Reply to the reviewers’ comments on the ACPD manuscript “Source attribution of European surface O3 using a tagged O3 mechanism” by Aurelia Lupașcu and Tim Butler

Below we address the comments of the reviewers and questions raised during the open discussion of the manuscript “Source attribution of European surface O3 using a tagged O3 mechanism”. We thank the two Anonymous Reviewers for the time and effort reviewing the manuscript. We believe it has improved thanks to their comments. We have listed all reviewers’ comments below and our answers are provided in blue. We also append a “track-changes” version of the revised manuscript as an appendix with all changes to the manuscript highlighted.

Response to Anonymous Referee #2 comments

This is a well-written paper that provides a unique analysis of all of the source contributions to surface ozone in Europe over the spring to autumn months in 2010. By creating additional tracers of NO, NO2 and their reservoirs to the chemical mechanism, the sources of ozone can be quantified without perturbing emissions (which changes the chemistry), as is frequently done for such analyses. This paper discusses in a comprehensive and clear manner the various contributions and their seasonal variation. A nice analysis of standard metrics (MDA8, W126, AOT40 and SOMO35) is also presented. I recommend publication after addressing the minor comments outlined below.

We thank the reviewer for their positive comments. Below you can find our point-by-point responses to all the issues raised.

1. There are numerous grammar errors (missing articles, plural/singular mismatch, etc.) that should be corrected.

   Thank you for the useful feedback. As suggested by both reviewers, the manuscript has been carefully revised and the grammatical, linguistic and spelling mistakes in the manuscript have been carefully checked and corrected.

2. In Section 3.1 more should be said about how similar this simulation is to the one evaluated in Mar et al. (2016) to assure the reader that the results of that evaluation are really relevant here.

   Following the reviewer’s suggestion, we updated the sentence as follows “An extensive evaluation of WRF-Chem using the MOZART chemical mechanism to predict long term meteorological data and O3 levels has been presented previously (Mar et al., 2016). The main differences between the set-up up used in this study and the model described by Mar et
al. (2016) include differences between the versions of the model used (3.7.1 vs. 3.5.1, respectively), horizontal resolutions (50kmx50km vs. 45x45km, respectively), microphysics (Morrison vs. Lin, respectively) and cumulus schemes (Grell-Freitas vs. Grell 3-D, respectively), simulation years (2010 vs. 2007, respectively), anthropogenic emissions inventory (TNO-MACC III vs. TNO-MACC II, respectively), and chemical input and boundary conditions (extended CAM-Chem version 1.2 with MOZART-4 vs. MOZART-4/GEOS-5 simulations found at http://www.acom.ucar.edu/wrfchem/mozart.shtml, respectively).

3. The table captions in the supplement should more clearly explain the contents (units, etc.) Following the reviewer’s suggestion, we updated the Tables caption as it follows: “Table 1. Percent contribution of local, European, long-range transported (LRT) and natural emissions sources to MDA8 O3 (ppb) at each receptor region during late spring, summer and early autumn 2010” and “Table 2. Percent contribution of different emission sources and types to total O3 at each receptor region as calculated for health and vegetation metrics. The metrics analysed are mean, MDA8 and 95th percentile (ppb) for the early "F" and late "S" simulation period, W126 (ppm-hours), SOMO35 and AOT40 (ppb-hours).”

Response to Anonymous Referee #3 comments
This is a very nice analysis that provides a lot of useful information and insight regarding the sources of ozone across Europe. The material is appropriate for ACP and I could recommend the paper for publication after it is revised according to my comments below.

We thank the reviewer for their constructive and valuable comments. Following the Reviewer’s suggestion, we revised the paper and addressed all the concerns raised by providing response to individual comments below. Our responses are in blue.

General comments: 1) My only concern about the analysis is with regards to the ALPS region. This region combines the high elevations of the Alps (strong influence from long range transport of European and intercontinental origin) with the low elevations of the Po Valley, which is shielded from long-range transport by the Alps and experiences localized and intense air pollution episodes. Given the high variability of source regions and the high variability of local emissions, I don’t think that any clear conclusions can be drawn for this region. The authors need to split this region into two parts: 1) the Po Valley; and 2) regions above 1500 m elevation. Then we should see that the high elevations have the greatest impact from long-range transport and the low elevations have the strongest impact from local emissions.
Following the recommendation of the reviewer, we have split the ALP source region into two receptor regions: the Po Valley and the high Alps. The manuscript was revised to account for these regions and the discussion was updated accordingly in the following sections:

- **2.2 (Experimental setup)** by adding the following sentences “Except for ALP, the source regions within the European domain are identical to receptor regions. Given the complex topography of the ALP source region, we split this region into two receptor regions: the Po Valley region and the high Alps (regions above 1500 m elevation).”

- **3.2 (Contribution of tagged precursor sources to the MDA8 O3 concentration)** by recalculating the contribution of O3 coming from different sources and types to total O3 mixing ratio in the Po Valley and the high Alps receptor regions. We noticed that the contribution of different sources to the total MDA8 O3 mixing ratio in the Po Valley and the (old) ALP receptor regions give fairly similar results. Therefore, the text has been updated by using the newly calculated contributions in the Po Valley receptor region instead of ALP.

- **3.3 (Tagged ozone precursor contributions to exceedances of MDA8 target values – case study)** by updating the manuscript as follows: “The relative contribution of emissions from different source regions to modelled MDA8 O3 and to observed MDA8 O3 values, after being scaled to account for the contribution of modelled sources of O3 types is generally similar for Po Valley and GEN receptor regions (see Fig. 6). In the Po Valley, we can pinpoint the main remote contributor as being MBS (see Fig. 6), followed by GEN, and FRA, suggesting a dominant westerly and northerly air flow. The recirculation of air masses in the Gulf of Genoa could accentuate the sea breeze and therefore more O3 coming from NOx associated with shipping activities in the Mediterranean will be transported to the coastal and inland station. The high Alps receptor region is less influenced by ALP emissions than the Po Valley, and is more influenced by remote sources (see Fig. 6). The increased contribution of O3 from CEN, ITA and FRA to both exceedance and non-exceedance days in the high Alps receptor region compared with the Po Valley receptor region highlights the impact of the transboundary transport of O3 and its precursors. Furthermore, the contribution of stratospheric as well as long-range sources was generally 6 % higher in this receptor region than in the Po Valley receptor region.”

- **3.4 (Tagged ozone precursor contributions to regulatory ozone metrics).** We have recalculated the contribution of O3 coming from different sources and types to diverse health and vegetation metrics in the Po Valley and the high Alps receptor regions. Thus, in the revised manuscript, the comparison of different ozone metrics highlights the modelled values in the Po Valley instead of the ALP receptor region.
We have updated the discussion in the Conclusion as follows: “To better understand the origin of MDA8 O3 exceedances, we compared modelled and observed values of MDA8 O3 concentration in the Po Valley, high Alps, Germany, and Benelux receptor regions. Throughout days exceeding the recommended thresholds of 120 µg/m^3, the contribution from local sources was ~41 %, 34 % and 38 % of modelled MDA8 O3 for Po Valley, high Alps, and GEN, respectively. Throughout days not exceeding recommended thresholds, local emissions explain ~27 %, 16 % and 23% of modelled MDA8 O3 for the Po Valley, high Alps, and GEN, respectively. Moreover, this tagging approach revealed that the main remote sources of MDA8 O3 are MBS, GEN, and FRA for the Po Valley receptor region, and are FRA, CEN and UKI for Germany and Benelux receptor region. In addition, these analyses identified a persistently high contribution of transboundary sources to background O3 concentration in the high Alps receptor region”.

We have also updated the tables in the Supplementary material accordingly. The details of the changed text could be also seen in the tracked changes version of the manuscript, appended here.

2) In general the standard of English is fairly good but it needs a lot of polishing. There are too many instances of grammatical errors or awkward phrasing for me to list individually, but here are a few examples from the first paragraph of the Introduction: “The World Health Organization air quality guideline report that high O3 concentrations can cause damages to humans and vegetation” “Moreover, it has been shown that tropospheric O3 also affects radiative forcing and therefore contributing to climate change.” “To maintain a good air quality and understand O3’s response to climate change, it is important to understand the contribution of different sources of its precursors to the tropospheric O3 concentration.” Another example is this sentence in the Conclusions, which is difficult to understand: “Thus, we have seen that during the exceedances days, the contribution from local sources sources is~45 % and 38 % of modeled MDA8 O3, whilst during nonexceedances values is~32 % and 2 3% for ALP, respectively GEN.”

Thank you for your kind suggestion. The manuscript has been carefully revised and the grammatical, linguistic and spelling mistakes in the manuscript have been carefully checked and corrected. Following the reviewer’s suggestion, we have updated the introduction as follows “Ground-level O3 is an important air pollutant that damages human health (Fleming et al., 2018) and vegetation (Mills et al., 2018). It also affects the radiative forcing (e.g. Ramaswamy et al., 2001; Stevenson et al., 5 2013), and therefore contributes to climate change. Impacts of O3 on human health are associated with lung disease, chronic disease, and death from respiratory ailments. To protect human populations from exposure to high
levels of O3, the World Health Organization (WHO, 2006, 2017) recommended an air quality guideline for ozone in which the maximum daily average 8-h (MDA8) for O3 should not exceed 100 µg/m³. The European Environmental Agency (EEA, 2017a) reported that the EU long-term objective concentration of 120 µg/m³ is often exceeded and that more than 90 % of the urban population of the European Union was exposed to O3 levels higher than the stricter recommendation set by the WHO. "To improve the air quality in certain areas, it is important to know the extent to which different precursors (NOx and VOCs) contribute to tropospheric O3 concentrations".

We realize that the sentence in the Conclusions creates confusion, therefore, we have rephrased this as follows: "To better understand the origin of MDA8 O3 exceedances, we compared modelled and observed values of MDA8 O3 concentration in the Po Valley, high Alps, Germany, and Benelux receptor regions. Throughout days exceeding the recommended thresholds of 120 µg/m³, the contribution from local sources was ~41 %, 34 % and 38 % of modelled MDA8 O3 for Po Valley, high Alps, and GEN, respectively. Throughout days not exceeding recommended thresholds, local emissions explain ~27 %, 16 % and 23% of modelled MDA8 O3 for the Po Valley, high Alps, and GEN, respectively."

Specific Comments:
Page 2, line 5 Here you state: “It has been shown that the background O3 concentrations have increased during the last several decades due to the increase of overall global anthropogenic emissions of O3 precursors (HTAP, 2010)” What is meant by background? HTAP uses the term global background to refer to natural ozone that would exist in the absence of anthropogenic emissions. This quantity cannot be measured but must be calculated by global models. Do you really mean to say that the global natural background has increased? Or do you mean that average observed global ozone has increased? According to the extensive review conducted by TOAR-Climate [Gaudel et al., 2018] the current in situ ozone monitoring network is insufficient to quantify ozone changes on the global or hemispheric scale; the available satellite products disagree on the trend, with some showing increases and some showing decreases.

We meant the surface ozone without contribution from local anthropogenic sources, which should more correctly be referred to as the “baseline” ozone. The text has been changed accordingly as follows: "A 2010 report from HTAP (HTAP, 2010) shows that the observed baseline O3 concentrations (concentrations without the contribution from local anthropogenic emissions) have increased throughout the last several decades since overall global anthropogenic emissions of O3 precursors have increased. However, a more recent study by Gaudel et al. (2018) has established that the global surface O3 trends exhibit high variability, and depend on several factors such as season, region, elevation and proximity to fresh
ozone precursor emissions. However, since the network capable of monitoring ozone levels is sparse, it is difficult to quantify the O3 changes on a global scale. Satellite-derived O3 measurements can be used to quantify changing levels of O3, but Gaudel et al. (2018) showed that these products are not capable of quantifying significant trends.”

Line 6 Here you want to demonstrate that ozone air pollution is a current issue, but you only provide one reference that is now 11 years old and only applies to China. Please find additional references that are more current and cover other regions of the world. TOAR has recently published three papers that report present-day ozone using metrics relevant to human health [Fleming et al., 2018], vegetation [Mills et al., 2018] and climate [Gaudel et al., 2018]. These papers also provide up-to-date reviews of the literature concerning the impacts of ozone on humans, vegetation and climate. These papers would be helpful for the Introduction.

Following the reviewer’s suggestion, we revised the sentence as it follows: “Surface O3 pollution due to urbanization and motorization processes are serious challenges for large cities (e.g. Chan and Yao, 2008; Folberth et al., 2015; Li et al., 2017, 2019). Paoletti et al. (2014) showed that in Europe and the United States of America, the average O3 concentration in the cities has increased at a faster rate than those observed in rural areas. Fleming et al. (2018) showed that the 4th highest daily maximum 8-hour O3 (4MDA8) are more ubiquitous at urban sites than at non-urban sites. This leads to a worsening of general air quality that, ultimately, affects human health and ecosystems (Paoletti et al., 2014; Monks et al., 2015; WHO, 2017; Fleming et al., 2018; Mills et al., 2018).”

In general the standard of English is fairly good but it needs some polishing, for example the following phrases in the first paragraph of the Introduction need more work: “The World Health Organization air quality guideline report that high O3 concentrations can cause damages to humans and vegetation” “Moreover, it has been shown that tropospheric O3 also affects radiative forcing and therefore contributing to climate change” To maintain a good air quality and understand O3’s response to climate change, it is important to understand the contribution of different sources of its precursors to the tropospheric O3 concentration.”

Another example is this sentence in the Conclusions, which is difficult to understand: “Thus, we have seen that during the exceedances days, the contribution from local sources sources is ∼45 % and 38 % of modeled MDA8 O3, whilst during nonexceedances values is ∼32 % and 2 3 % for ALP, respectively GEN.”

The reviewer has apparently made a duplicate comment since s/he had referred to these phrases in the “General comments” section, which we have already responded to.
Page 3, Line 21 Lefohn and Musselman stated that the W126 index “. . . would provide a more appropriate target for air quality management programs designed to reduce emissions from anthropogenic sources contributing to O3 formation”. I’m not sure why this quote is provided. It seems to imply that W126 is a better metric than AOT40, but there is no agreement among the scientists who study the impacts of ozone on vegetation as to which metric is best. W126 was developed for a few limited crops and trees and is not necessarily applicable to other types of vegetation. For example, Harmens et al. [2018] found that a particular type of wheat is not sensitive to ozone peaks, which means W126 is not the best metric. Mills et al. [2018] give an overview of various vegetation metrics and they point out that the flux-based methods are the most accurate, but TOAR did not include these methods because their calculation on the global scale is not yet feasible.

Considering the reviewer’s comment, we have simplified the paragraph for clarity. We have deleted the information less relevant to our manuscript since conflicts with other studies on this topic.


Corrected, thank you

Page 4, line 18 I don’t understand this phrase: “has been modified to enable to model capacity to be used”

Following the reviewer’s comment, we re-wrote the phrase as follows: “To overcome these limits, we modified the header file gdata.h, located in ~/KPP/kpp/kpp-2.1/src. Hence, the new gdata.h file considers a large number of species and reactions associated with this new chemistry option.”

Page 4, Line 19 Should this sentence be a part of the preceding paragraph?

Indeed. Thanks to the reviewer for pointing to this.

Page 5 line 31 Here and throughout you need to be consistent with regards to the term, ozone concentration. “Ozone concentration” is appropriate when using units of μg m−3, but when using units of ppb, the correct term is “ozone mixing ratio”

We corrected, thank you.

In many places in the paper the term “NOx precursors” is used. This seems to be a redundant phase. Just define NOx as a precursor gas at the beginning of the paper and then afterwards just use “NOx” as it will be clear that it is a well-known precursor.
Following the reviewer’s suggestion, in the “Introduction” we define NOx precursors as NOX and the use of the “NOx” term to refer to this precursor throughout the manuscript.

Page 8, line 18 “In all receptor regions, the MDA8 O3 concentration is dominated by O3 produced by remote anthropogenic precursors” I think this is overstated because it gives the impression that far more than half of the ozone is from remote anthropogenic precursors. But the range is 30-53%. Please re-phrase this sentence.

Following the reviewer’s comment, we re-phrase it as follows: “In all receptor regions, local anthropogenic sources have a lower contribution to MDA8 O3 mixing ratios than the sum of ozone due to anthropogenic sources in other European source regions and long-range transport of ozone from intercontinental source regions. The contribution of intercontinental transport to the total MDA8 O3 mixing ratio in Europe is consistent with previously reported results, i.e. Fiore et al. (2009) and Karamchandani et al. (2017), while this study allows us to identify which anthropogenic sources exert a strong influence on MDA8 O3 predicted in different regions.

Page 8 line 25 This sentence seems out of place and it should appear before the discussion of the stratospheric source.

Following the reviewer’s suggestion, we moved this sentence.

Page 8 line 29 “Arabic Saudi peninsula” should be Arabian Peninsula

Corrected, thank you

Page 9 line 11 This statement is not quite correct: “Another consequence of enhanced photochemical activity during the summer season is the reduction of stratospheric O3” It should say: “Another consequence of enhanced photochemical activity during the summer season is that it reduces the relative influence of stratospheric O3” But in addition to changing the relative impact, do the absolute values of stratospheric ozone also diminish in summer, relative to spring?

Indeed, the absolute ozone mixing ratio attributable to the stratosphere is reduced in our simulations in summer compared with spring. We have updated the sentence as follows: “Another consequence of enhanced photochemical activity during summer is that it reduces the influence of stratospheric O3 from a domain-wide mean MDA8 O3 mixing ratio of 4.4 ppb in the spring to 1.3 ppb in the summer (Figs. 2 and 3).”

Page 9 line 31 Is OCN in these studies defined in the same way as in your study? If not then OCN should not be used when referencing the other studies.
No, in these studies the total shipping emissions are assigned to OCN. In our study, we define three source regions associated with the shipping activities: OCN (Oceanic sources coming from boundaries and the Atlantic Ocean), MBS (the Mediterranean and the Black Sea) and BNS (Baltic and the North Sea). Following the reviewer's suggestion, we remove these references.

Page 12, line 34 I don’t understand what is meant by “efficiently complementing”. I think you are trying to say that they behave similarly.

Thanks for this suggestion. We change accordingly the text “Since the difference between AOT40 and SOMO35 is only a few percentage points, regardless of the receptor region, we were able to conclude that they behave similarly, according to thresholds used to define these metrics.”

Page 13, line 21 Here you say that W126 is more sensitive to local emissions because it does not include a threshold. But, in addition, isn’t it also more sensitive to local emissions because this metric places much more weight on the high ozone values and high ozone is likely to be produced under hot stagnant conditions when local emissions are more important?

We agree that this sentence was misleading, so we have removed it from the manuscript. We would also like to point out that on pages 13, line 32 of the original manuscript we have a paragraph that provides an explanation to the observed sensitivity of the W126 metric to higher ozone concentrations. This paragraph states “this behaviour is closely linked to the definition of these metrics. If the O3 mixing ratio is less than 40 ppb, W126 has a weighting factor lower than 0.03, while AOT40 has a weighting factor of 0. Above this threshold, AOT40 has a weighting factor of 1, while in the case of W126 only O3 values higher than 100 ppb have a weighting factor of 1. Due to way these metrics are defined, predicted O3 values in each grid cell are accounted for the W126, may not be accounted for the AOT40 index”.

Source attribution of European surface \( \text{O}_3 \) using a tagged \( \text{O}_3 \) mechanism

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**Abstract.** Tropospheric ozone (\( \text{O}_3 \)) is an important air pollutant that affects human health, ecosystems, and climate. The contributions of \( \text{O}_3 \) precursor emissions from different geographical source regions to the \( \text{O}_3 \) concentration can help to quantify the effects of local versus remote transported precursors on the \( \text{O}_3 \) concentration in a certain area. This study presents a “tagging” approach within the WRF-Chem model that attributes \( \text{O}_3 \) concentration in several European receptor regions to nitrogen oxides (\( \text{NO}_x \)) emissions from within and outside of Europe during April-September 2010. We also examine the contribution of these different precursor sources to various \( \text{O}_3 \) metrics and their exceedance events. Firstly, we show that the spatial distributions of simulated monthly mean MDA8 from tagged \( \text{O}_3 \) sources regions and types for late spring, summer and early autumn 2010 varies with season. For summer conditions, \( \text{O}_3 \) production is dominated by national and intra-European sources, while in the late spring and early autumn intercontinental transported \( \text{O}_3 \) is an important contributor to the total \( \text{O}_3 \) concentration. We have also identified shipping activities in the Mediterranean Sea as an important source of \( \text{O}_3 \) for the Mediterranean countries, as well as the main contributor to high modelled MDA8 \( \text{O}_3 \) concentration in the Mediterranean basin itself. Secondly, to have a better understanding of the origin of MDA8 \( \text{O}_3 \) exceedances, we compare modelled and observed values of MDA8 \( \text{O}_3 \) concentration in the “Alps-Po Valley” and “Germany-Benelux” receptor regions, revealing that the contribution from local sources is about 45-41% and 38% of modelled MDA8 \( \text{O}_3 \) during the exceedances days respectively. By examining the relative contributions of remote \( \text{NO}_x \) sources to modelled and observed \( \text{O}_3 \) exceedance events, we determine that model underrepresentation of long-range \( \text{O}_3 \) transport could be contributing to a general underestimation of modelled \( \text{O}_3 \) exceedance events in the Germany-Benelux receptor region. Thirdly, we quantify the impact of local vs. non-local \( \text{NO}_x \) precursors on \( \text{O}_3 \) production for each European receptor region using different \( \text{O}_3 \) metrics. The comparison between mean, MDA8 and 95th percentile \( \text{O}_3 \) metrics accentuate the importance of large contributions from locally-emitted \( \text{NO}_x \) precursors to the high-end of the \( \text{O}_3 \) distribution. When we compare the vegetation and health metrics, we notice that the SOMO35 and AOT40 indexes exhibit a rather similar behaviour, while the W126 index accentuates the importance of local emissions. Overall, this study highlights the importance of a tagging approach to quantify the contribution of local and remote sources to the MDA8 \( \text{O}_3 \) concentration during several periods as well to different \( \text{O}_3 \) metrics. Moreover, this method could be applied to assess different mitigation options.
1 Introduction

Tropospheric ozone (O₃) is formed primarily through reactions between nitrogen oxides (NOₓ) and volatile organic compounds (VOC) that occur in the presence of sunlight. The ground-level O₃ is an important air pollutant that damages human health (Fleming et al., 2018) and vegetation (Mills et al., 2018). It also affects the radiative forcing (e.g. Ramaswamy et al., 2001; Stevenson et al., 2013) and therefore contributes to climate change. Impacts of O₃ on human health are associated with lung disease, chronic disease and death from respiratory ailments. To protect human populations from exposure to high levels of O₃, the World Health Organization (WHO, 2006, 2017) recommended an air quality guideline (WHO, 2006, 2017) report that high for ozone in which the maximum daily average 8-h (MDA8) for O₃ concentrations can cause damages to humans and vegetation. It has been shown that the background should not exceed 100 µg m⁻³. The European Environmental Agency (EEA, 2017a) reported that the EU long-term objective target concentration of 120 µ is often exceeded and that more than 90% of the urban population of the European Union was exposed to O₃ levels higher than the stricter recommendation set by the WHO. A 2010 report from HTAP (HTAP, 2010) shows that the observed baseline O₃ concentrations have increased during (concentrations without the contribution from local anthropogenic emissions) have increased throughout the last several decades due to the increase of since overall global anthropogenic emissions of O₃ precursors (HTAP, 2010). Large cities are facing serious challenges in have increased. However, a more recent study by Gaudel et al. (2018) has established that the global surface O₃ trends exhibit high variability, and depend on several factors such as season, region, elevation and proximity to fresh ozone precursor emissions. However, since the network capable of monitoring ozone levels is sparse, it is difficult to quantify the O₃ changes on a global scale. Satellite-derived O₃ measurements can be used to quantify changing levels of O₃, but Gaudel et al. (2018) showed that these products are not capable of quantifying significant trends. Surface O₃ pollution due to urbanization and motorization processes (e.g. Chan and Yao, 2008). Moreover, it has been shown that tropospheric are serious challenges for large cities (e.g. Chan and Yao, 2008; Fofolberth et al., 2015; Li et al., 2017, 2019). Paoletti et al. (2014) showed that in Europe and the United States of America, the average O₃ concentration in the cities has increased at a faster rate than those observed in rural areas. Fleming et al. (2018) showed that the 4th highest daily maximum 8-hour O₃ also affects radiative forcing (e.g. Ramaswamy et al., 2001; Stevenson et al., 2013) and therefore contributing to climate change.

To maintain a good air quality and understand O₃’s response to climate change (MDA8) are more ubiquitous at urban sites than at non-urban sites. This leads to a worsening of general air quality that, ultimately, affects human health and ecosystems (Paoletti et al., 2014; Monks et al., 2015; WHO, 2017; Fleming et al., 2018; Mills et al., 2018). To improve the air quality in certain areas, it is important to understand the contribution of different sources of its know the extent to which different precursors (NOₓ and VOC to the VOCs) contribute to tropospheric O₃ concentration concentrations.

Emissions Information regarding levels of NOₓ and VOCs, as well as the emissions sources, VOC emissions and weather conditions are important to understand enhance our ability to predict the formation of the tropospheric O₃ in the troposphere. The continuous development of chemical transport models leads can lead to a better understanding of the processes that contribute to high O₃ episodes and can help the authorities to develop strategies to reduce the impact of O₃ on both human well-being and ecosystems by knowing the impact of source emissions of. Knowing the impacts of NOₓ and VOC
emissions from sources such as surface anthropogenic source activities, fires, soil, and the stratosphere on total O\textsubscript{3} production can help authorities develop strategies aimed at reducing the impact of high levels of O\textsubscript{3} on the well-being of both humans and ecosystems. Several approaches have been used to determine the source attribution—extent to which individual sources contribute to total levels—of O\textsubscript{3}. For example, estimations of the changes in O\textsubscript{3} concentration have been made by perturbation of different emission categories. Emission categories have allowed scientists to make estimations regarding the contributions of individual sources of O\textsubscript{3} to total O\textsubscript{3} levels (e.g., Fiore et al., 2009).

Tagging techniques have also been used in modelling studies to determine source attributions for pollutants/receptor relationships and how individual sources of pollutants contribute to total pollution levels at given locations and source/receptor relationships. Pollutants with relatively low chemical reactivities, such as carbon monoxide (CO), can be “tagged” according to their emission sectors or regions for attribution studies (e.g., Pfister et al., 2011). Sudo and Akimoto (2007), and Derwent et al. (2015) used O\textsubscript{3} tracers tagged by their region of formation. They have found that the to show that intercontinental transport of O\textsubscript{3} can occurring from polluted source region-regions, such as North America and East-Asia, appears to be the most important source of tropospheric O\textsubscript{3} in Europe. The other studies, including those of Wang et al. (2009) and Grewe et al. (2010, 2012, 2017) studies showed that the tagging method is used to identify contribution from individual sources due to its ability to track the have used tagging methods to identify the contribution of individual sources of O\textsubscript{3} to overall levels. This method has especially useful since it can track emitted NO\textsubscript{x} species during transport and chemical processing. Moreover, Grewe et al. (2012) showed the impact of the tagging method on mitigation measures, while Dahlmann et al. (2011) studied examined the contribution of O\textsubscript{3} sources to O\textsubscript{3} radiative forcing. The studies of Work by Emmons et al. (2012) and Butler et al. (2018) describe a procedure for tagging O\textsubscript{3} produced from NO\textsubscript{x} sources through updates to the MOZART chemical mechanism. In addition, Butler et al. (2018) has extended, and Butler et al. (2018) expanded the tagging technique to account for the VOC sources.

Based on Emmons et al. (2012) work the work of Emmons et al. (2012), Pfister et al. (2013) and Safieddine et al. (2014) used were able to use the WRF-Chem regional model to quantify the role contribution of inflow (defined as source of tagged O\textsubscript{3} and odd nitrogen species entering into the regional domain at the lateral boundaries) and of anthropogenic NO\textsubscript{x} precursors (named NO\textsubscript{x} in the following) on the surface O\textsubscript{3} levels. Using a slightly different methodology, Gao et al. (2016) have employed implemented within WRF-Chem a tagging-framework a tagging method based on Ozone Source Apportionment Technology (OSAT) (Yarwood et al., 1996) incorporated in the Comprehensive Air quality Model with extensions (CAMx).

Many efforts have been made to understand-Much effort has been focused understanding the origin of tropospheric O\textsubscript{3} and the key role played by the intercontinental transport, the contribution of stratospheric O\textsubscript{3} intrusion, and of different emissions sources to tropospheric O\textsubscript{3} concentration in a wide range of receptor regions. For a better understanding of these interactions, To better understand how these reaction interact it is necessary to know the relation between the amount-relation between levels of an emitted species and its atmospheric concentration. Thus we can-When this information is known, it is possible to quantify the contribution of different emission precursor sources to the overall O\textsubscript{3} concentration at levels at a particular receptor location. For this purpose, following we followed a strategy outlined in Emmons et al. (2012) and Butler et al. (2018), we implemented to implement a tagging technique into the regional WRF-Chem model tagging technique that. The model can
be used to quantify the source contributions to the tropospheric $O_3$ concentration, by “tagging” emissions of $NO_x$ emissions, and corresponding resulting products and following them to the products so that they can be traced to the final production of $O_3$.

Important objective when we are studying the effects of $O_3$ is its effect on humans and vegetation is of the utmost importance. Therefore, based on hourly averaged data, several exposure indexes have been defined in order to describe the relationship between $O_3$ and both human health and agricultural crop yield. These indexes are based on hourly averaged data. Musselman et al. (2006), Agathokleous et al. (2018), and Lefohn et al. (2018) present a literature overview on review literature describing $O_3$ metrics, while Paoletti et al. (2007) presents. Additionally, a work by Paoletti et al. (2007) has provided a list of common $O_3$ exposure metrics used to assess risk to human health and vegetation across Italy during the 2000-2001 period. Here we use some well-known $O_3$ metrics, such as MDA8, SOMO35, AOT40, and W126. The MDA8 index (Lefohn et al., 2018) has been defined as the maximum daily average 8-h (MDA8) $O_3$ values in parts per billion (ppb) (Lefohn et al., 2018). SOMO35 (WHO, 2001) has been determined by European protocols (EU directive 2008/50/EC, 2008) and it is defined as the annual sum of MDA8 $O_3$ with a cut-off of values of 35 ppb. Both MDA8 and SOMO35 are health-related metrics. The AOT40 and W126 vegetation metrics have been used to regulate air pollution in both Europe (EU directive 2008/50/EC, 2008) and the United States (U.S. EPA regulations https://www.gpo.gov/fdsys/pkg/FR-2015-10-26/pdf/2015-26594.pdf). In the European legislation (EU directive 2008/50/EC, 2008), the AOT40 metric is accumulated over the daytime period measured throughout daytime periods from May to July (growth season) and has a defined target limit of 18000 μg m$^{-3}$ h (9000 ppb – hours) and a long term objectives of 6000 μg m$^{-3}$ h (3000 ppb – hours). A standard of 15 ppm – hours is defined for the seasonal W126 index, which is averaged over three years. Lefohn and Musselman (2012, https://www.fcpotawatomi.com/wp-content/uploads/2015/01/Vegetation.pdf) stated that the W126 index “...would provide a more appropriate target for air quality management programs designed to reduce emissions from anthropogenic sources contributing to $O_3$ formation”. These metrics have been used side by side to assess the impact of mitigation strategies (Avnery et al., 2013), the impact of industry on air quality management issues (Vijayaraghavan et al., 2016), and the impact of high $O_3$ levels and temperatures on crops (Tai and Val Martin, 2017).

In this paper, we use a tagged $O_3$ mechanism in the WRF-Chem regional chemical climate model to understand the contributions of emitted $O_3$ precursor emissions to different geographical source regions and types on the modelled $O_3$ concentration in several European receptor regions. In Section 2 we briefly describe the details of the implementation this tagging technique pointing to the and describe changes made to both the chemical mechanism and WRF-Chem code. Section 2 also provides a description of describes the WRF-Chem configuration, simulation design, and input data used in the study. An analysis of the WRF-Chem simulations is presented in Section 3, while Section 4 summarizes our findings.
2 Model simulation

2.1 Tagging technique

In order to implement a WRF-Chem model simulation using a tagging approach, several changes must be implemented in the model code to accommodate additional tracers and reactions representing tagged constituents. Butler et al. (2018) describes in detail how the tagging technique was implemented in the Community Earth System Model. The tagging technique used in this study is based on the same approach and uses the same modified version of the MOZART chemical mechanism. Further detail on how the chemical mechanism was extended can be found in Butler et al. (2018).

In order to use the NO\textsubscript{x} tagging mechanism, a new chemistry option was added in the namelist.input file: chem...opt=113 through the code. The coupling of the new chemical scheme with microphysics and radiative processes requires several modifications to the code: 1) The first step is to create a new chemistry option. The package mozart..tag..kpp (chemopt==113) has been added to ~/WRFV3/Registry/registry.chem together with new model variables for tagged NO\textsubscript{x} species, for example, (e.g. O3...INI, O3...STR, etc). For this purpose, the pre-processing software described in Butler et al. (2018) was adapted in order to produce a new chemical mechanism; 2) The new chemistry package is a KPP option. Therefore, we created a new subdirectory in ~/WRFV3/chem/KPP/mechanisms/ directory containing the files (*.spc, *.eqn, *.kpp, and *.def) which defined the chemical model species and constants, chemical reactions in KPP format, model description, computer language, precision, and integrator.

The KPP chemical preprocessor, version 2.1 (Sandu and Sander, 2006) used by WRF-Chem has an upper limit of limits the numbers of species and reactions in the chemical mechanism. Thus, to overcome these limits, we modified the header file gdata.h, located in ~/chem/KPP/kpp-2.1/src, has been modified to enable model capacity to be used for. Hence, the new gdata.h file considers a large number of species and reactions associated with this new chemistry option. Further, we updated the subroutines in the chem directory to take into account these packages ~/WRFV3/chem directory consider the new chemistry package. The modules that we modified are described in the Appendix.

Although WRF-Chem uses the Advanced Research WRF (ARW) dynamic core in this simulation which conserves mass and scalar mass (Grell et al., 2005), the tagged O\textsubscript{3} species are advected independently. Thus, numerical errors associated with the advection scheme led to gradients in the sum of tagged species concentration compared to the “real” concentration; therefore, the relationship between these variables is not conserved. Since the advection scheme fails to reproduce the expected solution (in which the sum of the tagged species concentration at each grid point must be equal to “real” concentration), we solve this by fixing all undershoots and/or overshoots assuming that the sum of tagged species mass is proportional to the "real" concentration. This technique was also applied in Flemming et al. (2015), and Gromov et al. (2010).

Compared to Pfister et al. (2013) and Safieddine et al. (2014) work, the expanded tagging technique used in this study has the advantage that multiple tags can be defined in each model run.
2.2 **Experimental setup**

WRF-Chem version 3.7.1 was used for this study to account for the impact of different global and European O$_3$ precursor source regions to several European receptor regions during the April-September 2010 period. A single domain, that covers the area between 32° N and 70° N, and 29° W and 57° E, was used with 50-km grid spacing and 35 vertically-stretched layers from the ground up to 50 hPa. The physics options used for this study include the Morrison double-moment microphysics scheme (Morrison et al., 2009), the Grell-Freitas cumulus parameterization (Grell and Freitas, 2014), the Rapid Radiative Transfer Model (Iacono et al., 2008) for longwave and Goddard shortwave scheme (Chou and Suarez, 1994), the Yonsei University boundary-layer parameterization (Hong et al., 2006), and the Monin-Obukhov scheme for the surface layer (Jiménez et al., 2012). The initial and boundary conditions for meteorological fields are taken from the European Centre for Medium-Range Weather Forecasts (ECMWF) reanalysis. Anthropogenic emissions were obtained from the TNO-MACC III emission inventory for Europe (Kuenen et al., 2014). Because the model domain extends beyond the edges of the TNO-MACC III inventory, we used for completion emissions from the HTAP V2 inventory (http://edgar.jrc.ec.europa.eu/htap_v2). Biogenic emissions were computed on-line using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) model (Guenther et al., 2006). The biomass burning emissions are based on Fire INventory from NCAR (FINN) (Wiedinmyer et al., 2011).

For this WRF-Chem simulation, the tagged MOZART chemical mechanism for NO$_x$ emissions (Butler et al., 2018) is used to represent the gas-phase chemistry. The photolysis rates were computed using the Fast Tropospheric Ultraviolet and Visible (FTUV) Radiation Model (Tie et al., 2003; Li et al., 2005). The dry deposition was calculated following the Wesely (1989) resistance method, while the wet removal scheme for the tagged MOZART chemistry is based on Neu and Prather (2012).

In order to represent the impact of transported O$_3$ from different regions outside of the domain, for the trace gases we used chemical boundary conditions derived from the extended CAM-Chem version 1.2 global simulations. Butler et al. (in preparation) used the tagging approach within the CAM-Chem model for several HTAP2 source regions such as: ASI (Asia), NAF (North-Africa), NAM (North-America), OCN (Oceanic sources), RBU (Russia, Belarus, Ukraine), and RST (rest of the world), as well as for several source types: BIO (biogenic emissions), BMB (biomass burning emissions), LGT (lightning), and STR (stratospheric O$_3$). Using a division of source/receptor regions within the European model domain, we define 15 geographical regions for this study, as shown in Figure 1 and Table 1. Source regions within the European domain are identical to European receptor regions in our study. A similar division of European regions has been used by Christensen and Christensen (2007) and Otero et al. (2018) to address the main sources of uncertainty in regional climate simulations, as well as during the AQMEII project (i.e. Struzewsk a et al., 2015). Except for ALP, the source regions within the European domain are identical to receptor regions. Given the complex topography of the ALP source region, we split this region into two receptor regions: the Po Valley region and the high Alps (regions above 1500 m elevation).
For each receptor region, we analyse the impact of the anthropogenic NOx emissions coming from different source regions to the total O3 concentration. The BIO, BMB, LGT, and STR types are also included in the simulation, but without including them into the division of source/receptor regions.

### 2.3 Ozone metrics

Using different metrics to assess the impact of O3 impact metrics we determine which are the most important O3 precursor sources for different kinds - we can determine which precursor sources most highly influence the accumulation of O3 impact in different receptor regions, and thus to provide insight into appropriate mitigation measures insights into which type of mitigation measures will be useful for a particular geographic area. These metrics include the mean O3 concentration, the mean of the maximum daily 8-hour O3 (MDA8), the cumulative exposure to mixing ratios above 35 ppb (SOMO35) (Colette et al., 2012), and the 95th-99th percentile for surface O3, the impacts. Neither the impact of O3 exposure on trees, plants and ecosystems (W126) (Lapina et al., 2014), nor the AOT40 accumulation metric (the threshold is 40 ppb) were used to assess risk to vegetation from O3 exposure (UNECE, 2010).

The European Air Quality Directive (EU directive 2008/50/EC, 2008) defines a target specifies that O3 exposure should remain below a target MDA8 O3 value of 120 µg m⁻³ for the MD8 concentration, which can be exceeded up to 25 days per calendar year averaged over three years. The modelled daytime AOT40 (during local daylight hours 8 AM – 7 PM) was calculated according to Equation (1).

\[ AOT40 = \sum_{i=1}^{90 \text{ days}} \left( \sum_{h=8}^{19} max(O_{3i,h} - 40,0) \right) \]  

(1)

According to the European legislation (EU directive 2008/50/EC, 2008), the AOT40 metric is accumulated over the daytime period from May to July (growth season) and it has a defined target limit of 18000 µg m⁻³ h (9000 ppb – hours) and a long term objective of 6000 µg m⁻³ h (3000 ppb – hours). W126 is calculated, however, is described according to U.S. EPA regulations (https://www.gpo.gov/fdsys/pkg/FR-2015-10-26/pdf/2015-26594.pdf). A standard of 15 ppm – hours is defined for the seasonal W126 index averaged over three years, which is an average over a three-year period. For this study, the hourly surface O3 tagged outputs for April through September are used to calculate the highest 3-month W126 index values (see Eq. 2):

\[ W126 = \sum_{i=1}^{90 \text{ days}} \left( \sum_{h=8}^{19} O_{3i,h} \cdot \left( \frac{1}{1 + (4403 \cdot e^{-126 \cdot O_{3i,h}})} \right) \right) \]  

(2)

According to Lefohn et al. (1988), the W126 index includes all hourly O3 values within the specified time range, although a lower weight is given to hourly O3 concentrations below the inflection point at 65 ppb, whilst while values above 90 ppb the weighting factor is almost 1, are weighted with a factor of almost one. SOMO35 (WHO, 2001) is defined as the sum of the MDA8 O3 with a cut-off of 35 ppb (see Eq. 3). For this metric, the EU air quality directives do not prescribe a limit.
or a target values.

\[
SOMO35 = \sum_{h=1}^{6 \text{ months}} \max (\text{MDA8}_i - 35, 0, 0)
\]  

(3)

The contribution of tagged O₃ concentration to each metric is based on formulations of each metric and is calculated from the model output based on metric formulations. In the case of the MDA8 and 95th-95th percentile metrics, we searched for the specific period when the calculated values for in which calculated values of total O₃ concentration meet the requirements given by the formulation of these metrics. Once this is identified, the tagged O₃ concentrations are extracted for the same period which can then be used for further analysis. However, the contribution of these concentration of tagged O₃ concentrations to the cumulative metrics is slightly different and it uses on cumulative metrics are slightly different, a large proportion of each tagged species to is used to determine total O₃, as illustrated below for AOT40 at specific hour specific time period:

\[
AOT40_{\text{tag}} = \sum_{i=1}^{90 \text{ days}} \max \left( (O₃ - 40) \cdot \frac{O₃_{\text{tag}}}{O₃}, 0, 0 \right)
\]

(4)

Based on their formulation, we grouped these metrics into either non-cumulative (mean O₃, MDA8, and the 95th percentile) or cumulative (SOMO35, W126, and AOT40) categories. Since these metrics have different formulation (including hourly O₃ values of O₃ values above a specific threshold) and they do not cover the same period of time, to facilitate a more direct comparison between findings from multiple O₃ metrics, an analysis of the relative contribution of different source regions to the total O₃ in each receptor region using different O₃ metrics was determined. This was done using averaged values for non-cumulative metrics, 6-month- and 6-month sums for SOMO35, AOT40 calculated for cumulative metrics useful for evaluating effects on crops (cumulated over May-July period) and maximum of 3-months maximum of 3-month sums for every consecutive 3-month period determined using the W126 index.

3 Results and discussions

The discussion of the model results focuses on the April-September 2010 period. We first briefly evaluate the ability of WRF-Chem to reproduce meteorological parameters using measurements from the Global Weather Observation (GWO) dataset provided by the British Atmospheric Data Center (BADC), and observed O₃ concentration concentrations using the measurements included in the AirBase database, a European air quality database (EEA, 2017b). We then provide a more detailed analysis of the contribution of the different source regions and types to MDA8 values describing total O₃ for the analysed period.

3.1 Evaluation of meteorology and chemistry

Since the accurate simulation of meteorological parameters represents a key factor that affects the trace gases concentrations affecting the concentrations of trace gases, we briefly compare the modelled mean sea level pressure (MSLP), 2 m temperature (T2M),
10 m wind speed (WS10M) and direction (WD10M) variables against the GWO measurement. Predicted model variables were then evaluated against observations using statistical scores that include normalized mean bias (NMB), and the correlation factor between simulated and measured values (r).

An extensive evaluation and discussion of the WRF-Chem using the MOZART chemical mechanism to predict long-term meteorological data and O3 model performance of WRF-Chem using the MOZART chemical mechanism levels has been presented by Mar et al. (2016), previously (Mar et al., 2016). The main differences between the set-up used in this study and the model described by Mar et al. (2016) include differences between the versions of the model used (3.7.1 vs. 3.5.1, respectively), horizontal resolutions (50kmx50km vs. 45x45km, respectively), microphysics (Morrison vs. Lin, respectively) and cumulus schemes (Grell-Freitas vs. Grell 3-D, respectively), simulation years (2010 vs. 2007, respectively), anthropogenic emissions inventory (TNO-MACC III vs. TNO-MACC II, respectively), and chemical input and boundary conditions (extended CAM-Chem version 1.2 with MOZART-4 vs. MOZART-4/GEOS-5 simulations found at http://www.acom.ucar.edu/wrf-chem/mozart.shtml, respectively).

Due to the coarse resolution of the domain that will not properly reproduce our domain, the air parcel dynamics associated with the complex topography in the mountainous areas we assessed of mountainous areas was not properly reproduced. Thus, we assessed the ability of the model to reproduce the meteorological variables using only those measurements sites located bellow sites located below 1500 m above ground sea level. MSLP is well reproduced at European scale data was well reproduced over the entire period (NMB of ≤ 0 % and r of = 0.98). In terms of spatial correlation, the model predicted T2M performs very well (r = 0.91), however the observed temperature is underestimated by 3 % (see Table 2). WS10M is was also fairly well reproduced both in terms of spatial and temporal variability (NMB = 8 %, r = 0.63). Yet, WD10M did not perform data could not be predicted as well as the other meteorological variables (NMB = 13 %, r = 0.47 and this behavior could be related to the existence of unresolved topography features (Jimenez and Dudhia, 2012). However, the model performance is similar to Mar et al. (2016) and Tuccella et al. (2012).

We also compare the compared modelled MDA8 O3 concentration against concentrations with observations provided by the publicly available publicly available AirBase dataset. The relatively coarse resolution of the domain might may not be representative for the changes in the changes in local emissions when the measurements are representative for urban condition, therefore further for the analysis we use taken from urban areas; therefore, to aid in the analysis, we used only those stations characterized as rural background. As can be seen from in Table 3, the model evaluation over the whole period shows that both tests perform quite well in terms of concentration (NMB = -5.2 %) evaluation of the model over entire period revealed that the model performs quite well with respect to the prediction of concentration and temporal evolution(r = 0.69). Mar et al. (2016) reported a mean bias (MB) value of 15.85 µg m^{-3} and an NMB of 17% for the June–August June–August 2007 period when the MOZART mechanism was used to assess the chemical performances of the model—whereas for the same period we obtain a MB. For the same time period, we obtained an MB value of -5.92 µg m^{-3} and a NMB an NMB value of -6.3%. Tuccella et al. (2012) reported an annual MB of -1.4 µg m^{-3} when the RADM2 chemical mechanism was used to simulate the year a period throughout 2007. Month-to-month analysis (Table 3) shows that the model reproduces the O3 concentration well compared to the Mar et al. (2016) and Tuccella et al. (2012) studies. Even though the model performance performance of the model in
terms of temporal variation is relatively good (r values fall between 0.58 and 0.71), it mostly underestimates the observed concentration underestimates concentrations of O₃, except in September, when the model overestimates the observed overestimated concentrations (NMB = 4.6%). The modelled errors could Errors of the model may be explained by a wide range of uncertainties related to the modelled physical and chemical processes such as grid resolution, vertical and horizontal transport, boundary layer mixing, emissions emission inventory, chemistry and photolysis rates, dry deposition and wet scavenging, etc as well as uncertainties in the measurements. As It is also possible that uncertainties in measurements contribute to observed errors. Since the focus of this study is on the contribution of different O₃ sources and of its precursors to the, and their precursors, to the total tropospheric O₃ concentration in a certain of a particular area, a more thorough analysis of the model ability of the model to reproduce the observed meteorological variables is beyond the scope of this paper.

### 3.2 Contribution of tagged precursor sources to the MDA8 O₃ concentration mixing ratios

Figure 2 shows the spatial distributions of simulated monthly mean MDA8 values from tagged O₃ source regions and types for late spring throughout late spring in 2010. The receptor regions are shown were mainly influenced by the overseas combination of NAM, ASI, OCN, and RST sources that together have a contribution varying from 25--combine to contribute from 23 % in the ALP region (that include Po Valley, characterized as one of the most polluted areas in Europe). Po Valley to up to 53.6 % in the UKI region (see Table S1). O₃ from RST (a 7.5 - 15 % contribution) is the main overseas source. The source from overseas O₃ coming derived from oceanic sources affects mostly the Atlantic coastal countries (up to a 16.1 % contribution in the UKI region), yet a small contribution of ~4-5 % can be seen over the was also observed within inland regions. The long-range transported Long-range transport of O₃ from Asia and North America contributes to significantly to total observed O₃ in Europe, accounting for 9.6 % of the total observed O₃ in ITA and up to ~22 % in UKI and SCA. After intercontinental transport, the O₃ produced elsewhere in within Europe is an important source of O₃ in the receptor regions, followed by O₃ coming from other types (LGT, BIO, and BMB). In general, for this time of the year, the contribution from the local sources to the total MDA8 O₃ concentration in the receptor regions is mixing ratio in receptor regions falls within a range from 8.5 % (SCA) to 21 % (RBU) (see Table S1). Emissions from local sources do not only affect local O₃ mixing ratios, but also impact O₃ levels of bordering countries due to strong horizontal pollution transport. In all receptor regions, the local anthropogenic sources have a lower contribution to MDA8 O₃ concentration is dominated by mixing ratios than the sum of O₃ produced by remote anthropogenic precursors, consistent with previous work due to anthropogenic sources in other European source regions and long-range transport of ozone from intercontinental source regions. The contribution of intercontinental transport to the total MDA8 O₃ mixing ratio in Europe is consistent with previously reported results, i.e. Fiore et al. (2009) and Li et al. (2016; Karamchandani et al. (2017), while this study allows us to identify which anthropogenic sources exert a strong influence on MDA8 O₃ predicted in different regions. Using observations, Danielsen (1968), Thouret et al. (2006) showed that the transport of O₃ from the stratosphere also contributes to tropospheric O₃. Here, the stratospheric O₃ contributes up to 7 ppb (12.5 % in SCA) to the total MDA8 O₃ concentration, similar to mixing ratio, which is a finding similar to that reported by Derwent et al. (2015). A similar tagged system, but for predicting O₃ levels, using the CAM-Chem model (Butler et al., 2018), also shows that the has also shown that stratospheric O₃ has a large contribution significantly contributes to the total
tropospheric O$_3$ concentration mixing ratio. The MOZART chemical mechanism used in this study does not explicitly treat the stratospheric chemistry; thus the surface stratospheric O$_3$ could be attributed to the vertical and horizontal transport of stratospheric O$_3$ coming from the boundary conditions. The emitted local sources do not only affect local O$_3$ concentrations, but they also impact the O$_3$ levels of bordering countries due to a strong horizontal pollution transport.

During June-August 2010, Western Europe was mostly influenced by a high-pressure system centered over the Atlantic (see Fig. S1). In the upper troposphere, a ridge influenced the vertical atmospheric structure, especially over southern Europe. Therefore, these “usual summer conditions” favoured the intrusion of warm air coming from Africa and the Arabic Saudi Arabian peninsula and led to a warm and dry climate characterized by subsidence, stability, clear sky and high solar radiation intensity skies and high-intensity solar radiation. Hence, the photochemical formation of O$_3$ formation is enhanced, leading to a stronger contribution from local emissions and influenced the stronger contribution of local emissions to the total concentration mixing ratio compared to the previous period examined. Figure 3 depicts the average MDA8 O$_3$ for June-August 2010. For most regions, we notice an enhancement that levels of O$_3$ produced from local sources in June-August compared with April-May from June-August compared with April-May were enhanced (Figure 2). Local sources can contribute to more than 20% of the mean MDA8 O$_3$ concentration mixing ratio (from 14.6% in SCA to 33.6% in ALP 35.7% in the Po Valley, see Table S1) showing that the local sources play a stronger role in the formation of O$_3$ formation throughout the June-August period, as has been previously shown by Jiménez et al. (2006) and Querol et al. (2018). Compared with late spring, the relative contribution of the overseas sources decreased in summer, varying from 42.8% 10.9% in the ALP Po Valley receptor region to 44.8% in the UKI region in July (see Figs. 2, 3 and the month of July (Figs. 2 and 3; Table S1). We notice a reduced spread of O$_3$ produced from European anthropogenic precursors over the bordering regions compared with late spring 2010 (see Figs. 2 and 3). The increase in average temperature combined with stable atmospheric conditions lead to an enhancement of the biogenic NO emitted into the atmosphere, especially in South-Eastern and Eastern Europe; thus, the BIO source type contributes up to ~9 ppb (13.2% of MDA8 O$_3$) in the RBU receptor region (see Fig. 3). The vegetation fires that took place across Russia in July and August (Gilbert, 2010; Huijnen et al., 2012) as well as in Portugal and Spain (European Commission, 2011) lead to a increases in the contribution of O$_3$ coming from BMB of up to 29 ppb (16%) in the RBU receptor region and up to 8.5 ppb (2.3%) in the IBE receptor region. The BMB emissions contribute domain wide more than 3.6% (ALP), the most affected receptor regions being domain wide more than 3% (Po Valley), with the greatest impacts modelled over RBU, IBA, SEE, SCA, and TCA. Another consequence of enhanced photochemical activity during the summer season is the reduction summer is that it reduces the influence of stratospheric O$_3$ that contributes in general up to ~3.4% of total from a domain wide mean MDA8 O$_3$ concentration at the surface mixing ratio of 4.4 ppb in the spring to 1.3 ppb in the summer (Figs. 2 and 3).

The decrease of the photochemical activity in September 2010 is reflected in the decrease of decreases in total O$_3$ concentration mixing ratios compared with the summer season of the same year, as well as in the reduction of a reduction associated with the local source contribution to the total O$_3$ concentration mixing ratio (Fig. 4). Thus, only in IBE, TCA, FRA, ALP and RBU region the Po Valley, the high Alps, and RBU regions were contribution of local sources to total MDA8 O$_3$ is higher than 20% (Table S1). On the other hand, we noticed an increase in O$_3$ coming from overseas anthropogenic...
sources and anthropogenic overseas sources and from lightning in autumn, stressing the seasonal variation in that seasonal variations exist within the outflow from other continents and the. There also is variation in the lifetime of O3 which is shorter shortest during the summer due to the enhanced photolytic sinks as a result of enhanced photolytic activity.

Although we have seen that long-range long-range transport plays a major role in total O3 concentrations: mixing ratios, the tagging technique helps to gain more insight into which region of the world dominates these concentrations mixing ratios in spring or autumn. In early fall, the Western European receptor regions exhibit a slight increase by of 1.6 % of O3 concentrations coming from North-America compared with the spring season, whilst mixing ratios coming from North America compared with spring, while the contribution of O3 concentrations coming from the mixing ratios coming from other overseas sources to the total O3 decreases. This could be linked to the prevailing westerly wind and the synoptic conditions seen during the first period of September, when the Azores High extended far to the east and north (Fig S1), creating such conditions that direct. This phenomenon creates conditions that are conducive to the transatlantic transport of American pollution can be seen far east in the eastern direction. For example, in autumn periods within the RBU receptor region, the North-American and oceanic sources contribute account for up to 14.6 % in spring and 11.4 % in autumn to of the MDA8 O3 concentration mixing ratios.

Apart from local and other type sources, the NOx emissions from shipping activities in the Atlantic Ocean combined with the oceanic O3 from boundary conditions are an important source of O3 that explains up to 16 % in late spring, 21 % in summer and 12% in early autumn of the MDA8 O3 concentration mixing ratio in the UKI, IBE, FRA, GEN, CEN and SCA. Our results are similar to those presented by Tagaris et al. (2017) and the references therein, and Mertens et al. (2018) who showed that OCN contributes to 20 % of total O3 in the North Atlantic and SCA regions. Butler et al. (2018) showed that O3 from oceanic sources reach a minimum level in the North Atlantic Ocean during the summer, yet this study shows that in the UKI, IBE, FRA, GEN, CEN and SCA receptor regions the oceanic O3 peaks its maximum contributions contribution peak in the summer. This implies that the nearby shipping emissions have a greater contribution in these areas on oceanic bordering countries rather than oceanic O3 from the boundary conditions. Furthermore, the NOx emissions from shipping activities in the Mediterranean and Black Seas contribute account for up to 14 % in late spring, 19 % in summer and 11 % in early autumn of the MDA8 O3 concentration mixing ratio predicted in the receptor regions situated along the shore of the Mediterranean Sea, such as IBE, ITA, SEE, ALP and FRA.

As can be seen from Figs. 2–4, Our model results has shown that the highest MDA8 O3 concentrations are predicted: mixing ratios are predicted to occur over the Mediterranean basin. This is due to the several more presence of favorable conditions for its formation like O3 formation including the presence of small deposition sinks and intense photochemistry. (Figs. 2–4). Several studies, such as Satieddine et al. (2014), Tagaris et al. (2017), Mertens et al. (2018), Querol et al. (2018) and the references therein, have used source attribution methods to establish the origin of tropospheric O3 observed over the Mediterranean Basin. The tagging technique used here shows that the O3 from shipping activities in the Mediterranean and Black Seas (MBS) explains, on average, 15 % in late spring, 20 % in summer and 12 % in early autumn of total MDA8 O3 predicted to accumulate within the MBS receptor region. These findings are similar to those of Aksoyoglu et al. (2016) that showed these emissions contribute within a range of 10 to 20 % to accounted for 10-20 % of the mean O3 in the
Mediterranean in the summer of 2006. Moreover, Tagaris et al. (2017) has shown that shipping emissions explain up to 30% of the MDA8 O₃ simulated for July 2006 over the Mediterranean Sea. This study has shown that the shipping activities contribute likely accounted for up to 35% of the MDA8 O₃ near the Strait of Gibraltar (see Figure 5) during the April-September 2010 period. The shipping emissions have the highest contribution to Shipping emissions contribute most highly to total O₃ in the Western Basin of the Mediterranean Sea. Aside from shipping activities, the other European source regions have a localized contribution to total MDA8 O₃ predicted in the Mediterranean Sea. Thus, ITA, ALP, GEN source regions contribute contribute mostly to the central basin; IBE and FRA are main contributors in the western basin and SEE and TCA in predominantly contribute to the eastern basin. Natural sources contribute on average up to 10% of MDA8 O₃ in the western basin, and up to approximately 25% of MDA8 O₃ in the eastern basin. The large-scale long-range of O₃ transport contributes up to 45% along the North African shore and it exhibits a zonal pattern, with low concentrations mixing ratios occurring in the North and high concentrations in the South mixing ratios occurring south of the Mediterranean Sea, a trend mostly due to O₃ concentrations mixing ratios from NAF and RST sources.

3.3 Tagged ozone precursor contributions to exceedances of MDA8 target values – case study

As previously mentioned, the European Air Quality Directive (EU directive 2008/50/EC, 2008) has defined a target value of 120 µg m⁻³ for the MDA8 O₃ concentration, which can be exceeded up to 25 days per calendar year averaged over three years (over a three-year span). In the following we call exceedances the values that surpass 120 µg m⁻³ and non-exceedances as exceedances, and values below 120 µg m⁻³ as non-exceedances. Figure S2 shows the spatial distribution of the number of exceedances observed and calculated throughout the April-September 2010 period for the AirBase rural stations. The observed MDA8 O₃ exceeds the target limits locally in Po Valley, Austria, Germany and the coastal area and Germany; in coastal areas of Portugal, Spain, France and Italy; and inland areas of Poland and isolated in Poland, and Slovakia. Yet, the modeled exceedances do not exhibit the same spatial pattern or intensity as observed values. Our use of tags allows for the identification of main source contributors to exceedances of modelled MDA8 O₃. Given the high number of stations that measure O₃, for simplicity, we will discuss the source contribution to the MDA8 O₃ exceedances only for the ALP Po Valley, high ALPs, and GEN receptor regions.

Figure 6 exhibits the contribution of each tagged source and type to the modeled MDA8 O₃ as well as the observed MDA8 O₃ samples value. Samples were taken at the location of the measurement stations, during throughout the April-September 2010 period. Figure 6 shows averaged conditions during the average conditions that occurred during the exceedance of the MDA8 O₃ target value, and also at times during which the target value was not exceeded. In order to perform the source attribution for the observed values, we have scaled these values proportionally by the relative concentrations of each tagged O₃ tracer in our model output.

The relative contribution of emissions from different source regions to the modelled MDA8 O₃ and to the observed MDA8 O₃ scaled by values, after being scaled to account for the contribution of modelled modelled sources of O₃ types is generally similar for both Po Valley and GEN receptor regions (see Fig. 6). In the ALP Po Valley, we can clearly pinpoint the main remote contributor as being MBS (see Fig. 6), followed by GEN, and FRA, suggesting a dominant westerly and northerly air flow.
The recirculation of air masses in the Gulf of Genoa could accentuate the sea breeze and therefore more O$_3$ coming from NO$_x$ precursors associated with shipping activities in the Mediterranean will be transported to the coastal and inland station.

The high Alps receptor region is less influenced by ALP emissions than the Po Valley, and is more influenced by remote sources (see Fig. 6). The increased contribution of O$_3$ from CEN, ITA and FRA to both exceedance and non-exceedance days in the high Alps receptor region compared with the Po Valley receptor region highlights the impact of the transboundary transport of O$_3$ and its precursors. Furthermore, the contribution of stratospheric as well as long-range sources was generally 6 % higher in this receptor region than in the Po Valley receptor region.

In GEN, the main remote source regions are FRA and CEN during the exceedance days and FRA and UKI during non-exceedance days (Fig. 6). Opposite to Po Valley, in GEN the model predicts less-fewer MDA8 O$_3$ exceedances days. Comparing the source contribution to both modeled and observed exceedances days, we notice that model underestimates the number of exceedances in GEN is half of the observed number of exceedances (Figure 6).

This kind of analysis can be applied to improve our knowledge of the origin of O$_3$ precursor-sources and their contribution to MDA8 O$_3$ health metrics. Hence, by the means of the tagging technique, the policy makers-policymakers can identify future actions required to control the NO$_x$ emissions at local and regional levels.

### 3.4 Tagged ozone precursor contributions to regulatory ozone metrics

In this section, we discuss the contribution of O$_3$ concentrations-mixing ratios from diverse emissions sources and types to several different metrics which quantify metrics that quantify the O$_3$ exposure-exposures of humans and ecosystems. From modelled hourly concentrations-mixing ratios of tagged O$_3$ sources and types, we have calculated different O$_3$ metrics, such as including non-cumulative (mean, MDA8, and the 95th percentile O$_3$) and cumulative (SOMO35, W126, and AOT40) metrics. We have chosen not to analyse the performance of the calculated cumulative metrics in comparison with the measured values, as was done in previous work by Tong et al. (2009). Their work showed that the poor performance of the cumulative metrics is closely related to the sensitivity of these metrics to the threshold values or weighting factors.

Figure 7 and Table S2 exhibit the percent-case contribution of different emissions sources to total O$_3$ as well as using health and vegetation metrics. The non-cumulative O$_3$ metrics employed in this study have a similar pattern displayed similar patterns for most of the receptor regions. The contribution of local and European sources to the total O$_3$ concentration-mixing ratios have been low when we applied to mean O$_3$ metric and high when we are looking at 95th percentile-emphasising using 95th percentile metric. These findings emphasize the importance of O$_3$ produced by local and neighbouring sources to the high end of the O$_3$ concentration mixing ratio distribution.
Splitting the non-cumulative metrics into early (April-June) and late (July-September) simulation periods clearly illustrates that the European receptor regions are more prone to being influenced by intercontinental transport during the early period than during the late period. The intercontinental contribution of intercontinentally transported O₃ contribution to mean O₃ values in different receptor regions is higher during the early period than during the late period and it spans between 22.8% and 54.3%.

In the late period it accounts for between 16% and 48.9% during the late season of total O₃ (see Fig. 7 and Table S2). Since in this case the O₃ associated with intercontinental transport is coming from, in this case, solely from boundary conditions, it implies that errors in boundary conditions affect the predicted concentration-mixing ratio of various chemical species, consequently and consequently, the contribution of the overseas sources to European overseas sources of O₃ to levels observed in Europe O₃ (Tang et al., 2007; Giordano et al., 2015; Im et al., 2018).

The lower shorter lifespan of O₃ lifetime-over remote ocean regions throughout the warm season combined with the synoptic conditions lead to a decrease of the intercontinental, combined with synoptic conditions, has led to decreased levels of intercontinentally transported O₃ to Europe. Thus, for most receptor regions, the O₃ coming from Asia and the rest of the world was reduced by more than half when compared with the cold period. The O₃ concentration-mixing ratio from the stratosphere is, in general, 2.5 times higher in the cold season than in the warm season which is consistent with Butler et al. (2018) study with the findings of a study by Butler et al. (2018) which showed that the stratospheric O₃ concentration-mixing ratio varies with altitude and its lifetime is influenced by season and latitude. The tagging technique also helps to quantify the impact of biogenic and biomass burning emissions of NOₓ on tropospheric O₃. The impact of biogenic NOₓ emissions to the on mean O₃ concentration-mixing ratios is between 3.3% in ALP-Po Valley and 5.9% in TCA in the early season, while during the late season it spans between 5.6% in ALP is between 5.4% in Po Valley and 13.4% in RBU. The biomass burning emissions explain a range account for variable percentages of mean O₃ concentration-mixing ratios. These span between 1.6% in ITA to 5.3% in RBU during the early season, and between 2.9% in ALP-3.8% in Po Valley and 16.3% in RBU during the late season. Most of the time, the natural-Natural sources do not usually vary greatly when different non-cumulative metrics are applied except for. An exception would be for the biomass burning emissions on RBU during the late season. Thus, BMB in RBU contributes to 16.3%, 17.6% and 28.8% to of the mean, MDA8 and 95th percentile 95th percentile, respectively.

Even though the SOMO35 and AOT40 metrics are not accumulated over the same time period (SOMO35 is accumulated over the entire simulated period, and AOT40-metric is accumulated over the May-July period) and they do not use same input data (daily MDA8 O₃ for SOMO35 vs daytime O₃ concentration-mixing ratios for AOT40), since they are based on threshold exceedances and are designed to measure the-exposure to high O₃ levels of humans (SOMO35) or and vegetation (AOT40), they give us the possibility there is a way to directly compare them. As can be seen in Fig. data from each metric type. As shown in Figure 7 and Table S2, the contribution of different emissions sources and types to the sources of emissions and types as a proportion of total SOMO35 and AOT40 metrics is are similar for most of the European receptor regions. Their spatial distribution (not shown) is also comparable, with minimum values over the UK, NW Europe and Scandinavia and maximum values over Italy, the Alps, south of Spain, east of Turkey and in the metropolitan area of Moscow, Russia. Consistent with the previous studies of. These results are consistent with previous studies performed by Aksoyoglu et al. (2014), and Anav et al. (2016). The overseas sources have a similar contribution to the contribute similarly to SOMO35 and AOT40 indexes (usually
less than 30 %) for most of the receptor regions used in this study. However, in UKI, the overseas sources have a contribution of account for 32 % of AOT40 and 38 % of SOMO35, and in SCA they have a contribution of contribute to ~22 % of AOT40 and 30 % of SOMO35, suggesting. This suggests that these metrics are sensitive more sensitive with respect to the O3 concentration mixing ratios from remote sources in areas having a low level of O3 pollution. In the RBU receptor region, these indicators are sensitive to O3 coming from biomass burning emissions (20 % of SOMO35 and 24 % of AOT40), whereas for the remaining receptor regions the contribution of natural sources to SOMO35 and AOT40 is similar. The local sources contribute within Local sources account for a range of ~12 % (SCA) – ~38 % (GEN) to these metrics, accentuating the of these metrics. These data highlight the occurrence of increased O3 production from local sources in comparison with northern European countries as well as large emissions of NOx in the GEN source region. Since the difference in-between AOT40 and SOMO35 is only a few percent, regardless percentage points, regardless of the receptor region, we could have been able to conclude that they are efficiently complementing each other mostly due to the use of a threshold behave similarly, according to thresholds used to define these metrics.

The tagging method allows a better understanding of the main precursor sources responsible for exceedances of regulatory O3 metrics. This information can help to inform further modelling studies aimed at investigating the effects of emission reduction strategies, and ultimately inform air quality policy. For example, in the ALP region, which includes the Po Valley Po Valley receptor region, the modelled AOT40 is up to 2.6-3.4 times higher than the target limit given by EU legislation (on average 23560.8-31218 ppb – hours). The observed and calculated AOT40 values depicted in Figure S3 clearly exhibit the exceedance of target limits in ALP. The Po Valley O3 coming from local sources explain 33.6 can explain 35.0 % of this value (AOT40 up to 9163 an average of 10909 ppb – hours). After the local sources, the main European anthropogenic sources contributing to high level of AOT40 in the ALP region are distinguished to be FRA (6.5 values in the Po Valley region are from FRA (6.6 %), GEN (7.6-7 %) and MBS (7.9-8.8 %) (Table S2). Generally, the O3 concentration mixing ratio and its precursors transported from other anthropogenic European sources to the ALP receptor regions explain ~39 %, the natural sources ~13 % and long-range transport ~15 into the Po Valley receptor regions account for ~39.5 %, while natural sources accounts for ~12.3 % and long-range transport accounts for ~13.4 % of the remaining AOT40 concentration mixing ratios. Thus, to reach at least the target limit in the ALP Po Valley receptor region, considerable emission reductions are still will still be needed, not only on a local scale but also on the European scale, especially within the MBS, GER, and FRA source region regions.

Figure 7 also shows the percent contribution of different emissions regions and types percentage that different types of emissions and emission regions contribute to the W126 index. Interestingly, for most of the receptor regions, the local NOx anthropogenic emissions cause the largest response in W126 values compared with the other cumulative metrics used here in this study. Thus, the local NOx precursors explain from 10.9 % (0.1 ppm – hours) in SCA to more than 40 % of W126 in GEN (45.9 %; 2.48 ppm – hours), and ALP (13.5 %; Po Valley (45.4 %; 8.7 ppm – hours)) of W126 index values calculated for each region. The effect of European transported plumes is also enhanced for when using the W126 index compared with the other metrics for most of the downwind receptor regions. This behaviour is related to the way in which this metrics have been defined. Due to its sigmoidal weighted formulation, as discussed in Westenburger and Frisvold (1995), and Lapina et al. (2014), W126 takes into account includes all daytime values rather than O3 levels above a
certain threshold, as is done using SOMO35 and AOT40; therefore lower weighting factors of less than 0.5 are given to low O₃ values and weighting factors above 0.5 are given to O₃ values situated above the inflection point of 67 ppb. Given that all daytime values are considered by W126 and they are not disregarded as done with SOMO35 and AOT40, we explain why W126 is more sensitive to local NOₓ precursors than other metrics.

The modeled mean AOT40 and W126 in the ALP receptor region are exceeding the standards (23560 values in the Po Valley receptor region exceeded standards (26368 ppb – hours for AOT40 and 24.5–28.9 ppb – hours for W126) during the May-July 2010 period). As shown in Fig. 7 and Table S2, the local sources are an important contributor to these metrics. To better understand why the W126 index is mainly influenced by local sources compared with the other cumulative metrics, a more thorough comparison between AOT40 and W126 over the ALP receptor region is presented in the following. Figure 8 presents the values for the Po Valley receptor region. As shown in Figure 8, a temporal series of hourly daylight values for mean O₃, W126 and AOT40 values averaged over the ALP receptor region was lower than W126 (Fig. 8a), W126 is value lower than AOT40 (Fig. 8d). This way of acting was most probably due to the weighting factor being less than 0.3, and above this concentration mixing ratio W126 tends to be higher than AOT40. This behavior is closely linked to the definition of these metrics. The O₃ concentration mixing ratio is less than 40 ppb, W126 has a weighting factor lower than 0.03, while AOT40 has a weighting factor of 0. Above this threshold, AOT40 has a weighting factor of 1, while in the case of W126 only O₃ values higher than 100 ppb have a weighting factor of 1. Due to the metrics definition way these metrics are defined, predicted O₃ values in each grid cell are accounted for the W126, and may not be accounted for the AOT40 index.

In addition, the visual analysis of the time series also revealed that when the O₃ concentrations-mixing ratios from local sources are ~20 ppb, these concentrations-mixing ratios have a higher contribution to W126 than to AOT40. To better understand this observation, we have further analyzed the relationship between mean O₃ values from ALP sources (O₃-ALP) and the percent contribution of these O₃ tracers to mean O₃, W126, and AOT40 metrics. Figure 9 presents the scatter plots that relate the contributions of these concentrations on mean O₃, W126, and AOT40. In addition, the linear regression of Y vs X (Y=a*X+b) using all data sets has been applied. It can be seen that, in general, high mean O₃-ALP concentrations contribute more mixing ratios contribute more highly to W126 than to AOT40; this is also confirmed by the highest slope (1.64) attained when the linear regression was applied to W126 vs. O₃-ALP. The averaged O₃-ALP and mean O₃ as well as O₃-ALP and W126 are highly correlated (r=0.97, and respectively 0.96, and r=0.93), while O₃-ALP and AOT40 have a lower correlation are correlated more loosely (0.88). The high correlation of level of correlation between O₃-ALP with both mean O₃ and W126 could be related to the fact that these metrics account for all modeled values, whilst AOT40 considers only O₃ values above 40 ppb.
Extending this analysis to all receptor regions, we can explain why the W126 index is more sensitive to O$_3$ coming from local sources compared with the other cumulative metrics. In addition, W126 accentuates the contribution of BIO and BMB in RBU, TCA and SEE, most likely because this metric considers all daytime values, and not only just those above a certain threshold. Thus, the use of W126 highlights the considerable impacts of BIO and BMB emissions which are important sources of total O$_3$ during the summer seasons and vegetation fires mixing ratios throughout the summer and from burning vegetation that ultimately influence the extent to which O$_3$ damage causes damage to vegetation.

We have seen that the contribution of different NO$_x$ precursors to total O$_3$ varies with metrics and with the region depending on metrics and regions considered. Hence, the tagging method could help design different emission control strategies in specific source regions depending on which impacts need to be reduced in specific receptor regions.

4 Conclusions

Here, we implemented into the WRF-Chem model a new chemical mechanism within the WRF-Chem model to account for source attribution of O$_3$ from NO$_x$ precursors. We investigated the origin of surface O$_3$ using the “tagging” technique during from April-September 2010, as well as the contribution of different sources to O$_3$ metrics, and their exceedance events.

Using tagged simulation from WRF-Chem, we show that the spatial distribution of simulated monthly mean MDA8 from tagged O$_3$ source regions and types for throughout late spring, summer, and early autumn of 2010. The contribution of different sources to O$_3$ production varies with season. We have identified the intercontinental transported O$_3$ as an important contributor to the total O$_3$ concentration mixing ratio, especially in the late spring and early autumn, while during summer. During summer, however, the O$_3$ production is dominated by national and intra-European sources. We have also identified shipping activities in the Mediterranean Sea as an important source of O$_3$ for the IBE, ITA, SEE, ALP and FRA peripheral maritime receptor regions. We also analysed which are the main sources of MDA8 O$_3$ over the Mediterranean Basin and our study has identified the main contributors to high we have the main factors that contribute to MDA8 O$_3$ concentration mixing ratios to the greatest degree. These were mainly shipping activities and the localized contribution from the bordering countries.

To have a better understanding of better understand the origin of MDA8 O$_3$ exceedances, we compared modelled and observed values of MDA8 O$_3$ concentration in the Alps and Germany, Po Valley, high Alps, Germany, and Benelux receptor regions. Thus, we have seen that during the exceedance days Throughout days exceeding the recommended thresholds of 120 µg, the contribution from local sources sources is ~45 % was ~41 %, 34 % and 38 % of modeled modelled MDA8 O$_3$ for Po Valley, high Alps, and GEN, respectively. Throughout days not exceeding recommended thresholds, local emissions explain ~27 %, whilst during non exceedance days values is ~32 % and 2-3 % for ALP, respectively GEN16 % and 23 % of modelled MDA8 O$_3$ for the Po Valley, high Alps, and GEN, respectively. Moreover, this tagging approach revealed that the main remote sources of MDA8 O$_3$ are MBS, GEN, and FRA for the Alps–Po Valley receptor region, and are FRA, GEN, and UKI for the Germany and Benelux receptor regions. In addition, these analyses identified a persistently high contribution of
transboundary sources to the background O₃ concentration in the ALP high Alps receptor region. Furthermore, by showing that the contribution of precursor sources to modelled O₃ target value exceedances in the GEN region is systematically different to from the contribution of precursor sources to modelled O₃ when exceedances are observed but not modelled, we have identified a possible reason (underestimation of long-range transport) for the poor performance of our model at reproducing the observed number of O₃ target value exceedances in the GEN region.

By means of Through comparisons with different O₃ metrics, we quantified the impact of local vs. non-local NOₓ precursors on O₃ production for each European receptor region. The comparison between mean, MDA8 and 95th percentile O₃ metrics accentuate the importance of large contributions from different NOₓ precursors to the high-end of the O₃ distribution. By analysing these metrics for two periods (April-June and July-September), we can clearly distinguish the contribution of different NOₓ precursors to total O₃ concentration mixing ratios in each region for different times of the year. When we compare the cumulative metrics, we noticed that the SOMO35 and AOT40 indexes exhibit a rather similar behaviour. Considering that these metrics are not calculated over the same time period nor do they use same input data, the similar behaviour is likely due to the similar threshold values applied to define these metrics.

The use of the W126 index accentuates the importance of local emissions. To confirm this, we investigated the behaviour of modeled mean AOT40 and W126 in the ALP values in the Po Valley receptor region. We noticed that when the O₃ concentrations from local sources are approximately 20 ppb, these concentrations have a higher contribution to W126 than they do to AOT40 and determined that the difference was mostly due to the definition of W126 which takes into account all O₃ values, not only those that are above a certain threshold.

Overall, this study has identified the local and remote contribution factors that contribute to the MDA8 O₃ concentration mixing ratio during several periods as well as within different O₃ metrics. Furthermore, the method applied here could be used to design improved emission control strategies depending on which impacts need to be reduced.

Appendix A

- chemics_init.F;
- module_input_chem_data.F;
- module_plumerise1.F and module_add_emiss_burn.F to account the source attribution of biomass burning emissions to O₃ concentration;
- module_emissions_anthropogenics.F to account for the impact of anthropogenic emissions on O₃ concentration;
- module_bioemi_megan2.F and module_data_mgn2mech.F to see the impact of biogenic emissions on O₃ concentration;
- module_lightning_nox_driver.F for lightning-generated nitrogen oxides.
Dry and wet deposition of tagged trace gases are treated by module_dep_simple.F and module_mozcart_wetscav.F, thus all tagged species have the same dry deposition velocities and wet removal rates with the corresponding non-tagged species;

- module_ftuv_driver.F to consider the photolytical reaction of the new packages;
- emissions_driver.F;
- chem_driver.F.

Code and data availability. The WRF-Chem model is publicly available on http://www2.mmm.ucar.edu/wrf/users/download/get_source.html. The modification introduced and described in Section 2 as well as the model data can be provided upon request to the corresponding author.

Author contributions. AL and TB designed the research. AL adapted the automatic mechanism-rewriting and code-generation tools and in implemented into WRF-Chem source code. AL performed the model runs and subsequent analysis. AL wrote the paper with contribution from TB.

Acknowledgements. This work was hosted by IASS Potsdam, with financial support provided by the Federal Ministry of Education and Research of Germany (BMBF) and the Ministry for Science, Research and Culture of the State of Brandenburg (MWFK). The authors would like to thank Kathleen Mar for helping with the emissions preprocessing as well as to Jane Coates for her help with some of the plots.
References


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Paoletti, E., De Marco, A., Beddows, D., Harrison, R., and Manning, W.: Ozone levels in European and USA cities are increasing more than at rural sites, while peak values are decreasing, Environmental Pollution, 192, 295–299, https://doi.org/10.1016/j.envpol.2014.04.040, 2014.


Table 1. List of tagged European source/receptor regions

<table>
<thead>
<tr>
<th>Acronym</th>
<th>List of countries</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBS</td>
<td>Mediterranean, and Black Seas</td>
</tr>
<tr>
<td>BNS</td>
<td>Baltic, and North Seas</td>
</tr>
<tr>
<td>CEN</td>
<td>East Austria, Hungary, Czech Republic, Slovakia, Estonia, Latvia, Lithuania, Poland</td>
</tr>
<tr>
<td>ALP</td>
<td>West Austria, Switzerland, and North Italy (including Po Valley)</td>
</tr>
<tr>
<td>ITA</td>
<td>South Italy, and Malta</td>
</tr>
<tr>
<td>SEE</td>
<td>Bulgaria, Romania, Moldavia, Albania, Slovenia, Croatia, Serbia, Montenegro, Macedonia, Greece, and Cyprus</td>
</tr>
<tr>
<td>IBE</td>
<td>Spain, and Portugal</td>
</tr>
<tr>
<td>UKI</td>
<td>United Kingdom, and Ireland</td>
</tr>
<tr>
<td>GEN</td>
<td>Belgium, Netherland, Luxembourg, and Germany</td>
</tr>
<tr>
<td>SCA</td>
<td>Finland, Norway, Sweden, Denmark, and Island</td>
</tr>
<tr>
<td>FRA</td>
<td>France</td>
</tr>
<tr>
<td>RBU</td>
<td>Russia, Belarus, and Ukraine</td>
</tr>
<tr>
<td>TCA</td>
<td>Turkey, Azerbaijan, Armenia, and Georgia</td>
</tr>
</tbody>
</table>

Table 2. Observed mean and simulation summary statistics for meteorological parameters. The normalized mean bias (NMB) and correlation coefficient (R) are calculated between simulated and observed meteorological observation from GWO during April – September 2010 period

<table>
<thead>
<tr>
<th>Variable</th>
<th>Observed</th>
<th>Modeled</th>
<th>NMB (%)</th>
<th>R</th>
</tr>
</thead>
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<tr>
<td></td>
<td>min</td>
<td>mean</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>MSLP (hPa)</td>
<td>1000.96</td>
<td>1014.3</td>
<td>1022.06</td>
<td>969.05</td>
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<td>T2M (°C)</td>
<td>-17.14</td>
<td>14.99</td>
<td>32.10</td>
<td>-22.50</td>
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<tr>
<td>WS10M (m/s)</td>
<td>0.36</td>
<td>3.37</td>
<td>10.83</td>
<td>0.00</td>
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<tr>
<td>WD10M (°)</td>
<td>0</td>
<td>190</td>
<td>360</td>
<td>31.91</td>
</tr>
</tbody>
</table>
Table 3. Observed mean and simulation summary statistics for MDA8 O$_3$ concentrations ($\mu$g/m$^3$) at rural background sites. The normalized mean bias (NMB) and correlation coefficient (R) are calculated between simulated and observed O$_3$ concentrations from the AirBase dataset during April – September 2010 period.

<table>
<thead>
<tr>
<th>Analyzed period</th>
<th>Observed</th>
<th></th>
<th>Modeled</th>
<th></th>
<th>NMB (%)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>mean</td>
<td>max</td>
<td>min</td>
<td>mean</td>
<td>max</td>
</tr>
<tr>
<td>April</td>
<td>52.5</td>
<td>97.0</td>
<td>140.8</td>
<td>36.5</td>
<td>90.8</td>
<td>134.5</td>
</tr>
<tr>
<td>May</td>
<td>41.0</td>
<td>87.9</td>
<td>143.0</td>
<td>28.0</td>
<td>83.2</td>
<td>124.6</td>
</tr>
<tr>
<td>June</td>
<td>44.2</td>
<td>96.2</td>
<td>162.3</td>
<td>32.0</td>
<td>89.7</td>
<td>132.6</td>
</tr>
<tr>
<td>July</td>
<td>43.8</td>
<td>97.0</td>
<td>178.2</td>
<td>26.0</td>
<td>90.8</td>
<td>147.7</td>
</tr>
<tr>
<td>August</td>
<td>40.3</td>
<td>87.5</td>
<td>145.2</td>
<td>27.3</td>
<td>82.6</td>
<td>130.8</td>
</tr>
<tr>
<td>September</td>
<td>33.4</td>
<td>77.5</td>
<td>135.4</td>
<td>26.5</td>
<td>81.1</td>
<td>129.6</td>
</tr>
<tr>
<td>Total</td>
<td>40.5</td>
<td>90.5</td>
<td>160.5</td>
<td>28.4</td>
<td>86.3</td>
<td>135.9</td>
</tr>
</tbody>
</table>

Figure 1. Tagged European source/receptor regions
Figure 2. Contribution to MDA8 O₃ (ppb) of each O₃ source region for the April-May 2010 period.
Figure 3. Same as Fig. 2, but for the June-August 2010 period.
MDA8 O3 (ppb) - September 2010

Figure 4. Same as Fig. 2, but for September 2010
**Figure 5.** Average MDA8 O₃ mixing ratio (upper left panel) and contribution of each tagged O₃ region and source over the Mediterranean Sea for the April-September 2010 period. The unit is ppb.
Figure 6. Mean modeled and observed MDA8 O$_3$ mixing ratio filtered by a threshold of 120 µg m$^{-3}$ for ALP-Po Valley (top panel), high Alps (third from top panel) and GEN (second-fifth from top panel) and percent contribution to MDA8 O$_3$ from different emissions sources and types for ALP-Po Valley (third-from-top second panel), high Alps (fourth) and GEN (bottom panel) during April-September 2010 period. In each case the contributions of tagged sources to the total O$_3$ are shown. The tagged contributions to observed O$_3$ are obtained by scaling the observed O$_3$ by the relative contributions of these tagged sources to modeled O$_3$. The total number of exceedances (and non-exceedances) of the MDA8 O$_3$ target value is indicated at the top of each column.
Figure 7. Comparison of percent contribution to O₃ metrics from different emissions sources and types. The metrics analysed are mean, MDA8, 95th percent (ppbv), W126 (ppm hrs), SOMO35 (ppbv days), AOT40 (ppb hrs). The white dashed lines on each panel separate different categories (intercontinental transport, natural sources, and local and other European sources).
Figure 8. April-September 2010 time series of daytime a) hourly O$_3$ (ppb), b) hourly AOT40 index (ppb □ hours), c) hourly AOT40 W126 index (ppb □ hours), and d) differences between W126 and AOT40 indexes (ppb □ hours) averaged over ALP-Po Valley receptor region.
Figure 9. Scatter plots showing the ozone concentration from local sources versus the contribution to Mean O$_3$ (black dots), W126 (red dots) and AOT40 (blue dots). The solid lines are the lines of best fit.