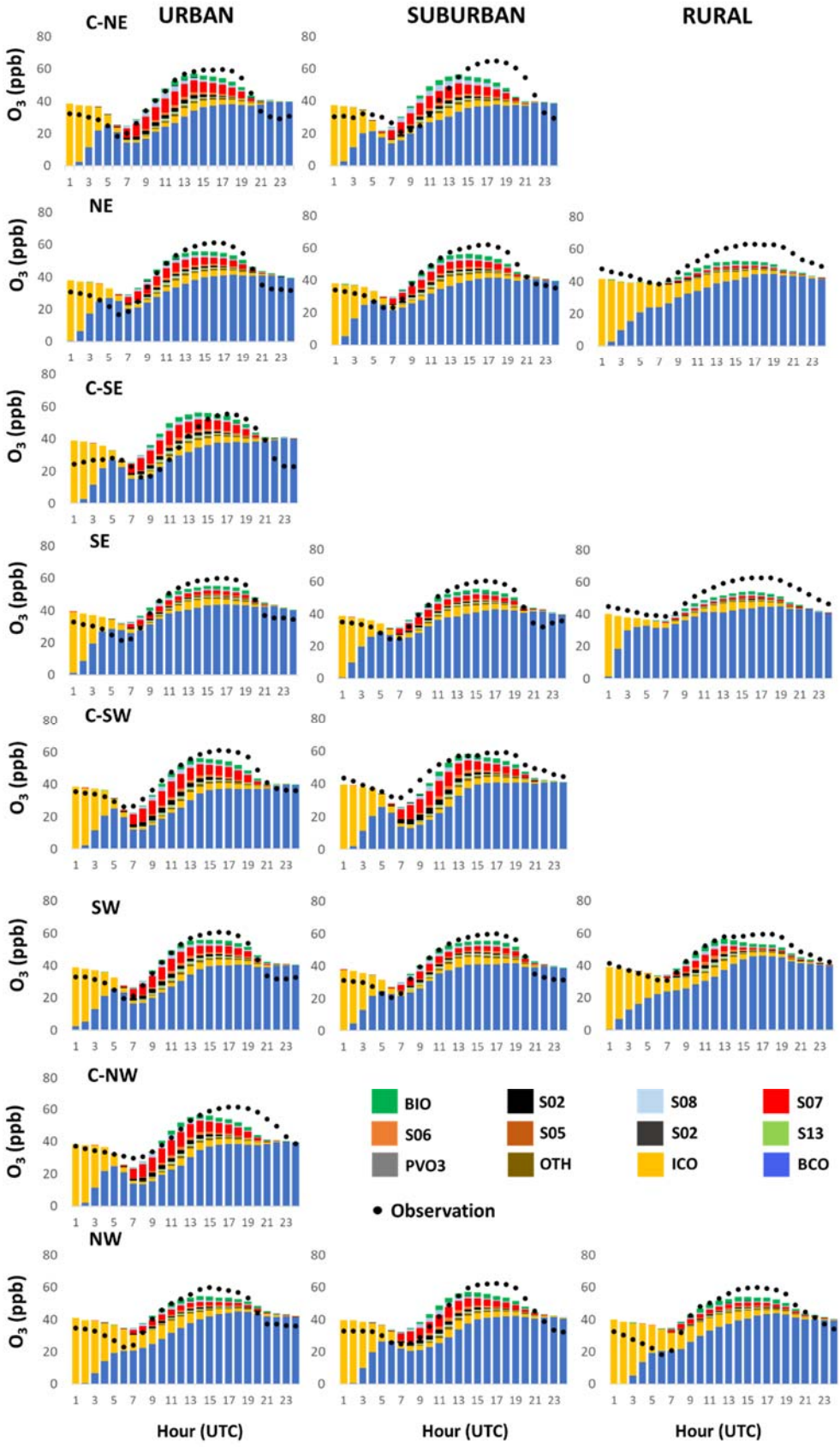

Figure S14. Hourly contribution (ppb) for the monthly average at the location of monitoring sites by geographical quadrant.

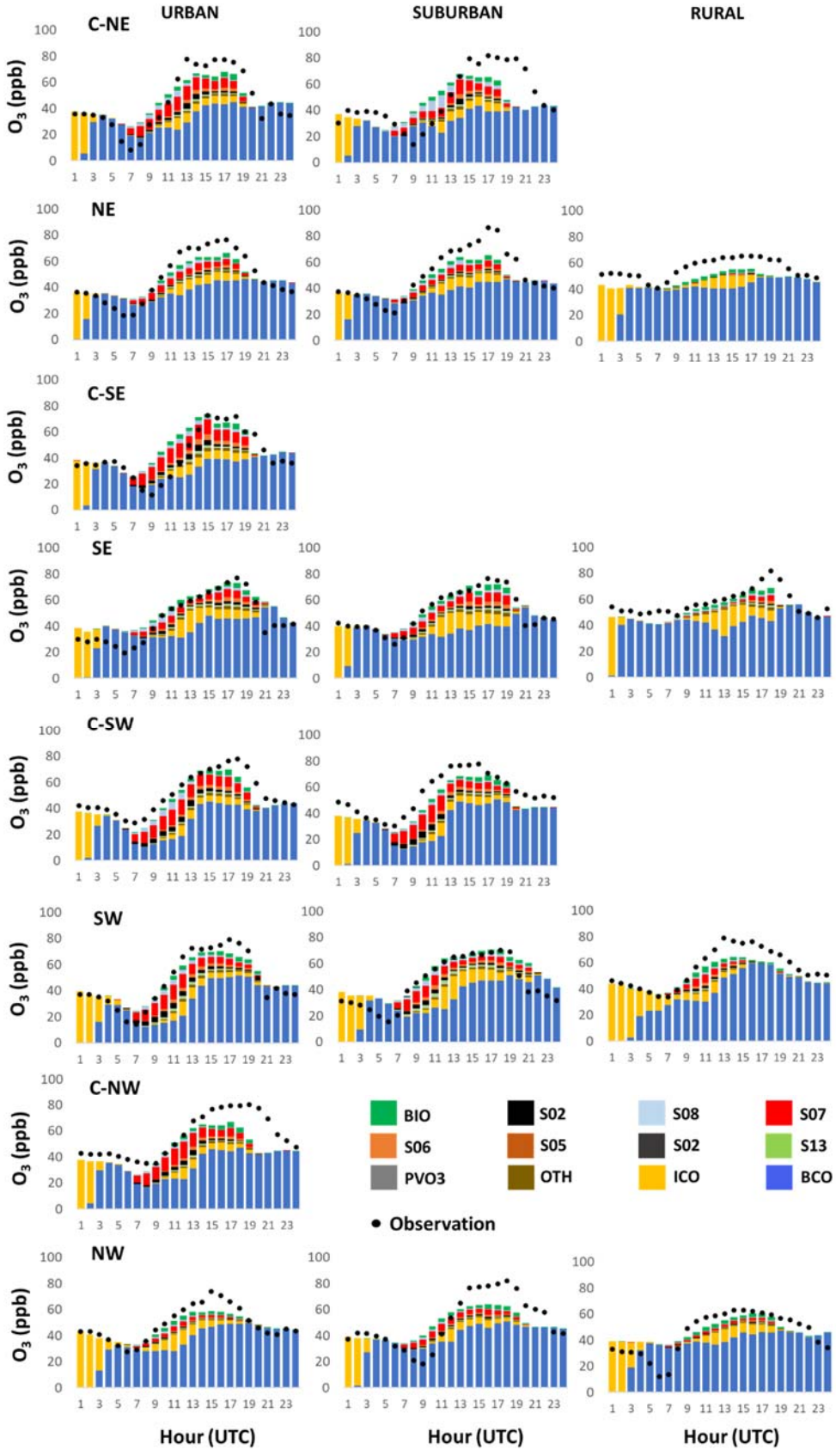

Figure S15. Hourly contribution (ppb) for July 27th, 2016 at the location of monitoring sites by geographical quadrant.

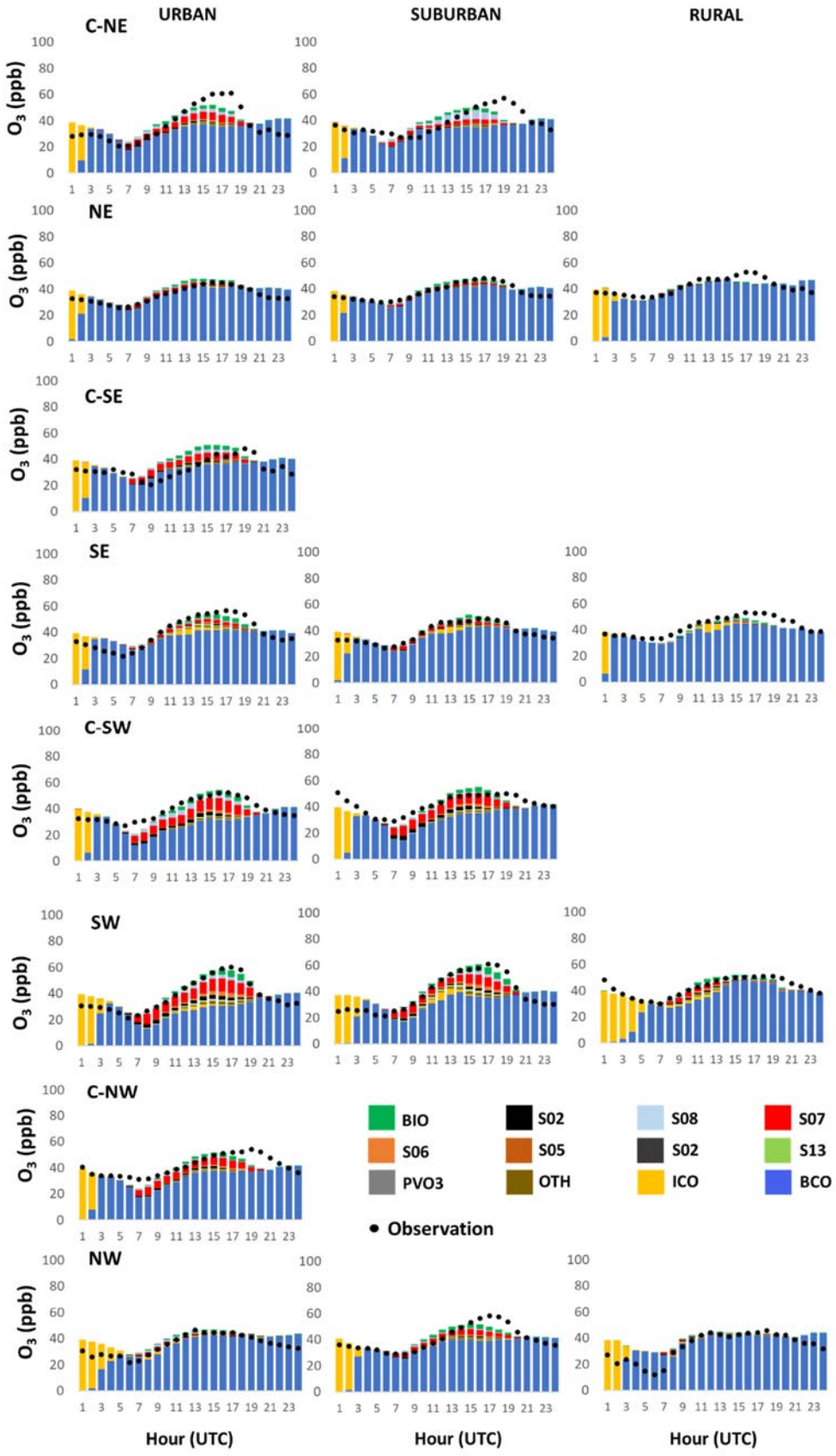

Figure S16. Hourly contribution (ppb) for July 13th, 2016 at the location of monitoring sites by geographical quadrant.

~~**Table S4. Model performance statistics by station type for ground-level O3 concentration.**~~

~~Station~~	~~FAC2~~	~~MB (µg m-3)~~	~~MGE (µg m-3)~~	~~NMB~~	~~NMGE~~	~~RMSE (µg m-3)~~	~~r~~	~~IOA~~
~~Industrial~~	~~0.95~~	~~7.8~~	~~14.5~~	~~0.10~~	~~0.18~~	~~18.7~~	~~0.84~~	~~0.71~~
~~Rural~~	~~0.98~~	~~-2.9~~	~~13.8~~	~~-0.03~~	~~0.14~~	~~18.1~~	~~0.76~~	~~0.68~~
~~Suburban~~	~~0.94~~	~~2.4~~	~~17.15~~	~~0.03~~	~~0.20~~	~~23.3~~	~~0.74~~	~~0.69~~
~~Urban background~~	~~0.89~~	~~8.3~~	~~20.4~~	~~0.10~~	~~0.25~~	~~27.1~~	~~0.69~~	~~0.65~~
~~Urban traffic~~	~~0.88~~	~~10.8~~	~~19.9~~	~~0.14~~	~~0.25~~	~~26.5~~	~~0.73~~	~~0.65~~