Response to Editor decision (publish subject to minor revisions)

Dear editor, thank you for the opportunity to refine our submission according to the points raised by both reviewers in the second revision round. Once more, we acknowledge them for the time devoted to our manuscript and for fruitful suggestions that definitively helped us to improve our work.

In the document attached we provide point-to-point responses to each of their additional questions and comments for your final consideration. Consistently with the response to reviewers previously submitted, the author comments are structured according to ACP guidelines and follow the recommended sequence: comments from the referees (report #2 and report #1) are shown in blue, then we provide our responses in black and the corresponding changes made in the manuscript and/or supplementary material (over the corresponding R1 versions) are included in red.

Responses to report #2 (Anonymous referee #1)

The authors have done a good job in revising the manuscript. Before I can recommend the manuscript for publication, however, a few details still need to be clarified:

Thank you for your contributions to improve our manuscript and for further recommendations to clarify remaining minor issues.

1) Figure 2: Please add the unit (%) to the axis. Moreover, I wonder if it would be much more helpful for the reader if the figure would show the share of the emissions during the analyzed period and not for the whole year (the share of biogenic emissions might be much larger during summer as for the annual mean?).

Yes, we agree that is a good point. Now Figure 2 refers exclusively to the temporal span of the modeling exercise (July 2016). We have added the % to the x axis and removed the description of the tagged sectors since it is now shown in Table 1, according to the following suggestion from Reviewer #1.

While emissions from vegetation (SNAP 10 and SNAP 11 sectors) represent 42.2% of total VOC emissions on an annual basis, this share raises to 72.2% specifically for this summer month.

Of note, in the process of double-checking emission figures we found an error regarding NO_X emissions from soils, included in this tag. While emissions inputs are correct, they were mistakenly reported in Figure AC6 within the responses to reviewers during the first revision of our manuscript. They are relatively small (around 224 t in this period, distributed as shown in Figure AC1 below), but by no means negligible. They represent 3.8% of total NO_X emissions, which is very similar to the estimate of MEGAN for the whole Europe according to Visser et al. (2019). These authors, however, point out that actual NO_X emissions from agricultural soils may be larger. That would be consistent with other estimates at global scale that suggest that soils may be responsible for up to 15% of total NO_X emissions (Weng et al., 2020). According to Lu et al. (2021), NO_X emissions from agricultural soils may be a significant limitation towards meeting O_3 standards since they significantly reduce the sensitivity of ozone to anthropogenic emissions. This specific issue may be addressed by further future specific studies to clarify to what extent this source may be diminishing the potential of anthropogenic emission abatement strategies.

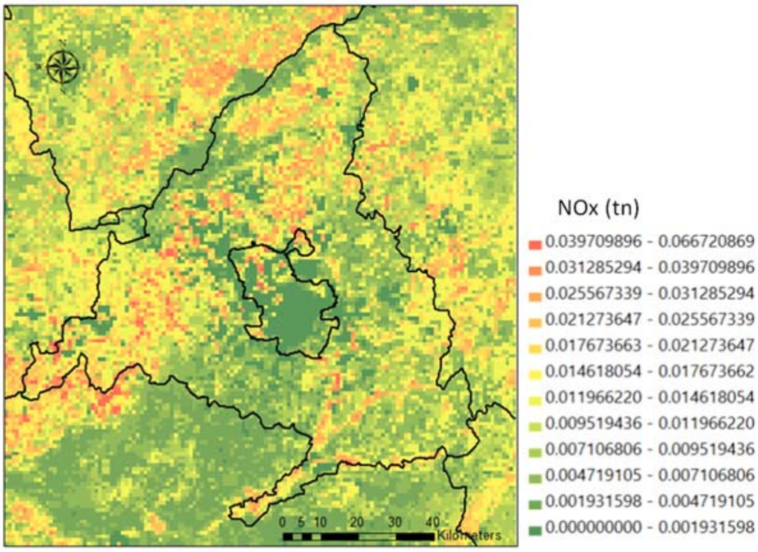

Figure AC1. Soil NO_X emissions (t) estimated in our modeling domain for July 2016

We revised section 2.4 of our manuscript to adjust the discussion to monthly percentages and to correct the discussion regarding NO_X emissions from soils. We included Table 1 for the sake of clarity and revised the manuscript for a consistent use of the abbreviations defined in the 3rd column to refer to tagged ozone sources. Section 2.4 now reads (changes in red):

"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-temporally resolved for modeling purposes (Borge et al., 2008b; Borge et al., 2018) and consistently combined for the different modeling domains (Borge et al., 2014).

Emissions from power generation and industrial activities (SNAP 01, SNAP 03 and SNAP 04 groups according to the Selected Nomenclature for Air Pollution nomenclature) were merged due to their limited presence in this modeling domain. Since emissions from agriculture (SNAP 10) in the region are mainly significant for VOCs from plants, they have been tagged along biogenic VOC (BVOC) emissions from vegetation (SNAP 11) (labeled as SNAP 10-11 in Figure 12). Soil-NO_X emissions provided by MEGAN 2.1 (Yienger and Levy, 1995) are also included in this group and their share to total NO_X emissions is around 4% in this period, consistently with MEGAN results reported European scale (Visser et al., 2019).

Consequently, 8 emission sources (Table 1) were tagged for the source apportionment analysis of ambient O_3 in the region. The share of NO_X and VOC emissions of each of them for July 2016 is summarized in Figure 2. The emission breakdown on an annual basis can be found elsewhere (Borge et al., 2022). Figure 2 shows that they account for the totality of emissions in the modeling domain and identifies road traffic (SNAP 07) as the main source of NO_X (66% of total emissions), followed by other mobile sources (SNAP 08). Since emissions from the residential, commercial and institutional sector (SNAP 02) occur almost exclusively in winter, the contribution from this sector is relatively small (around 7%) and is related to combustion units in agriculture and forestry. VOC emissions are dominated in this period by emissions from plants. The combined contribution of forests and agriculture represents 72% of total VOCs. Solvent use (SNAP 06) is the main anthropogenic source of this O_3 precursor with a total share of 22% (nearly 80% of anthropogenic VOC emissions).

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. 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."

Table 1. Tagged sectors for the O_3 source apportionment analysis

Tagged sources	Description	Abbreviation
SNAP01 – SNAP03 – SNAP04	Power generation (S01), Industrial combustion (S03) and Industrial processes without combustion (S04)	S01-03-04
SNAP02	Non-industrial combustion plants	S02
SNAP05	Extraction and distribution of fossil fuels	S05
SNAP06	Use of solvents and other products	S06
SNAP07	Road Transport	S07
SNAP08	Other mobile sources and machinery	S08
SNAP09	Waste treatment and disposal	S09
SNAP10 – SNAP11	Agriculture and nature	S10-S11

OTHER	Non-tagged emissions, including online computations (none in this study)	OTH
ICON	Initial conditions	IC
BCON	Boundary conditions	BC
PVO3	Stratospheric ozone (potential vorticity)	ST

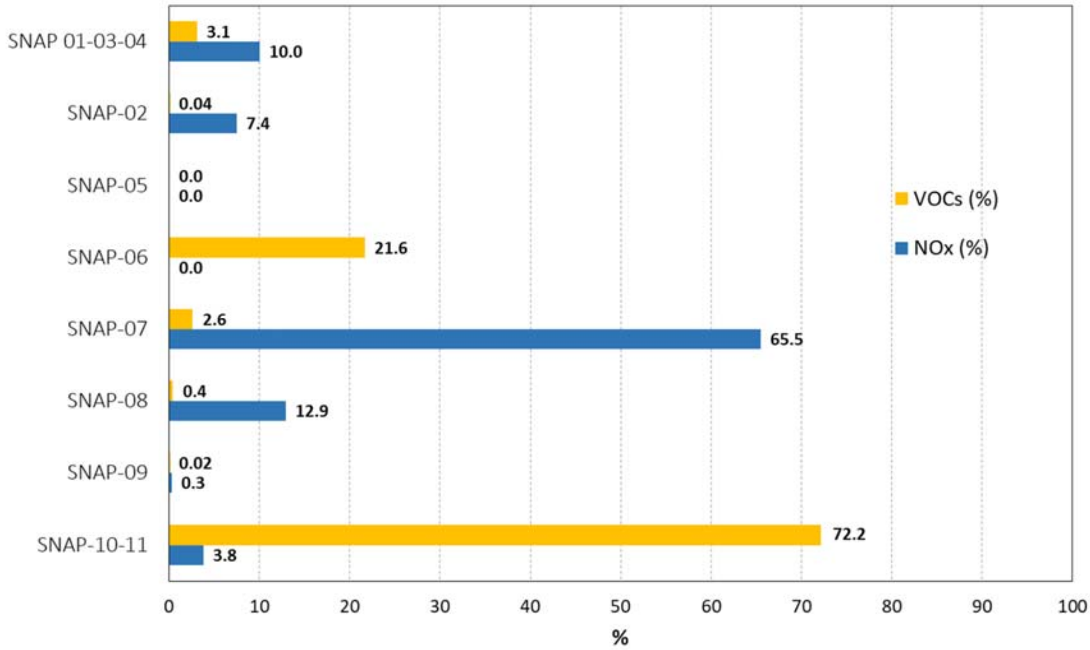

Figure. 2. NO_X and VOC emissions of tagged sectors for July 2016 (percentage over total emissions in the modeling domain) for the source apportionment analysis.

References added:

- Visser et al. (2019): https://doi.org/10.5194/acp-19-11821-2019

2) To my opinion a table which lists all the tagged sectors including a short description would be very helpful. Figure 2 lists only the emissions, Fig. 12 lists all tagged sectors but using acronyms only i.e. the reader has to search for the meaning of "OTH" or "PVO3". Also the tagged biogenic emissions are labeled SNAP10-11 in Figure 2 and BIO in Figure 12. Please use a unique naming scheme.

We made the necessary changes to incorporate this suggestion as discussed in the previous response. Figure 12, Figure S1, Figure S2, Figure S14, Figure S15 and Figure S16 have been modified by following this unique naming scheme.

3) I think the newly added discussion on the contribution of biogenic emissions in Sect. 3.2 is interesting, but the section seems unbalanced to me. The authors write: "O3 apportionment to biogenic emissions is not considered in Figure 4 because i) they have less interest from the point of view of possible abatement measures (Oliveira et al., 2023) and ii) their contribution is relatively

small". After this statement they add one page of discussion on biogenic emissions and only after this discussion the figure is discussed further. I feel this newly added part would much better fit into a dedicated "Discussion" section (or at the end of Sect. 3.2)

We concur with reviewer #1. We adopted a better-balanced structure where section 3.2 is split in two subsections (3.2.1. Non-anthropogenic sources and 3.2.2. Anthropogenic sources) with the following brief introduction:

"3.2. Spatial analysis of the source apportionment assessment

In this section, we discuss the contribution to ground-level O_3 of the tagged sources (Table 1) both, for monthly average and high values (illustrated by the 90th percentile, hereinafter P90). O_3 apportionment focusses on anthropogenic sources since they have more interest from the point of view of possible abatement measures (Oliveira et al., 2023) and have a larger contribution than that of SNAP10-11 (below 4% to total O_3 levels in this period). However, it is not a negligible apportionment since these groups 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). Non-anthropogenic emissions have been reported to play an important role on atmospheric photochemistry and they interact with manmade emissions so, they need to be considered in the process of designing policies to reduce tropospheric O_3 levels. Therefore, we discuss the potential role of emissions from agriculture and nature as well."

Furthermore, we added a brief discussion on the potential effects of NO_x emissions from agricultural and forest soils within new subsection 3.2.1 (lines 289-293 of the revised manuscript):

"Of note, SNAP 10-11 include NO_X emissions from soils (see section 2.4). Although they represent less than 4% of total NO_X emissions in the domain, they may be underestimated by MEGAN (Visser et al., 2019). According to other studies, i.a. Weng et al. (2020), emissions from agricultural soils may be substantially higher and could pose a significant constrain towards the control of O_3 levels (Lu et al., 2021). Methods to reduce the uncertainty of NO_X emissions estimates from soils as well as their role for O_3 control policies specifically for this region may be addressed in future research."

We added the later to the potential future research lines in the last paragraph of the conclusions section (lines 490-491):

"…speciation for specific sources. Furthermore, the role of biogenic NO_X and VOC emissions may be further studied to understand the implications for O_3 control strategies in the Madrid region."

References added:

- Visser et al. (2019): https://doi.org/10.5194/acp-19-11821-2019
- Weng et al. (2020): https://doi.org/10.1038/s41597-020-0488-5
- Lu et al. (2021): https://doi.org/10.1038/s41467-021-25147-9, 2021

4) Please clarify L426: "This relates to second-order interactions between sources (U.S. EPA, 2022). This represents a negligible fraction in this study, i.e. ISAM could attribute the virtual totality of O3 to any of the other sources" What is meant by " second-order interactions between sources"?

We appreciate the reviewer for pointing out these lines of text. We realize that the term "second-order" has specific mathematical meaning and could lead the reader to confusion. What we mean here is that this contribution is negligible and minor. We also provide a reference where the reader can find more information about this issue. In our opinion, it would not be prudent to distract the reader from the main points of our work here with the lengthy explanation about this while another reference is available. Taking this suggestion into considerations, we made the following changes to the manuscript (lines 411-414):

"Although 100% of emitting sectors have been tagged, Figure 12 shows as well the contribution from "others" (OTH). This contribution is typically negligible and relates to minor model interactions between sources and species not considered by the ISAM model. Details are fully explained in the documents provided with the model release (U.S. EPA, 2022)."

5) Please fix wrong usage of citations with (author) instead of author (e.g. (Paoletti et al., 2014))

We have carefully checked the reference style and made 12 corrections, including Paoletti et al. (2014).

Responses to report #1 (Referee #2: Johana Romero Alvarez)

The authors addressed the previously suggested comments, enhancing the manuscript's contribution to understanding the role of different emission sources in ozone formation. To improve the clarity of the discussion, I recommend the following specific revisions:

Thank you for the time devoted to our manuscript and for making additional suggestions to polish our manuscript.

Typographical and Citation Format Consistency:
I recommend a comprehensive review of the manuscript to check for typographical errors such as missing commas or periods in citations (e.g., Collet et al., (2018), should be Collet et al. (2018))

Thank for spotting that typo. We have carefully checked the reference style and made 12 corrections, including Collet et al. (2018).

Clarification on the Significance of Biogenic Emissions (Line 260):
The manuscript states that biogenic emissions account for 27% (monthly mean) and 22% (P90) of total O3 but are described as not negligible. To strengthen the narrative, it would be beneficial to elaborate on why these percentages, despite being lower than anthropogenic contributions, hold significant implications for ozone formation strategies and understanding.

Following reviewer #1's recommendation, we split section in two subsections dedicating one of them to the discussion of biogenic emissions (3.2.1. Non-anthropogenic sources). Now, we include a brief introduction in lines 247-254 (reproduced below) where we make this point explicit. We believe this helps to strengthen the narrative and makes clear the rationale to specifically discuss the role of emissions from agriculture and nature (SNAP 10-11).

"3.2. Spatial analysis of the source apportionment assessment

In this section, we discuss the contribution to ground-level O_3 of the tagged sources (Table 1) both, for monthly average and high values (illustrated by the 90th percentile, hereinafter P90). O_3 apportionment focusses on anthropogenic sources since they have more interest from the point of view of possible abatement measures (Oliveira et al., 2023) and have a larger contribution than that of SNAP10-11 (below 4% to total O_3 levels in this period). However, it is not a negligible apportionment since these groups 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). Non-anthropogenic emissions have been reported to play an important role on atmospheric photochemistry and they interact with manmade emissions so, they need to be considered in the process of designing policies to reduce tropospheric O_3 levels. Therefore, we discuss the potential role of emissions from agriculture and nature as well."

In addition, we reflected the need to further understand the role of non-anthropogenic emissions as a future research lines in the last paragraph of the conclusions section (lines 494-495):

"…speciation for specific sources. Furthermore, the role of biogenic NO_X and VOC emissions may be further studied to understand the implications for O_3 control strategies in the Madrid region."

Comparison with Previous Studies (Line 263):
When discussing the comparison of your findings with those of previous studies (e.g., Sartelet et al., 2012), it would be beneficial to briefly outline the methodologies or data employed in these referenced studies, especially if they diverge from your approach. This detail will provide readers with a clearer understanding of the reasons behind any similarities or discrepancies in findings, enriching the discussion.

We acknowledge the suggestion although we feel that discussing the methodological differences with previous studies regarding biogenic contributions would be out of the scope of this paper. Nonetheless, we summarize the main methodological features that may lead to discrepancies within the new subsection 3.2.1. (lines 266-269):

"… 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. In addition to the apportionment methodology itself, the results may differ depending on the emission inventory used, the modeling scale and resolution, temporal span and sources tagging scheme."