Reply to Anonymous Referee #1:
We are thankful for the detailed review. While we think that some of the reviewers arguments are based on misinterpretations, they also points at some crucial details of our tagging scheme, which are caused by necessary tradeoff between practicability and accuracy. Assumptions and simplifications are required in such a complex diagnostics. We thought that we have addressed it in our manuscript, but we are happy to discuss in more detail, since it is important to know the limitations. To clarify this we include a new section on the limitations of this approach.

Reviewer Comment:
General comments
The manuscript by Grewe et al. describes the design and implementation of a novel system for attribution of species concentrations in numerical models to the precursor emissions which produce those concentrations, or "tagging". Some initial results of the system are also presented. Tagging is a useful method for source attribution in numerical models of atmospheric chemistry. There are already a diversity of approaches for such source attribution, including several currently-existing systems which use a tagging approach. This reviewer believes that the community benefits when a large number of diverse approaches to the problem of chemical source attribution exist, and are able to provide results which can be intercompared. For this reason I would ultimately like to see the manuscript published. Before publication however, I believe there appear to be serious issues which the authors should ideally fix, or at least openly acknowledge and thoroughly discuss in their manuscript. There are two problems with the approach as currently described, which lead to the production of unphysical results, which I will describe in more detail below.
Authors' Comment:
We are happy that the reviewer supports publication of the manuscript, in principle, and we will clarify the two addressed issues (see below).

Reviewer Comment:
One of the most interesting aspects of the TAGGING approach is that it considers both NO_x *and VOC precursors of ozone simultaneously. Earlier tagging approaches used in scientific applications have tended to focus on just one of these precursors at a time. Emmons et al. (2012), for example attribute all ozone formation to* NO_x *precursors, while Butler et al. (2011) attribute all ozone formation to VOC precursors. The present manuscript attempts to simultaneously attribute ozone formation to both VOC and* NO_x *precursors by using a combinatorial approach that effectively gives equal weight to* NO_x *and VOC precursors. While potentially very interesting, the discussion of this approach ignores the conventional wisdom that tropospheric ozone can be produced under different chemical regimes which are typically referred to as "NOx-limited" or "VOC limited" (see eg. Sillman et al. 1995).*
Authors' Comment:
The reviewer is right that we haven't addressed how the tagging mechanism responses in NO_x and VOC-limited regimes, and instead have focused on other examples. However, the question is indeed intersting and was partly also addressed by Grewe et al. (2010). NO_x and VOC-limited regimes imply that increases of VOC and NO_x, respectively, doesn't lead to increases in the ozone production. Still both components

are required for ozone production. While Dunker et al (2002) attributes all ozone produced in a $\mathrm{NO_x}$ sensitive regime to the respective $\mathrm{NO_x}$ source, we are arguing that either VOCs, CO, or $\mathrm{CH_4}$ are necessary to produce ozone and attribute, as the reviewer stated correctly, to both. The factor 0.5, which is a result (not an assumption) of the combinatorial ansatz. Details are, e.g., given by Grewe et al. (2010). As an example we focus on reaction R1 (see manuscript and below). At reaction level, the production, which can be associated to emission category i ($= P^i_{R1}$) can be split up into 3 parts: NO^i reacts with HO^i_2, NO^i reacts with HO^j_2 from any other category ($j \neq i$), and HO^i_2 reacts with NO^j from any other category ($j \neq i$). Note that at reaction level, the reaction of HO^i_2 with NO^j for $i \neq j$ is accounted for by 50% to emission category i and j:

$$\begin{aligned}
P^i_{R1} &= k_{R1}\left(NO^i\ HO^i_2 + \sum_{j\neq i}\frac{1}{2}NO^i\ HO^j_2 + \sum_{j\neq i}\frac{1}{2}NO^j\ HO^i_2\right) && (1)\\
&= k_{R1}\left(NO^i\ HO^i_2 + \frac{1}{2}NO^i(HO_2 - HO^i_2) + \frac{1}{2}HO^i_2(NO - NO^i)\right) && (2)\\
&= \frac{1}{2}k_{R1}\left(\frac{NO^i}{NO} + \frac{HO^i_2}{HO_2}\right). && (3)
\end{aligned}$$

Therefore, the production of ozone via this reaction can be written as

$$\begin{aligned}
P_{R1} &= k_{R1} NO\ HO_2 && (4)\\
&= k_{R1}\sum_{i=1}^{N} NO^i \sum_{j=1}^{N} HO^j_2 && (5)\\
&= \sum_{i=1}^{N}\frac{1}{2}k_{R1}\left(\frac{NO^i}{NO} + \frac{HO^i_2}{HO_2}\right) && (6)\\
&= \sum_{i=1}^{N} P^i_{R1}. && (7)
\end{aligned}$$

At concentration level, the ODE

$$\frac{d}{dt}O^i_3 = P^i - D^i, \qquad (8)$$

determines the concentration change of O^i_3 and implicitely includes effects wrt. $\mathrm{NO_x}$ and VOC saturated regimes (see below). The derived factor of 0.5 describes a basic principle and per se is not including explicitely any information on limited regimes. On the other side, the concentrations of ozone and the tagged ozone are revealing these regimes.

As an example, we assume a $\mathrm{NO_y}$ concentration of 80 ppbv and VOC of 1.5 ppmv, leading to an ozone steady-state concentration of 100 ppbv. The regime is $\mathrm{NO_x}$ limited. Now the tagging scheme attributes 50 ppbv ozone to $\mathrm{NO_y}$ and 50 ppbv to VOCs, leading to an attribution of 0.625 ppbv $\mathrm{O_3}$ per ppbv $\mathrm{NO_y}$ and 33 ppbv $\mathrm{O_3}$ per ppbv-VOC. Increasing the VOC emissions leads to 2 ppmv VOC and to the same ozone concentration, since we have a $\mathrm{NO_x}$-limited/VOC-sensitive regime. Therefore, the $\mathrm{NO_y}$ attribution remains unchanged and the VOC attribution is effectively reduced from 33 to 25 ppbv O3 per ppbv $\mathrm{NO_y}$, nicely attributing less ozone per VOC molecule.

Text changes: We now explain this in more detail in Section 2.

Reviewer Comment:
Earlier work described by Dunker et al. (2002) uses a technique for attributing ozone production to either NO_x or VOCs depending on the chemical regime, which has mostly seen application in regulatory modelling. In order to place their work in more context, the authors should discuss how their approach of equally weighting NO_x and VOC precursors of ozone fits with the previous work of Emmons et al (2012), Butler et al. (2011) and Dunker et al. (2002).
Authors' Comment:
The contribution calculations can be divided into two categories, which we refer to as "Perturbation-Method" and "Contribution-Method". Note that there is no consensus in literature about the naming. For the Contribution-Method, tagged species obtain production and loss terms in relation to the tagged source concentration. This method is applied by Lelieveld and Dentener, 2000; Grewe, 2007; Emmons et al., 2012, for the NO_x-O_3 tagging and by Butler et al., 2012 for the VOC-O_3 tagging.
With the "Perturbation-Method" sensitivities are attributed to soures terms. This can be emissions changes, e.g. Hoor et al. (2009). Dunker et al. (2002) used similar techniques as for the "Contribution-Method", but took as production terms the ozone change depending on the chemical regime and by this analyzed ozone sensitivities and thereby achieved a good agreement of their source contribution with calculated sensitivities (see their Figure 4). Hence this method, by definition, is similar to the "Perturbation-Method", since it diagnoses the origin of ozone changes.
Both approaches are answering different research questions and should not be mixed (see also discussion in the Introduction; A detailed analysis between these approaches is given by Grewe et al. (2010) and Grewe et al. (2012).
Text changes: Two text passages are added to the introduction, including the suggested references.

Reviewer Comment:
An unphysical result stemming from this equal-weight assumption is described by the authors near the end of Section 4.2 and shown for example in Figure 5. The TAGGING submodel attributes a certain proportion of VOC and CO to production from lightning. This is unphysical. Lightning is a source of NO_x, not carbon. "CO due to lightning" has no physical meaning, yet is an output of the TAGGING submodel. The authors describe this as "fully consistent with the chosen tagging approach", which while true, omits to mention that this is also unphysical. In a revised version of this manuscript I would like to see the authors acknowledge this result as being unphysical, and being due to the blending of NO_x and VOC precursor tags during the production of tagged PAN (and subsequently produced NO_x and VOC products of PAN degradation inheriting this mixture of tags), which is a direct consequence of the equal-weight assumption.
In a future version of the TAGGING scheme, the authors could consider adding 10 additional PAN tracers to their scheme (one per source sector), making it possible to track "PAN from NO_x precursors" and "PAN from VOC precursors", and thus reducing these particular unphysical results.
Authors' Comment:
The reviewer is right that CO, and equally ozone, OH and HO_2, is not emitted by lightning. The tagging scheme shows, however, which species are effectively influenced by individual sources categories.

For example NO_x emitted by traffic may react with hydrocabons from, e.g., biogenic emissions to form PAN, which is then transported over longer distances. After being transported over a long distance it decomposes into NO_y and VOCs. The biogenic emissions contributed to PAN, made a transport over a long distance possible and hence the decomposed NO_y gets a biogenic tag, although it was not initially emitted by the biogenic source, considered. This is meant by "fully consistent with the chosen tagging approach". A different question is whether this is what we want to diagnose. Hence, it is not a question of "physical" or "unphysical", but a question of the objective.
Text changes: We clarify this in Sec. 4.2 and introduce a new Section on limitations.

Reviewer Comment:
Unfortunately PAN is not the only reactive chemical species containing both carbon and nitrogen. For example, most modern chemical mechanisms include one or more alkyl nitrate species. In order to avoid NO_x*-only tags (such as lightning) being passed on to carbon-containing molecules, duplicate tracers would need to be defined for all kinds of organic nitrates in the model chemical mechanism (or more minimally, just two sets of 10 additional tracers covering an "organic nitrate family"). Their transformations in and out of the VOC and* NO_y *families would also need to be tracked by the TAGGING submodel. Clearly this would add extra complexity to the system, and likely also increase the runtime of the submodel. Low runtime overhead is one of the nice features of the TAGGING submodel as currently described. In their revised manuscript, the authors may wish to discuss this tradeoff between complexity and correctness in their design of the TAGGING scheme.*
Authors' Comment:
Totally agreed. Thanks - that is an important point. The discussion of pros and cons in the conclusion section was meant to include this statement, but unintentionally this got lost.
Text changes: We include a section on limitations.

Reviewer Comment:
I believe that a much more serious problem than that described above results from the use of a single chemical "family" to describe all of the VOC species belonging to each tag. This family includes all anthropogenic and biogenic VOCs, their oxidation products, and the oxidation products of methane. The problem with this approach is that not all VOC are created equally. Some VOC are highly reactive in the atmosphere, with very short lifetimes (eg. isoprene), while others have lifetimes orders of magnitude longer (eg. ethane). Different VOC also have different degradation pathways, which can lead to differences in intermediate oxidation products, radical recycling efficiency, and tropospheric ozone production yields between these VOC. I believe that lumping all of these diverse species together into a single tagged species may result in a significant loss of information about the diverse effects of different classes of VOC, in some cases leading to unphysical results from the TAGGING submodel.
The manuscript does not go into enough detail to describe the way in which this VOC family is treated in the model, in particular how the chemical tendencies obtained from the "real" chemistry are used to modify the concentrations of tagged VOC, and how the effects of "real" reactions involving VOC on radicals, ozone and PAN are distributed to the tagged VOC. Does the TAGGING submodel simply obtain the total VOC tendency

in each grid cell from the chemical solver, then apply this tendency to the individually tagged VOC family tracers present in that grid cell? If this is the case, then I see the following problem with this approach: Imagine that a plume of anthropogenically emitted VOC is advected over a forest with large biogenic isoprene emissions. The anthropogenic plume will contain a high fraction of relatively long-lived species such as ethane. With a lifetime of many weeks, such a plume would be capable of being advected over long distances. If a significant amount of isoprene is emitted into this plume, then this will be quickly removed through rapid chemistry, leading to a high negative tendency of the whole VOC family. If this negative tendency is applied equally to each of the tagged VOC species, the result will be that the anthropogenicly tagged VOC is removed at the same rate as the biogenic VOC, leading to an artificially short lifetime for the anthropogenic tag, and an artificially long lifetime for the biogenic tag, thus losing information about the unique properties of each of these VOC sources.

Similarly, the effects of VOC on other species such as radicals and PAN may tend to be smeared, or aliased over the different tags. This effect can actually be seen in Figure 5 of the manuscript, where PAN production has been partially attributed to methane emissions. In both our current understanding of reality, and our current state-of-theart models of atmospheric chemistry, there is no chemical pathway by which methane emissions can form PAN in the atmosphere. Methane contains one carbon atom. All oxidation products of methane (methyl radical, methyl peroxy radical, formaldehyde, methyl hydroperoxide, carbon monoxide, carbon dioxide, etc. . .) also contain one carbon atom. PAN (peroxy acetyl nitrate) contains two carbon atoms. Formation of PAN from methane is unphysical, but the TAGGING submodel nevertheless attributes a proportion of PAN formation to methane. I believe that this unphysical result stems from the use of aggregated family tendencies from the chemical solver being applied equally to each tag.

I would like to see a revised version of the manuscript in which the authors acknowledge that this result (PAN production attributed to methane) is unphysical, explain clearly and in detail how this comes about, offer their thoughts on further unphysical results which may be similarly expected from their approach, and what consequences this has for limiting its usefulness. For example, I believe that the authors should refrain from interpreting the PAN attribution results from the TAGGING system as currently implemented.

In a future version of the TAGGING scheme, the authors could consider adopting approaches used variously by Dunker et al. (2002) to mitigate the problem of different VOC reactivities, and Butler et al. (2011) to ensure that chemical production pathways are respected. Dunker et al. (2002) assign different decay rates to each VOC tag based on the kOH rate constants for each source category, so that (for example) biogenically tagged VOC will decay more quickly than anthrophgenic VOC. Butler et al. (2011) explicitly follow the degradation pathways of each emitted molecule, ensuring that only expected intermediate products are attributed to the original emissions. Both of these approaches would involve an increase in the complexity of the TAGGING submodel. In their revised manuscript, the authors may wish to discuss this tradeoff between complexity and correctness in their design of the TAGGING scheme.

Authors' Comment:

Thanks for pointing this out. We include a Section on limitations and discuss some pros and cons of the tagging approach in more detail, and discuss future directions to overcome shortcomings.

Reviewer Comment:
Specific comments
Line 15: this diagnostics package. . .
Line 38: Emmons et al. (2012) is already cited below, but should also be listed here as an example of tagging schemes previously used in global models.

Authors' Comment:
Text adapted accordingly

Reviewer Comment:
Line 40: NO_x *is technically a chemical family, not a species. Are the authors using the term here as a convenient shorthand for all oxides of nitrogen, or are they describing the implementation of* NO_x *in their model as a chemical family?*
Authors' Comment:
Here, we have simplified the description. The chemical scheme MECCA is simulating individual species, whereas the diagnostics package TAGGING is summarizing the reaction rates, obtained from MECCA and applied to a family concept. We have rephrased the sentence and clarify that we are talking about a family of reactive nitrogen compounds, which is tagged.

Reviewer Comment:
Line 94: The reaction following the parenthesised text is not the reaction described in the parenthesised text. This is confusing, please be clearer here about what you mean.
Authors' Comment:
Text adapted

Reviewer Comment:
Line 96: Ozone production also depends on RO2.
Authors' Comment:
Correct. Though here we are concentrating exemplarily on one reaction, only, as clearly indicated in this paragraph. The regarded reaction, as written, depends on NO and HO_2.

Reviewer Comment:
Line 102: Please provide a forward reference to where tagging of HO2 is described.
Authors' Comment:
included

Reviewer Comment:
Line 184: A table listing the members of the NO_y *and VOC families would be useful.*
Line 217: Please also list the members of this "effective ozone" family.
Authors' Comment:
A table is given in the supplement, which includes the ozone family. We include a reference to the

supplement.

Reviewer Comment:
Table 3: This table appears to be incomplete. Photolysis of formaldehyde should also be an important source of HO2. Is this considered? Are there any other sources left out of this table?
Authors' Comment:
This reaction is included in MECCA, but it is not included in the present version of the TAGGING scheme. Though, most of the OH production (globally) is covered by the chosen set of reactions. However, the reviewer is right that this reaction is indeed important for the OH budget and we have identified the reduced set of reactions as a shortcoming of the OH tagging scheme. Currently, a colleague is preparing a follow-up paper (Rieger et al., in preparation) on the OH tagging scheme with a full set of reactions. Here, 'full' refers to the set of reaction used in the MECCA chemistry scheme. First results are promising and do locally show changes; however the global picture and results presented here for HO_x, NO_y, and ozone are hardly affected. A comment is added to the new Section on limitations.

Reviewer Comment:
Line 380: Did you mean to write that your simulation shows a lower contribution from stratospheric ozone in the Northern Hemisphere? This would be consistent with the previous work as described in the previous sentence.
Authors' Comment:
Unfortunately, the text is misleading. Emmons et al. (2012) give absolute numbers (mixing ratios). Those are lower on the southern hemisphere than on the northern hemisphere, while the relative contributions in percent are larger on the southern hemisphere than on the northern because of the larger background concentrations on the northern hemisphere. Text is adapted.

Reviewer Comment:
References
Butler, T., et al.: Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach, Atmos. Env., 45, 4082-4090, 2011.
Dunker, A., et al.: Comparison of source apportionment and source sensitivity of ozone in a three-dimensional air quality model, Environ. Sci. Tech., 36, 2953-2964, 2002.
Emmons, L., et al.: Tagged ozone mechanism for MOZART-4, CAM-chem and other chemical transport models, Geosci. Model Dev., 5, 1531-1542.
Sillman, S.: The use of NO_y, H2O2, and HNO3 as indicators for ozone-NO_x- hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100, 14175-14188, 1995.

Authors' Comment:
References included.

Reply to Anonymous Referee #2:
We are thankful for the detailed review. We like to point out two important comments, which can be summarized as a better description of limitations (similar to the reviewer #1) and a better explanation of the factor 1/2 in the final tagging equation. We have included a section on limitations to clarify the reviewer's questions and we included some more equations in the mathematical re-formulation concerning the factor 1/2. For a couple of other comments, however, we have the feeling that the reviewer assumes and even demands that the tagging diagnostics package performs identical to the perturbation approach. This is neither our intention nor do we pretend it. In contrast, we clearly described the difference and stated that a combination of both approaches gives a good insight in atmospheric processes.

Reviewer Comment:
This new model development by Grewe et alii continues the development of tagging tracers in various ways to attribute environmental degradation to specific emissions (or possibly other actions). The method is reasonable but certainly not a unique or singularly correct approach to derive the environmental damage for a given set of actions. Grewe has made some very specific assumptions about how to partition a key species like tropospheric O3 into a unique sum of causes. The choices made are plausible, but there are readily available other methods (e.g., the 'perturbation method', line 50, which goes back decades before the Grewe references listed here indicate). I tend to concur with the other RC1 review in that a diversity of approaches can always teach us something. Thus, with some chemical model revisions and with a recognition that tagging does not just give us the "contribution", the model should be published.

Authors' Comment:
We are happy that the reviewer acknowledge, in principle, the publication of this method. We think that it is important to stress that different methods often address different questions. And hence, we agree that no unique, best, or better technique exists in quantifying e.g., anthropogenic impacts on atmospheric chemistry and climate change. We already state in the introduction
"The combination of both approaches leads to much better insights in the reasons how emission changes lead to concentration changes",
and hence clearly agree and support both reviewers view that the more diagnostics we have, the more we learn. We agree that the "perturbation method" has been used previously, frequently, and by many more authors, which we thought is obvious. The reference to our own work was actually meant to strengthen the point that we use both approaches and that we are not trying to rate one over the other, in general. For different purposes, though, one method might be, and actually is, better suited than the other. On the other hand, our experience is that the different aspects of different diagnostic packages are sometimes not well differentiated. Hence, we tried to define a wording in the beginning of the paper, which clarifies our understanding of the wording "contribution" and "change". There is no unique definition. But to our understanding, our choice is at least meaningful. And it is important to acknowledge that there is a difference, which the reviewers are obviously aware of, but others may not.

Reviewer Comment:
There are several serious problems with this GMDD paper as written that might be cleared up with major revisions affecting both the (i) chemical modeling and (ii) the authors' choice to describe the tagging method as the true 'correct' method and thus discussing the errors, for example, in the perturbation method. There is an additional

(iii) potential problem here in that the extensively expanded TAGGING here may still lack the full chemical coupling across species and regions that has been demonstrated in perturbation experiments with fully coupled models. There are some very interesting results here, but the paper needs to be a bit better balanced and informative.

Authors' Comment:

We are happy to provide more information and equally happy to adapt the wording to better balance our enthusiasm on our own work.

Reviewer Comment:

(i) The chemical model has some clear problems in language or concept. For example, CH4 does NOT make NMHCs. The production of NMHCs (e.g., C2H6 etc) comes from the sources. CH4 is a major source for H2CO in the remote troposphere but that species is not listed here and is not an NMHC. At best it might be a VOC. The NMHC reactions in the table make no sense.

Authors' Comment:

We have the impression that there might be a misunderstanding, which we probably have caused by using the word 'tagging' for both, the conceptual approach and the way we implemented it in the current model version. The mathematical concept 'tagging' is a decomposition of the equations in order to derive, what we called, contributions. No further assumptions, linearizations, or other limiting processes are applied. Hence, we do not see any problems with the mathematical concept. On the other hand the implementation requires simplifications. These are now better addressed in a Section by its own. We think that this might have caused some irritations. We think that the way we have implemented the mathematical concept of tagging provides useful information. However, work is still required to deal with shortcomings.

Reviewer Comment:

Another mistake appears to be the lack of photolysis of O2 as an important source of O3 in the tropical upper troposphere. This is well established and I can only take it that the old photolysis lookup tables used here have cut off this process in the troposphere? Otherwise the explanation for tropospheric O3 sources does not makes sense.

Authors' Comment:

Ozone is often divided up into stratospheric and tropospheric ozone, which either means ozone produced in the stratosphere and troposphere, respectively, or ozone present in the stratosphere or troposphere, respectively. Here, we are referring to ozone production terms in a way that we call ozone produced by oxygen photolysis, regardless where it happens, as stratospheric ozone production, since it is a process typical for the stratosphere. In the same way, we name ozone production via other chemical reactions, e.g. $NO+HO_2 \longrightarrow NO_2+OH$, as tropospheric ozone. We focus on the type of production terms, regardless of where it happens. However, we know that the one is a typical stratospheric ozone production and the other a tropospheric ozone production term. (Note that we have one chemical mechanism, from the surface to the middle atmosphere.) We think that this is justified, since the primary goal is to discriminate ozone production from surface emissions from other sources. The tropopause region is actually characterized by both processes. A split into also ozone produced in the tropopshere and stratosphere is feasible, but beyond the scope of this work. We have adapted the text in the introduction to Section 3.

Reviewer Comment:
Putting
in N2O emissions is interesting, but I do not see where it is then listed as a source of tropospheric NOx (0.1 Tg-N/yr)? Moreover, the N2O-CH4-O3 system in the stratosphere is quite complex and controls the net trop influx of O3 and NOy. That system is also established as a coupled perturbation, but is not accurately represented in this tagging model.
Authors' Comment:
The mechanism requires a complete set of NO_x emissions and loss terms (see introduction to Section 3). Therefore stratospheric NOx production is included. We do not understand the comment with respect to the coupled system.

Reviewer Comment:
Almost all modern scavenging algorithms for species such as H2O2 and HNO3 and others follow the rainout and washout AND re-evaporation of these species in layers below the original uptake. The method of tagging here would seem to be inadequate to deal with this.
Authors' Comment:
No, the 3D-tendencies are obtained from the scavenging submodel. Negative tendencies are interpreted as losses due to washout, positive tendencies are re-evaporation.

Reviewer Comment:
(ii) The tagging method as best I understand is built to achieve a zero sum in that a certain level of, say O3 concentration, is partitioned into the different sources so as to sum correctly. This is clearly a personal choice, since I would prefer the linearized tangent approach in which the differential evaluated at the current atmospheric state is used to calculate the change in O3.
Authors' Comment:
This actually seems to be the source of a misunderstanding. We are not considering changes in ozone. We are not investigating, how ozone would change if we were changing the strength of any emission source. This question, as discussed in our manuscript in the introduction section, would be best answered by the perturbation approach. Diagnostic packages as that favored by the reviewer or the tagging, we are proposing are adding additional information so that the physical and chemical reasons for these ozone changes can be understood. Here, we are investigating one simulation with one specific chemical regime and attributing emissions to ozone concentrations. In our view that is best described by the wording 'contribution of an emission sector to the atmospheric concentration of ozone' and it is different from 'contribution of changes in emission sectors to change atmospheric concentrations of ozone', to which, at least as far as we understand the comments, the reviewer is referring to.

Reviewer Comment:
This of course will not lead to a sum of all the components being zero because the chemistry is non-linear over the range from zero to full industrial emissions. This has a similar issue with CO2 and radiative forcing

attribution, since the RF of CO2 goes as the log of its concentration. In this case we have the "which came first?" or "straw that broke the camel's back" problem. Recent increase in CO2 has a lower impact than earlier ones. For many of us the only fair way is to do the perturbation experiment (flat slope at high CO2) and then realize that the sum of all tangent additions if scaled to zero would not be equal to the current state. This is the same problem with the attribution of say biomass burning, and there is no single correct answer. This paper needs to realize and carefully explain the arbitrary choices made.

Authors' Comment:

We agree that the fundamental problem is the "straw that broke the camel's back". Please note that there is a difference between ozone and carbon dioxide, which, in our opinion, questions the approach suggested by the reviewer. It is well established that for a certain NOy concentration any increase in NOy reduces the net-ozone production (Ehalt and Rohrer, 1994 and many others). Hence an increase in any NOx emission source potentially leads to a lower ozone concentration. And this is then the case for all emission sectors. Defining the contributions on the basis of this approach hence leads even to an overall negative contribution of emissions to ozone. So what process actually produces ozone to close the budget? Note that in this case, we are considering only the "last straw" as relevant ozone prodcution terms. In our approach, we argue that air chemistry is not making any difference from which source a NO molecule has been emitted. A NO molecule from industry or from traffic emissions has the same likelihood to react with HO2. The reaction kinetics are the same.

Reviewer Comment:

There is a worrisome statement in the introduction that somehow demonstrates the absurdity of the different approaches. The idea that tagging is the 'correct' answer is just incorrect. It is indeed one of the answers, but not necessarily the best: "For example, the change in ozone due to a 100% reduction in road traffic emissions is smaller by a factor of 5 than the contribution of the road traffic emissions to ozone." The tagging method is obviously defined here to be "the contribution of ", but as a policy maker who wants to know what happens if I reduce road traffic, I would prefer a 100% reduction as the correct answer, or I might choose the 5% reduction times 20. Clearly if I reduce road traffic by 5% or by 100%, the perturbation run, not the tagging run, is the correct value. Does the tagging method do any better than a series of 5% reductions scaled across different emission sources? Moreover, one would not be interested in attributing the background basic atmospheric state (e.g., lightning emissions) in a proportional basis with those of industry, since the background state is not billable for damages as an anthropogenic perturbation is.

Authors' Comment:

We clearly stated that the perturbation method is the adequate method to answer the question how changes in road traffic emissions affect ozone or any other atmospheric species (see Introduction). So we still are puzzled how the reviewer got another impression. We are interested in understanding atmospheric chemistry. We are interested in how much lightning is contributing to the ozone concentration. Not everything is about "billing for damages". Agreed, that is important. But we also think that understanding the simulated changes is equally important and our diagnostics package is contributing to this understanding.

Reviewer Comment:
The authors continue to use the English word contribution as a code word for their own specific method for dividing up species concentrations. Lines 530-535 argue that the perturbation method "underestimates this contribution" by a factor of 2. I would assert that the "tagging-contribution" is larger than the perturbation by a factor of two and that one of the causes may be the lack of full tagging. The other reason is the apparent need to tag everything including background processes in a similar way to pollution sources. Personally I am not sure that the treatment of the background atmosphere by tagging is done well (e.g., the stratosphere) and thus the partitioning here may be specific to the assumptions made.
Also the authors really need to explain their 1/2 factor throughout the equations (starting with eqn 3). It is far from obvious since a simple Taylor expansion would not give 1/2. Please help us out. If it does not apply to small perturbations but only when trying to ensure that the sums are balance, then explain.
Authors' Comment:
Again and similar to our previous comment, the reviewer implicitely assumes that we are investigating changes or perturbations, because she or he is mentioning the Taylor-approximation, which is based on estimating effects of a small perturbation. Since we have foreseen such a discussion, we already have included a whole Section on tagging basics, where we clearly state that the tagging principle does not include any approximations or linearizations. An additional explanation on the factor 1/2 is given above. At reaction level, looking at reaction kinetics, rather than concentration level, where we consider solutions of a ODE, the reaction rate for the above considerer reaction is P=k [NO] [HO_2]. The chemistry mechanism is not discriminating between NO from different sources. The reaction rate P is not adapted whether NO from road traffic or from lightning is reacting with HO_2. The molecules NO and HO2 are both equally important for this reaction. See also answer to reviewer 1. We have included a discussion on this point in Section 2.

Reviewer Comment:
(iii) There are clearly identified global chemical coupling patterns that reach across species and regions (strat vs. trop). They are readily identified in models through perturbation simulations. For example, these early chemical feedbacks of tropospheric OH-CH4 and the N2O-NOy-O3 in the stratosphere have been demonstrated to work across many models in various IPCC model comparisons. These are important because they affect the lifetime of a perturbation and hence the attributable damage of emissions. They are most surely in the full MESSY model. From the couplings of this tagging method, I do not believe that these fundamental couplings are present in the tagging model. If you could demonstrate that both of these feedbacks can be derived from the tagging then it would be convincing. Otherwise it shows that tagging really cannot include the dominant chemical feedbacks of the lower atmosphere. This lack of full coupling in the TAGGING model means that one cannot be sure what chemical feedbacks are not included.
Authors' Comment:
The tagging method, as a diagnostic package, is controlled by the MECCA chemistry, which includes

feedback processes. And can be analyzed, as suggested, by perturbations of the system. In the paper we have described the feedback of NOx emission changes to the ozone production efficiency: A decrease in, e.g., road traffic emission leads to lower NOx concentrations. This may lead to larger net-ozone production rates. Hence this is a negative feedback. The lower NOx emissions (with unchanged) net-ozone production rates leads to lower ozone concentrations. However, since the net-ozone production rates increase, the ozone reduction is reduced. This is a negative feedback process, which can be deduced only in the comparison of two simulations. Another interpretation is that the unchanged, e.g., lightning emissions, also experience the enhanced net-ozone production rates decrease, and hence the ozone produced by lightning NO is larger than in the previous simulation. During the simulation and more importantly also in reality, a NO molecule has no remembrance of its source of emission. Hence, no difference is made between the reaction of a NO molecule with HO2, whether it originates from lightning or road traffic. Feedbacks are always related to changes with respect to a base situation, whereas tagging is analysing a base situation by itself. So we think that asking for feedbacks to be included in the tagging is simply trying to achieve the same results from the tagging method as a perturbation method is providing. However, this is not the intention and not the case. Both methods are valid and usable, however, answering different questions.

Reviewer Comment:
Other issues: (iv) The method is described as low cost and non-intrusive, but the only global example given is for T42 resolution (2.8 deg). This is very low resolution for current global models, yet this is only a GMD paper to establish the development of the model. OK, but can you run at T159 (1.1 deg) for example with all the memory requirements for the tagged tracers to be transported? I had thought that tracer transport was one of the dominant costs of high-res CTMs. Indeed, line 564 seems to indicate that you already have memory limitations at T42.
Authors' Comment:
Actually, EMAC is not a CTM. I am not quite sure, with which coupled troposphere-to-mesosphere chemistry-climate model, multi-decadal simulations were performed at T159. The most recent models, which will participate in the upcoming IPCC via CCMI have actually a similar resolution as we have used in our study (Morgenstern et al., 2017; their table 3). Moreover, the sensitivity study presented in Section 5.1 has a horizontal resolution of 10 km or 0.1°.

Reviewer Comment:
(v) What was the STE flux of O3 and NOy as a function of latitude and season. This would seem to be very important since the background atmosphere shares the attribution in this scheme. Please denote.
Authors' Comment:
We have estimated the net ozone flux from the stratosphere in the EMAC model for the years 2000-2004. Using the residuum method, i.e. STE=Burden change-Prod+Loss+Deposition, the ozone STE is calculated to be 393 +- 25 TgO3 per year (Jöckel et al., 2006), which is in agreement with other modeling studies (Stevenson et al., 2006). Note that this method includes net fluxes, i.e. upward and downward fluxes of ozone through the tropopause. The calculation of the stratosphere-to-troposphere ozone flux was performed by using a diagnostic tracer Strat-O3, which is nudged to ozone in the stratosphere and experiences loss terms (chemistry and deposition) in the tropopshere, only. The accumulated loss terms provide a measure for the stratosphere-to-troposphere ozone flux and is 1198 +- 28 TgO_3 per year (see

also Jöckel et al., 2006, Table 2). The analysis of the impact of STE on the composition of the troposphere is indeed an important question, but beyond the scope of this paper. Generally, it was shown with a similar approach used here that stratospheric ozone changes and STE variations lead to variations in tropospheric ozone (e.g. Grewe, 2007). The concentration of the tagged tracer for stratospheric ozone is basically a result of the ozone produced by O_2 photolysis, transport to the tropopshere and tropspheric loss processes.

Reviewer Comment:
(vi) The idea that the Mediterranean Sea contains ”pristine areas” anywhere is at least humorous - thanks.
Authors' Comment:
You're welcomed. Text adapted.

Reference:

Morgenstern, O., Hegglin, M. I., Rozanov, E., O'Connor, F. M., Abraham, N. L., Akiyoshi, H., Archibald, A. T., Bekki, S., Butchart, N., Chipperfield, M. P., Deushi, M., Dhomse, S. S., Garcia, R. R., Hardiman, S. C., Horowitz, L. W., Jckel, P., Josse, B., Kinnison, D., Lin, M., Mancini, E., Manyin, M. E., Marchand, M., Marcal, V., Michou, M., Oman, L. D., Pitari, G., Plummer, D. A., Revell, L. E., Saint-Martin, D., Schofield, R., Stenke, A., Stone, K., Sudo, K., Tanaka, T. Y., Tilmes, S., Yamashita, Y., Yoshida, K., and Zeng, G.: Review of the global models used within phase 1 of the ChemistryClimate Model Initiative (CCMI), Geosci. Model Dev., 10, 639-671, doi:10.5194/gmd-10-639-2017, 2017.

Manuscript prepared for Geosci. Model Dev.
with version 2014/09/16 7.15 Copernicus papers of the LaTeX class copernicus.cls.
Date: 2 May 2017

Contribution of emissions to concentrations: The TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52)

Volker Grewe[1,2], Eleni Tsati[1], Mariano Mertens[1], Christine Frömming[1], and Patrick Jöckel[1]

[1]Deutsches Zentrum für Luft- und Raumfahrt, Institut für Physik der Atmosphäre, Oberpfaffenhofen, Germany
[2]also at: Delft University of Technology, Aerospace Engineering, Section Aircraft Noise and Climate Effects, Delft, Netherlands

Correspondence to: Volker Grewe (volker.grewe@dlr.de)

Abstract. Questions such as "What is the contribution of road traffic emissions to climate change?" or "What is the impact of shipping emissions on local air quality?" requires a quantification of the contribution of specific emissions sectors to the concentration of radiatively active species and air quality related species, respectively. Here, we present a diagnostics package, implemented in the Modular Earth-System Model MESSy, which keeps track of the contribution of source categories (mainly emission sectors) to various concentrations. The diagnostics package is implemented as a submodel (TAGGING) of EMAC (European Centre for Medium-Range Weather Forecasts - Hamburg (ECHAM)/Modular Earth Submodel System (MESSy) Atmospheric Chemistry). It determines the contributions of 10 different source categories to the concentration of ozone, nitrogen oxides, peroxyacytyl nitrate, carbon monoxide, non-methane hydrocarbons, hydroxyl and hydroperoxyl radicals (=tagged tracers). The source categories are mainly emission sectors and some other sources for completeness. As emission sectors, road traffic, shipping, air traffic, anthropogenic non-traffic, biogenic, biomass burning, and lightning are considered. The submodel obtains information on the chemical reaction rates, online emissions such as lightning, and wash-out rates. It then solves differential equations for the contribution of a source category to each of the seven tracers. This diagnostics package does not feed back to any other part of the model. For the first time, it takes into account chemically competing effects: For example the competition between NO_x, CO, and NMHCs in the production and destruction of ozone. We show that the results are in-line with results from other tagging schemes and provide plausibility checks for concentrations of trace gases such as OH and HO_2, which have not previously been tagged. The budgets of the tagged tracers, i.e. the contribution from individual source categories (mainly emission sectors) to, e.g., ozone, are only marginally sen-

sitive to changes in model resolution, though the level of detail increases. A reduction in road traffic emissions by 5% shows that road traffic global tropospheric ozone is reduced by 4% only, because the net ozone productivity increases. This 4% reduction in road traffic tropospheric ozone corresponds to a reduction in total tropospheric ozone by ≈0.3%, which is compensated by an increase in tropospheric ozone from other sources by 0.1%, resulting in a reduction in total tropospheric ozone of ≈0.2%. This compensating effect compares well previous findings. The computational costs of the TAGGING submodel are low with respect to computing time, but a large number of additional tracers are required. The advantage of the tagging scheme is that in one simulation and at every time step and grid point, information is available on the contribution of different emission sectors to the ozone budget, which then can be further used in upcoming studies to calculate the respective radiative forcing simultaneously.

1 Introduction

Nitrogen oxides (NO_x), carbon monoxide (CO), methane (CH_4) and non-methane hydrocarbons (NMHC) are precursors of tropospheric ozone (O_3). The assessment of the contribution of individual emissions of these precursors on air quality and climate requires a detailed analysis of the chemical conversion, transport and deposition of these species in numerical atmosphere-chemistry simulations. A frequently used method is called 'tagging' (Horowitz and Jacob, 1999; Lelieveld and Dentener, 2000; Meijer et al., 2000; Dunker et al., 2002; Grewe, 2004; Gromov et al., 2010; Butler et al., 2011; Emmons et al., 2012; Grewe et al., 2012). Technically, this method adds a set of diagnostic tracers for each chemical species or chemical family considered, i.e. one additional tracer per source category for each chemical species or family considered. For example, for the ~~species~~ family of reactive nitrogen compounds NO_y a set of tagged tracers NO_y^{ant}, NO_y^{rt}, NO_y^{shp}, NO_y^{air}, NO_y^{bio}, NO_y^{bb}, NO_y^{lig}, NO_y^{ch4}, NO_y^{n2o}, and NO_y^{str} is added, which describes the NO_y concentration from anthropogenic non-traffic (e.g. industry, households), road traffic, ships, air traffic, biogenic, biomass burning, lightning, methane and nitrous oxide decomposition and stratospheric ozone production. The idea is that these tagged tracers experience the same chemical conversions, sources, and loss processes (such as deposition), as the simulated tracer NO_y. If all emissions of NO_y are considered and tagged, the sum of all tagged diagnostic NO_y tracers equals the simulated NO_y tracer in this approach. A full partition of the simulated tracer concentration with respect to emission sectors can be achieved. Thus, the contribution of an emission sector, such as industry, road traffic, etc. to a concentration is provided by the tagging method.

The abundances of carbon compounds (CO, CH_4, NMHCs) and nitrogen oxides are both limiting factors for tropospheric ozone production (Sillman, 1995). Many tagging mechanisms for global applications concentrate on NO_x compounds (Horowitz and Jacob, 1999; Lelieveld and Dentener, 2000; Meijer et al., 2000; Grewe, 2004; Grewe et al., 2012), only. Butler et al. (2011) tags the sources for hydrogen carbons. Dunker et al. (2002) tags ozone sensitivities and attributes them to either nitrogen oxides or volatile organic compounds (VOCs) depending on the chemical regime. This latter mechanism is a very helpful tool in understanding the underlying chemical processes and especially sensitivities. However, the mechanism differs in principle from other tagging mechanisms. One consequence is that the sum of all contibutions is not adding up to the ozone concentration. The focus on the ozone sensitivities makes that scheme more similar to the perturbation approach.

~~A different approach, the~~ This perturbation approach (e.g. Hoor et al., 2009; Grewe et al, 2007, and many others), where results from two simulations are compared which differ in the strength of an individual emission source, identify the impact of changes in emissions (e.g. by mitigation options) on the atmospheric composition. It is important not to confuse both approaches. For example, the change in ozone due to a 100% reduction in road traffic emissions is smaller by a factor of 5 than the contribution of the road traffic emissions to ozone (Grewe et al., 2012). Emmons et al. (2012) showed that similar results (factor of 3) are obtained for biomass burning NO_x emissions and the impact on ozone. Clearly, the non-linearity in the ozone chemistry leads to these large differences. Any reduction in NO_x emission leads mostly to a larger ozone production efficiency. Grewe et al. (2012) showed that in the simulation without road traffic NO_x emissions, the obvious large reduction in ozone from the reduced road traffic contribution to ozone is compensated by larger contributions from other emission sectors, not because these emissions are changed, but because the ozone production efficiency is increased.

These two different approaches answer two different questions. The perturbation approach quantifies how much a concentration changes if emissions are changed, whereas tagging addresses the contribution of an emission to the concentration. The combination of both approaches leads to much better insights in the reasons how emission changes lead to concentration changes (Grewe et al., 2012). Note also that the perturbation approach often requires the identical meteorology in either simulation to enhance the signal-to-noise ratio enabling a robust signal. However, this is not feasible in fully coupled chemistry-climate models unless run in a so-called "QCTM-mode", which replaces instantaneous chemical feedbacks by climatological values (Deckert et al., 2011, see also below).

Most tagging approaches address a straight process chain from the emission of e.g. NO_x to a concentration of e.g. ozone. Grewe et al. (2010), as well as Grewe (2013a) and Tsati (2014) proposed a more general tagging approach, where competing mechanisms in the production of ozone can be taken into account, e.g. both NO_x and carbon compounds (CO, CH_4, NMHCs) are precursors of ozone. This more general tagging approach allows the contribution of road traffic NO_x, CO, and NMHC emissions to ozone, for example, to be determined. This generalised method has also been successfully applied to a non-chemical application, namely temperature in an energy balance model (Grewe, 2013b).

Here, we present a submodel (TAGGING) of an Earth-System-Model (EMAC), which applies this general tagging approach to allow the contribution of NO_x, CO and NMHC emissions from a variety of emission sectors to ozone and HO_x chemistry to be quantified. Hence, it combines NO_x-ozone tagging approaches (Emmons et al., 2012) with VOC-ozone tagging approaches (Butler et al., 2011). In Section 2 we present the basic equations of the tagging scheme, whereas in Section 3 we present what emissions are addressed and how the tagging method is implemented. In Section 4 we show results of a base simulation and compare them with other modelling studies. Since no measurements are available for contributions of emissions to ozone concentrations, a direct comparison with observational data is not possible. Instead, we show that the results are in agreement with other studies. Since the tagging of HO_x components is new, we discuss those results in more detail, especially with the focus on aviation and shipping emissions. Finally, we address sensitivities of the methodology (Sec. 5), with respect to the resolution and emission changes, and provide a comparison of the perturbation and tagging method.

2 Basics on tagging

The tagging approach, which we adopt here is based on Grewe et al. (2010) and Grewe (2013a). We first describe the basic mechanism and describe in Sec. 3 how this mechanism is applied in the submodel TAGGING. Exemplarily, we concentrate on the main reaction for tropospheric ozone production: ~~(rate limiting step; NO_2 is photolysed and recombines with O_2 to form ozone):~~

$$NO + HO_2 \longrightarrow NO_2 + OH. \tag{R1}$$

Note, this reaction is not producing any ozone, but NO_2 is photolysed and recombines with O_2 to form ozone and reaction (R1) is the rate limiting step for this chain of reactions. The ozone production rate P_{R1} depends on the abundance of NO and HO_2, and the reaction rate coefficient k_{R1} (Reaction R1). The NO concentration in turn depends on emissions of NO from different emission sectors (here N in total), such as industry and road traffic with the respective concentration NO_x^{ind} and NO_x^{rt}. Thus, the ozone production rate P_{R1} has to be distributed to the sectors industry, road traffic, etc. This is achieved by a combinatoric redistribution according to the concentrations of the tagged family and species of NO_x and HO_2, respectively. Note that a full description of the applied TAGGING mechanism, including the tagging of OH and HO_2, is given in the next Section. This means that all possible combinations between a tagged NO_x species and another tagged HO_2 species are evaluated and its probability calculated consistently with the calculation of the chemical production rate P_{R1}. This is just a full partitioning of the production rate P_{R1} (following Grewe et al., 2010):

$$
\begin{aligned}
P_{R1} &= k_{R1} NO\, HO_2 && (1)\\
&= k_{R1} \sum_{i=1}^{N} NO^i \sum_{j=1}^{N} HO_2^j && (2)\\
&= k_{R1} \sum_{i=1}^{N} \left(NO^i\, HO_2^i + \sum_{j\neq i} \frac{1}{2} NO^i\, HO_2^j + \sum_{j\neq i} \frac{1}{2} NO^j\, HO_2^i \right) && (3)\\
&= \sum_{i=1}^{N} \frac{1}{2} k_{R1} \left(\frac{NO^i}{NO} + \frac{HO_2^i}{HO_2} \right) && (4)\\
&= \sum_{i=1}^{N} P_{R1}^i . && (5)
\end{aligned}
$$

Here i and j represent a counter for all N source categories; We have chosen $N = 10$ source categories (see Sec. 3). The factor $\frac{1}{2}$ stems from the split of the part of the ozone production $k_{R1}\, NO^i\, HO_2^j$ $(i \neq j)$, which is equally attributed to emission category i and j. Note that no approximation, linearization, or Taylor approximation is used in this approach. ~~With this combinatorial approach, Grewe et al. (2010) showed (here as an example for industry) that the reaction rate~~ For the ozone production due to NO_x from industry (NO_x^{ind}) and due to HO_2^{ind} from industry we hence obtain: ~~P_{R1}^{ind}, that is the ozone production due to NO_x from industry (NO_x^{ind}) and due to HO_2^{ind} from industry equals:~~

$$
P_{R1}^{ind} = P_{R1} \frac{1}{2} \left(\frac{NO^{ind}}{NO} + \frac{HO_2^{ind}}{HO_2} \right) . \qquad (6)
$$

Note that this includes the reactions of NO_x^{ind} with all other HO_2 molecules and vice versa HO_2^{ind} with other NO_x molecules without any double counting. The relevant differential equation for the tagged species is then

$$
\frac{d}{dt} O_3^{ind} = P^{ind} - D^{ind}, \qquad (7)
$$

where P^{ind} and D^{ind} are the sum of all relevant production and loss terms. With this approach, Grewe et al. (2010) showed that the sum of all emissions contributions adds up to the total concentration of the respective species. For example, the ozone field is completely partitioned into emission sectors contributions, if all emission sectors are included, leading to

$$
\sum_{i=1}^{N} O_3^i = O_3 . \qquad (8)
$$

Note that the factor 0.5 in Eq. (6) is a result of the combinatorical ansatz and not an assumption. It reflects that in reaction R1 both species are required and similar to the reaction rate coefficient it constitutes a basic principle. This should not be confused with effects of different chemical regimes on the ozone productivity, which are reflected in the concentrations of ozone and the tagged ozone fields. For example, when increasing NO_x emissions in a VOC-limited regime (i.e. any changes in nitrogen oxide emissions hardly change the ozone production), the ozone productivity or sensitivity attributed to NO_x will descrease, whereas that of VOCs remains unchanged.

This approach is identical to a different formulation, which describes the right hand side of the differential equation more generally as the relative sensitivity of the individual production and loss terms with respect to the emission sector considered (Grewe, 2013a):

$$P_{R1}^{ind} = P_{R1} \frac{S^{ind^T}\,\nabla_S P_{R1}}{S^T\,\nabla_S P_{R1}}, \tag{9}$$

where S is the vector of all chemical compounds, e.g.,

$$S^T = (NO_x, CO, NMHC, O_3, ...)^T, \text{and} \tag{10}$$

$$S^{ind^T} = (NO_x^{ind}, CO^{ind}, NMHC^{ind}, O_3^{ind}, ...)^T, \tag{11}$$

and

$$\nabla_S P_{R1} = \frac{d}{dS} P_{R1} \tag{12}$$

providing two different interpretations of the differential equation (7).

To summarise, this tagging approach fully partitions individual chemical fields into the contribution of individual emission sectors. There is no linearisation required and the approach utilises the identical chemical parameterisation as the underlying chemical scheme, with respect to the probability that a reaction occurs. Note that the new aspect of this tagging approach compared to other tagging approaches (Grewe, 2007; Lelieveld and Dentener, 2000; Emmons et al., 2012) is the competing effect of NO_x and carbon compounds in producing ozone. Since the differential equation for the tagging scheme (7) fully relies on the reaction rates and concentrations, the tagging scheme can be implemented independently from the main chemical solver. However, details on many reaction rates have to be transferred from the chemical solver to the tagging scheme.

In the following, and actually this also applies to the previous sections, we use the wording 'contribution of emissions from a sector X to the atmospheric concentration of species (or family) Y', when we are referring to that part of the concentration Y, which can be attributed to the emission sector X, by a decomposition of the chemical reactions (see above). This implies that no changes in chemical reaction rates is assumed, e.g., for natural and anthropogenic emissions, which would represent differerent atmospheric situations for pre-industrial and today's atmospheric chemical regimes. Obviously, other authors may have other definitions for this wording.

3 Implementation in EMAC/MECO(n)

The objective of the implementation of this tagging scheme is to be able to monitor online, i.e. at every model's timestep, the contribution of individual emission sectors to ozone and OH, allowing a competition between ozone precursors, linearisation to be avoided, and applicable in decadal simulations. The tagging approach requires to quantify all sources of the species considered. Therefore, in

Table 1. Brief description of the submodels used together with the TAGGING submodel. A complete list can be found in the supplement of Mertens et al. (2016).

Submodel	Description	Reference
CLOUD	large scale cloud/rain properties	based on Roeckner et al. (2003) see also Jöckel et al. (2006)
CONVECT	convective cloud/rain properties and related transport)	Tost et al. (2006a)
DDEP	dry deposition of trace gases	Kerkweg et al. (2006a)
JVAL	photolysis rates	Landgraf and Crutzen (1998), see also Jöckel et al. (2006)
LNOX	lightning NO_x emissions	Tost et al. (2007b) and Grewe et al. (2001)
MECCA	tropospheric and stratospheric gas-phase chemistry	Sander et al. (2011)
OFFEMIS	prescribed emissions of trace gases	Kerkweg et al. (2006b) (named OFFLEM therein)
ONEMIS	online calculated emissions of trace gases	Kerkweg et al. (2006b) (named ONLEM therein)
SCAV	wet deposition and scavenging of trace gases	Tost et al. (2006b)

addition to the emission sectors considered, there are additional source categories considered, such as ozone produced by photolysis of oxygen, which predominantly occurs in the stratosphere and which we therefore name stratospheric ozone production. Note that also in the upper tropopshere, ozone is produced by this reaction. In the following the base models are described for which the tagging scheme is developed, an overview on the tagging scheme is given, and the tagging chemistry is described.

3.1 Description of MESSy, EMAC and MECO(n)

The TAGGING model described here (see also Tsati, 2014) is written as a submodel of the Modular Earth Submodel System (MESSy), which comprises a standard interface to couple different processes, a simple coding standard and a set of different submodels (Jöckel et al., 2005). The TAGGING submodel is implemented in MESSy2 (Jöckel et al., 2010) and consists of two parts, the SubModel Interface Layer (SMIL) and the SubModel Core Layer (SMCL). The SMIL part is mainly important for data management, defining and handling the tracers (using the TRACER submodel described in Jöckel et al. (2008)) and the diagnostic output fields using the CHANNEL submodel (Jöckel et al., 2010). The coupling for the necessary input fields are also handled via the CHANNEL submodel. These input fields comprise, for example, lightning NO_x emissions and chemical production/loss-rates from the chemical solver MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere, Sander et al. (2011)).

The TAGGING submodel is implemented in EMAC (ECHAM5/MESSy Atmospheric Chemistry) and MECO(n) (MESSyfied ECHAM and the Consortium for Small-Scale Modelling model COSMO nested n-times). While EMAC uses ECHAM5 as a global circulation model, MECO(n) consists of COSMO/MESSy as a regional-scale model with EMAC as the driving model (Kerkweg and Jöckel, 2012a), which are coupled online. The SMCL of the TAGGING submodel is independent of the base

Table 2. Submodels which provide the source terms (emissions or production terms) for the individual emission sectors (first column) and tagged species (columns 2-4).

Sector	Tagged species with emissions and other sources			
	NO_y	CO	NMHC	O_3
—— Anthropogenic ——				
Non-traffic	OFFEMIS	OFFEMIS	OFFEMIS	-
Road Traffic	OFFEMIS	OFFEMIS	OFFEMIS	-
Ships	OFFEMIS	OFFEMIS	OFFEMIS	-
Air Traffic	OFFEMIS	OFFEMIS	OFFEMIS	-
—— Natural ——				
Lightning	LNOX	-	-	-
Biogenic	ON-/OFFEMIS	ON-/OFFEMIS	ON-/OFFEMIS	-
N_2O	MECCA	-	-	-
CH_4	-	-	MECCA	-
Strat-O_3	-	-	-	MECCA
—— Mixed ——				
Biomass Burning	OFFEMIS	OFFEMIS	OFFEMIS	-

model and consists mainly of the code needed to solve the relevant equations. A detailed description of the TAGGING submodel, including individual subroutines of the SMIL and the SMCL, are provided in the supplement. The model set-up is identical to that of Mertens et al. (2016). A detailed list of applied submodels can be found in the supplement of Mertens et al. (2016) (page 42, therein). Table 1 describes only those submodels, which are of direct relevance for the TAGGING submodel. An evaluation of the model configurations of EMAC and MECO(n) with respect to the chemical composition of the atmosphere can be found in Jöckel et al. (2016) and Mertens et al. (2016).

3.2 TAGGING overview: families, emission sectors and workflow

The objective of the tagging scheme is to determine the contribution of emissions from various sectors. Here, we discriminate between ten different sources, four anthropogenic: non-traffic anthropogenic (industry, energy, households), road traffic, ships, and air traffic, five natural sources: lightning, emissions from biogenic sources including soils, decomposition of N_2O, decomposition of CH_4, stratospheric ozone production by photolysis of O_2, and a mixed class: biomass burning (see Table 2).

We use a configuration of the chemical scheme MECCA (Sander et al., 2011), which consists of 72 species. We only tag a reduced set of species, which resemble the main species and families for tropospheric chemistry, in order to limit the required memory. Besides CO, O_3, peroxyacytyl nitrate (PAN), HO_2, and OH, 2 families are considered: NO_y and NMHC which include all chemically active nitrogen compounds (15) and hydrocarbons (42) (see supplement for more details). All together, the tagging scheme consists of 7 species times 10 emission sectors, thus 70 tagged tracers. For each tracer initialisation, transport (except for OH and HO_2), emissions, dry and wet deposition, and chemical conversion has to be deduced from the base model (Figure 1). The tagging scheme utilises the EMAC submodels, e.g. for tracer transport, for emissions computed online during the simulation, and for emissions prescribed by inventories (Table 1; for details see supplement), such as industry, road traffic, etc. (Figure 1, middle column). It further obtains information on online emissions (lightning, soils), dry and wet deposition, background tracers and reaction rates (left column). This information is processed in tagging core routines (right).

Here, we concentrate on the TAGGING submodel (Figure 1, right column). For the initialisation of the tagged tracers two options are available. First, the variables can be initialised from files, or second the tagged tracers can be initialised according to their key characteristics. In this case, the tagged stratospheric ozone is initialised by the ozone field above the tropopause and all other tagged ozone fields are zero above the tropopause and vice versa. Below the tropopause, all but the tagged stratospheric ozone tracer, obtain one ninth of the tropospheric ozone concentration.

At each time step during the simulation, the online emissions (soil emissions) are added to the respectively tagged tracer (Table 2). The emission rate is obtained by recording the concentration of NO_x before and after the calculation of online emissions. The tagged lighting NO_y tracer obtains the same lightning emissions as the chemical NO tracer, which is provided by the lightning submodel LNOX (Tost et al., 2007b; Grewe et al., 2001). Dry and wet deposition is treated as a bulk process. Changes in the concentration of all relevant chemical species are calculated in a practical and simple manner, by the difference in the respective concentrations before and after dry and wet deposition is calculated. This tendency of the concentration is provided to the tagging submodel and distributed among the tagged species according to their relative contribution to the total concentration.

3.3 TAGGING chemistry

The core of the tagging submodel is the distribution of the chemical tendencies to the tagged tracers as introduced in Sec. 2. Therefore, the individual production and loss terms have to be determined adequately to calculate concentration changes via Eq. (7). Here, we consider effective ozone production and loss terms according to Crutzen and Schmaizl (1983). This implies that a family is considered for ozone (see supplementary material for more details), which includes all fast exchanges between ozone and other chemical species. The ozone production basically requires splitting up an oxygen molecule. For the identification of ozone production and loss reactions, we apply the tool *ProdLoss* (see supplementary material for more detailed information), which identifies the effective production and loss reactions for a family in the selected chemical mechanism. This family for effective ozone is hereafter referred to as ozone for simplicity. This results in two ozone production terms, which are applied to any tagged ozone field with the exception of stratospheric ozone. This is reaction (R1) and the combination of reactions of the type (see supplementary material for more detailed information)

$$NO + RO_2 \longrightarrow NO_2 + RO, \tag{R2}$$

with reaction rate P$_{R2}$. The production and loss terms of these tagged ozone fields are then

$$\begin{aligned} PO_3^{tag} &= \frac{1}{2}P_{R1}\left(\frac{NO_\mathrm{y}^{tag}}{NO_\mathrm{y}} + \frac{HO_2^{tag}}{HO_2}\right) \\ &+ \frac{1}{2}P_{R2}\left(\frac{NO_\mathrm{y}^{tag}}{NO_\mathrm{y}} + \frac{NMHC^{tag}}{NMHC}\right) \end{aligned} \tag{13}$$

$$\begin{aligned} DO_3^{tag} &= \frac{1}{2}P_{R3}\left(\frac{OH^{tag}}{OH} + \frac{O_3^{tag}}{O_3}\right) \\ &+ \frac{1}{2}P_{R4}\left(\frac{HO_2^{tag}}{HO_2} + \frac{O_3^{tag}}{O_3}\right) \\ &+ \frac{1}{2}P_{R5}\left(\frac{NO_\mathrm{y}^{tag}}{NO_\mathrm{y}} + \frac{O_3^{tag}}{O_3}\right) \\ &+ \frac{1}{2}P_{R6}\left(\frac{NMHC^{tag}}{NMHC} + \frac{O_3^{tag}}{O_3}\right) \\ &+ P_{R7}\frac{O_3^{tag}}{O_3}, \end{aligned} \tag{14}$$

with tag denoting one of the ten source tags and with the reaction rates P$_{R3}$, P$_{R4}$, P$_{R5}$, P$_{R6}$, P$_{R7}$ referring to the reactions

$$OH + O_3 \longrightarrow HO_2 + O_2 \tag{R3}$$

$$HO_2 + O_3 \longrightarrow OH + 2\,O_2 \tag{R4}$$

$$\text{Effective ozone loss via } NO_y \tag{R5}$$

$$RO_2 + O_3 \longrightarrow RO + 2\,O_2 \tag{R6}$$

$$OH + O_3 \longrightarrow HO_2 + O_2 \tag{R7}$$

The tagged species NO$_\mathrm{y}$, CO, NMHC, and PAN are treated similarly and will be discussed here only briefly, while more detailed information is provided in the supplement. Figure 2 sketches the principal relations between the tagged species. Methane (not tagged) is depleted and the chemical products are then tagged as "NMHC from methane". The species in the NMHC family are eventually transformed into CO and further into CO$_2$. The decomposition of N$_2$O (not tagged) constitutes a source for "stratospheric NO$_\mathrm{y}$". Reactions between NO$_\mathrm{y}$ and NMHCs form PAN (not included in NO$_\mathrm{y}$). PAN is an important species which can be transported over long distances before it thermally decomposes (Roberts, 2007).

HO$_\mathrm{x}$ chemistry (Figure 3 and Table 3) and the calculation of the individual contributions to the concentrations of OH and HO$_2$ is much more complex, hence we discuss it here in more detail. The

Table 3. Reactions and reaction rates used for the calculation of OH and HO_2 contributions.

			Reaction Rate			
Reaction			OH		HO_2	
			Prod	Loss	Prod	Loss
$H_2O + O(^1D)$	$\longrightarrow$	2 OH	$0.5\ P_1^{OH}$			
$HO_2 + O_3$	$\longrightarrow$	$OH + 2\ O_2$	P_2^{OH}			$L_1^{HO_2}$
$NO + HO_2$	$\longrightarrow$	$NO_2 + OH$	P_3^{OH}			$L_2^{HO_2}$
$OH + CO$	$\xrightarrow{O_2}$	$HO_2 + CO_2$		L_1^{OH}	$P_1^{HO_2}$	
$OH + CH_4$	$\xrightarrow{O_2}$	$NMHC + H_2O$		L_2^{OH}		
$OH + O_3$	$\longrightarrow$	$HO_2 + O_2$		L_3^{OH}	$P_2^{HO_2}$	
$OH + NMHC$	$\xrightarrow{O_2}$	$NMHC + H_2O$		L_4^{OH}		
$OH + HO_2$	$\longrightarrow$	$H_2O + O_2$		L_5^{OH}		$L_3^{HO_2}$
$OH + NO_2$	$\longrightarrow$	HNO_3		L_6^{OH}		
$NMHC + NO$	$\longrightarrow$	$NMHC + HO_2 + NO_2$			$P_3^{HO_2}$	
$NMHC + HO_2$	$\longrightarrow$	$NMHC + O_2$				$L_4^{HO_2}$
$HO_2 + HO_2$	$\longrightarrow$	$H_2O_2 + O_2$				$L_5^{HO_2}$

main source of OH is the reaction of H_2O with $O(^1D)$. The chemical reactions between OH and HO_2 involve species such as CO, CH_4, NO_y, and NMHC. Losses of HO_x are the formation of H_2O_2 and HNO_3, which are soluble and can be easily rained out.

Since the lifetime of both OH and HO_2 is short, we assume steady-state for the contributions. We regard the main HO_x reactions, for which the production and loss rates are calculated in and provided by the MECCA submodel (see also Table 2).

The steady-state assumption for the contributions to the OH and HO_2 concentrations, i.e., OH^{tag} and HO_2^{tag} implies that the individual production terms equal the individual loss terms:

$$P_{OH}^{tag} = L_{OH}^{tag} \tag{15}$$

$$P_{HO_2}^{tag} = L_{HO_2}^{tag}. \tag{16}$$

Again the more complex part of the tagging chemistry is to derive the production and loss terms. Using the reactions in Table 3 and the approach from Grewe et al. (2010), we obtain for the production and loss of OH^{tag}:

$$\begin{aligned} P_{OH}^{tag} &= P_1^{OH}\frac{O_3^{tag}}{O_3} + \frac{1}{2}P_2^{OH}\left(\frac{HO_2^{tag}}{HO_2} + \frac{O_3^{tag}}{O_3}\right) \qquad (17) \\ &+ \frac{1}{2}P_3^{OH}\left(\frac{NO_y^{tag}}{NO_y} + \frac{HO_2^{tag}}{HO_2}\right) \end{aligned}$$

$$\begin{aligned}
L_{OH}^{tag} &= L_1^{OH}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{CO^{tag}}{CO}\right) \\
&+L_2^{OH}\left(\frac{OH^{tag}}{OH}\right) \\
&+L_3^{OH}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{O_3^{tag}}{O_3}\right) \\
&+L_4^{OH}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{NMHC^{tag}}{NMHC}\right) \\
&+L_5^{OH}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{HO_2^{tag}}{HO_2}\right) \\
&+L_6^{OH}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{NO_y^{tag}}{NO_y}\right)
\end{aligned} \tag{18}$$

This set of equations includes the assumption that exchanges within a family are fast enough to achieve equally distributed tags among family members. For example, concerning P_1^{OH}, the contribution of one source to O(^{1}D) equals that of O$_3$, i.e. $\frac{O(^1D)^{tag}}{O(^1D)} = \frac{{O_3}^{tag}}{O_3}$.

Similarly, we derive the individual production and loss terms for HO$_2$:

$$\begin{aligned}
P_{HO_2}^{tag} &= P_1^{HO_2}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{CO^{tag}}{CO}\right) \\
&+P_2^{HO_2}\frac{1}{2}\left(\frac{OH^{tag}}{OH}+\frac{O_3^{tag}}{O_3}\right) \\
&+P_3^{HO_2}\frac{1}{2}\left(\frac{NMHC^{tag}}{NMHC}+\frac{NO_y^{tag}}{NO_y}\right)
\end{aligned} \tag{19}$$

$$\begin{aligned}
L_{HO_2}^{tag} &= L_1^{HO_2}\frac{1}{2}\left(\frac{HO_2^{tag}}{HO_2}+\frac{O_3^{tag}}{O_3}\right) \\
&+L_2^{HO_2}\frac{1}{2}\left(\frac{HO_2^{tag}}{HO_2}+\frac{NO_y^{tag}}{NO_y}\right) \\
&+L_3^{HO_2}\frac{1}{2}\left(\frac{HO_2^{tag}}{HO_2}+\frac{OH^{tag}}{OH}\right) \\
&+L_4^{HO_2}\frac{1}{2}\left(\frac{HO_2^{tag}}{HO_2}+\frac{NMHC^{tag}}{NMHC}\right) \\
&+L_5^{HO_2}\frac{HO_2^{tag}}{HO_2}.
\end{aligned} \tag{20}$$

Now the Eqs. (15) and (16) can be written as

$$0 = A^{tag} - L^{OH}\frac{OH^{tag}}{OH} + P^{OH}\frac{HO_2^{tag}}{HO_2} \tag{21}$$

$$0 = B^{tag} + P^{HO_2}\frac{OH^{tag}}{OH} - L^{HO_2}\frac{HO_2^{tag}}{HO_2}, \tag{22}$$

with

$$A^{tag} = P_1^{OH}\frac{O_3^{tag}}{O_3} + \frac{1}{2}P_2^{OH}\frac{O_3^{tag}}{O_3} + \frac{1}{2}P_3^{OH}\frac{NO_y^{tag}}{NO_y} - \frac{1}{2}L_1^{OH}\frac{CO^{tag}}{CO} - \frac{1}{2}L_3^{OH}\frac{O_3^{tag}}{O_3} - \frac{1}{2}L_4^{OH}\frac{NMHC^{tag}}{NMHC} - \frac{1}{2}L_6^{OH}\frac{NO_y^{tag}}{NO_y} \tag{23}$$

$$B^{tag} = \frac{1}{2}P_1^{HO_2}\frac{CO^{tag}}{CO} + \frac{1}{2}P_2^{HO_2}\frac{O_3^{tag}}{O_3} + \frac{1}{2}P_3^{HO_2}\frac{NMHC^{tag}}{NMHC} + \frac{1}{2}P_3^{HO_2}\frac{NO_y^{tag}}{NO_y} - \frac{1}{2}L_1^{HO_2}\frac{O_3^{tag}}{O_3} - \frac{1}{2}L_2^{HO_2}\frac{NO_y^{tag}}{NO_y} - \frac{1}{2}L_4^{HO_2}\frac{NMHC^{tag}}{NMHC} \tag{24}$$

$$P^{OH} = \frac{1}{2}\left(P_2^{OH} + P_3^{OH} - L_5^{OH}\right) \tag{25}$$

$$L^{OH} = \frac{1}{2}\left(L_1^{OH} + 2L_2^{OH} + L_3^{OH} + L_4^{OH} + L_5^{OH} + L_6^{OH}\right) \tag{26}$$

$$P^{HO_2} = \frac{1}{2}\left(P_1^{HO_2} + P_2^{HO_2}\right) \tag{27}$$

$$L^{HO_2} = \frac{1}{2}\left(L_1^{HO_2} + L_2^{HO_2} + L_3^{HO_2} + L_4^{HO_2} + 2L_5^{HO_2}\right) \tag{28}$$

The Eqs. (21) and (22) can easily be solved resulting in

$$OH^{tag} = \frac{A^{tag}L^{HO_2} + B^{tag}P^{OH}}{L^{OH}L^{HO_2} - P^{OH}P^{HO_2}}OH \tag{29}$$

$$HO_2^{tag} = \frac{A^{tag}P^{HO_2} + B^{tag}L^{OH}}{L^{OH}L^{HO_2} - P^{OH}P^{HO_2}}HO_2. \tag{30}$$

The quantity A^{tag} (B^{tag}) represents the contribution of chemical tracers (tagged and non-tagged, other than OH and HO_2) to the net OH production (net HO_2 production). The terms L^{OH} and P^{OH} are primarily contributions to OH loss and production rates, which depend on the contribution to OH (OH^{tag}) and HO_2 (HO_2^{tag}), respectively. Only the reaction of OH with HO_2 forming water vapour and molecular oxygen constitutes an exception, since the loss of OH is dependent from both OH and HO_2 (L_5^{OH}). Therefore, it also contributes to P^{OH} (see Eq. (25)), the last term in equation (21), which depends on HO_2. Note that in this case it does not lead to a production but destruction of OH.

4 Present-day simulation and comparison to other studies

In this Section, we present results of a present day simulation. An actual validation of the tagging method is not feasible, since only the full quantities can be measured, e.g. the ozone concentration, but not the contribution from individual sources. Therefore, we concentrate on a comparison to earlier studies. In the following sections we present the simulation set-up and give a plausibility check for contributions to the HO_x concentration based on shipping and aviation, focussing on the ozone concentration.

4.1 Simulation set-ups

4.1.1 EMAC

To evaluate the TAGGING submodel we conduct two different simulations, one base simulation with all emissions and a second simulation where we reduced all road traffic emissions by five percent. The set-up follows the "Specified Dynamics Reference Simulation" for the Chemistry Climate Model Initiative, and is identical to the RC1SD-base10a set-up described and evaluated by Jöckel et al. (2016), however, extended by the TAGGING module, which we described above.

The simulation is performed with a spectral resolution of T42 and a vertical resolution of 90 levels (up to 0.01 hPa). For the anthropogenic emissions we use the MACCity emissions dataset with a resolution of $0.5°$ described by Granier et al. (2011). The lightning emissions are calculated online using the parameterisation described by Grewe et al. (2001). Emissions of NO from soil and biogenic origin as well as biogenic isoprene ($\mathrm{C_5H_8}$) are calculated online by the MESSy submodel ONEMIS (described as ONLEM in Kerkweg et al. (2006b)). The submodel ONEMIS uses an algorithm based on Yienger and Levy (1995) for NO and Guenther et al. (1995) for isoprene. The dynamic state of the atmosphere is relaxed towards ERA-Interim reanalysis data (Dee et al., 2011) using a weak Newtonian relaxation ("nudging") of the four prognostic variables temperature, divergence, vorticity and the logarithm of surface pressure (Jöckel et al., 2006). Sea-surface temperature and sea-ice concentration are taken from ERA-Interim as well.

One important difference of our simulation to the RC1SD-base10a set-up is the use of the QCTM-mode of EMAC (Deckert et al., 2011). This QCTM-mode decouples the chemistry and the dynamics by using monthly climatologies (here derived from the RC1SD-base10a simulation) in the radiation code and for the heterogeneous stratospheric reactions. The application of the QCTM mode is important for overcoming the problem of a low signal to noise ratio in the case of a direct comparison of a base case simulation with one with a small chemical perturbation, which would be present with a fully coupled system. The dynamical and chemical differences between the RC1SD-base10a and our base simulation are shown in the supplement. The simulation covers the period 2004-2010 and is initialized from the RC1SD-base10a simulation. The first year was used as a spin-up period, resulting in an evaluation period from 2005-2010.

4.1.2 MECO(n)

The COSMO/MESSy simulation shown in Sec. 5.1 covers the European domain, including parts of the Eastern Atlantic and North Africa, with a resolution of $0.44°$ ($\approx$ 50 km). Simulated is the period from July 2007 until December 2008, with the six months of 2007 used as spin-up phase. The driving EMAC model is applied at a resolution of T42 with 31 horizontal levels and is relaxed towards ERA-Interim reanalysis as well. The same QCTM mode as described above is applied for EMAC and COSMO/MESSy. Both model instances use the anthropogenic MACCity emissions, as well as online calculated soil/biogenic emissions as described above. The simulation differs, however, from the EMAC simulation described above, by using the lightning parameterisation after Price and Rind (1992) to simulate the lightning $\mathrm{NO_x}$ emissions on the global scale. In COSMO/MESSy we use the same emissions as on the global scale by regridding the corresponding emissions from EMAC. We have chosen this approach to have emissions as comparable as possible in both model instances. More detailed information about this simulation, including an evaluation of chemical tracer concentrations, is provided by Mertens et al. (2016).

4.2 Contributions of emission sectors to $\mathrm{NO_y}$, CO, NMHCs, and $\mathrm{O_3}$

The six year annual average contributions of the ten emission sectors to the ozone concentration are shown in Figure 4. We compare these results with an earlier model version, which only tags $\mathrm{NO_y}$ and ozone (Grewe, 2007, Figure 5b therein), and to earlier similar studies by Lelieveld and Dentener (2000) and Emmons et al. (2012). This comparison aims at verifying that the implementation of the TAGGING mechanism is correct by comparing contribution patterns and magnitudes. We have to keep in mind that the approach is conceptually different from earlier studies and takes into account all ozone precursor emissions and not only $\mathrm{NO_y}$. Hence the individual contributions have to be smaller and no agreement can be expected, except for pattern and magnitude. The only direct intercomparison can be performed for the stratospheric ozone mixed into the troposphere, since this process is independent from any precursors. Here Lelieveld and Dentener (2000); Lamarque et al. (2005); Grewe (2007); Emmons et al. (2012) (hereafter denoted as LD00, L05, G07, and E12, respectively) estimated a 5 to 40% contribution from stratospheric ozone to tropospheric ozone in the Southern Hemisphere and mostly systematically lower values of 10% to 25% in the Northern Hemisphere, while tropical values are below 10% (Table 4). Our simulation shows also a minimum of the stratospheric ozone mixing ratios in the tropics and lower mixing ratios ~~values~~ in the Southern Hemisphere compared to the Northern Hemisphere. The mixing ratios for January and July are very similar to those of Emmons et al. (2012, not shown).

Ozone formed from lightning $\mathrm{NO_x}$ (Figure 4) shows a maximum in the tropics and upper troposphere and larger contributions in the Southern Hemisphere than in the Northern Hemisphere, which is in agreement with G07 and LD00. The maximum contribution from lightning is around 25-30%

and thus lower than G07 (40%) and LD00 (50%), because here we regard the ozone production of all precursors, whereas in G07 and LD00 only NO_x as a precursor is considered (see above).

Agreement between the studies LD00, G07, E12, and our work can also be found with respect to the contribution of anthropogenic emissions to tropospheric ozone. These emissions (here: anthropogenic non-traffic, road traffic, shipping and aviation) predominantly contribute by 30 to 50% in the Northern Hemisphere. The ozone contribution from biomass burning peaks in the lower tropical troposphere with values of around 10% to 15% which compares well with G07 and LD00 (20%). Around 15% of the tropospheric ozone originates from methane, which reacts with OH and contributes to NMHC compounds and eventually to CO and CO_2.

Figure 5 shows the contribution of the individual emission sectors to the tropospheric budgets of NO_y, CO, NMHC, PAN, and O_3. Lightning and non-traffic anthropogenic emissions show the largest contributions to NO_y. The emitted NO_y from lightning and aviation remains much longer in the atmosphere compared to a surface source such as non-traffic anthropogenic NO_y, since lightning and aviation emit mainly in the upper troposphere. Aviation, shipping, and biomass burning have approximately the same contribution.

The different emission sectors have very different emission characteristics. Some are only emitting NO_y, such as lightning, or NO_y and NMHCs, such as most anthropogenic sources. This is well reflected in the budgets (Figure 5). Since NO_y is required to form PAN, the decomposition of PAN also produces NO_y and NMHCs with the original tag, e.g. the lightning tag. This is fully consistent with the chosen tagging approach and leads to minor contributions of non-CO and non-NMHC emitting emission sectors to the CO and NMHC budgets (lightning, stratosphere, aviation). For example, NO_x emitted by road traffic may react with hydrocabons from, e.g., biogenic emissions to form PAN, which is then transported over longer distances. When decomposed after being transported over a long distance, the products obtain tags from both sources. Hence hydrocarbons, which may not have been emitted by road traffic obtain in this process a road traffic tag. The reasoning behind this is that only the PAN formation allowed the long-range transport of either species and hence both emission sources have effected this. While this case is a wanted tagging effect, other situations may lead to unwanted side-effects or even unphysical effects (see discussion in Section 6 for more details). The formation of PAN and hence contributions to PAN (Figure 5, second row) requires both NO_y and NMHCs. None of the ten emission sectors has a large contribution from both. And hence, the contributions of each of the ten sectors to PAN are almost equally distributed around 10%. One exception is methane, which contributes largely to NMHC concentrations but not to NO_y. In addition, the NMHCs from methane are predominantly occurring in areas with low NO_y background, which reduces the impact on PAN. The contribution to tropospheric ozone (Figure 5, second row) reflects the distribution presented in Figure 4, with major contributions from lightning, stratosphere, anthropogenic non-traffic emissions and methane.

4.3 Contribution of emission sectors to HO_x concentrations

In this Section, we present the effects of a surface source (shipping) and a higher altitude atmospheric source (aviation) on their contribution to the HO_x concentrations. We have chosen the Mediterranean Sea for shipping, since it includes ~~pristine~~ areas in the middle of the Sea on the one hand, as well as areas which are largely affected by other sources e.g. in southern France (Marseilles) and Italy (harbour areas such as Genoa, Figure 6), on the other hand.

We have identified four areas (A-D) with different chemical characteristics (Table 5, see also Figure 6): Highly polluted areas with high concentrations of NO_2 (A and B) and with large (some) impact from shipping in region A (B); a more remote ~~pristine~~ area with some impact from shipping on NO_x and O_3 (C), and a ~~pristine~~ more remote area with a larger values of shipping ozone (D).

Large NO_x concentrations in the background (A and B) impact the chemistry and net production efficiencies, i.e. the ozone enhancement per NO_x is decreasing with increasing NO_x concentrations (e.g. Dahlmann et al., 2011). The reaction (R1), which transforms HO_2 into OH, in principle increases (decreases) the OH (HO_2) concentration in the region where large amounts of shipping NO_x is present. However, this reaction only dominates the OH to HO_2 ratio if enough ozone is available for the HO_x production. In region A, the very low ozone concentration due to ozone titration by NO_x limits the availability of OH and the contribution of shipping NO_x to OH is even negative. Region B is less polluted than region A and has lower values of shipping NO_x and therefore reaction (R1) dominates the OH and HO_2 contributions from shipping leading to positive contributions to OH and negative to HO_2. The tagged shipping ozone is larger in area D compared to A and B (not shown). This leads to a larger contribution to OH via the main production reaction of H_2O with $O(^1D)$, where the $O(^1D)$ originates from the tagged ozone (see also Table 3). The close coupling of OH with HO_2 also enhances the tagged HO_2 especially in region D. These processes then lead to a complex picture. It shows negative contributions to OH in region A, mainly due to low ozone concentration limiting the OH availability which is even more pronounced by shipping emissions. The shipping contribution to HO_2 in the polluted areas A and B are negative mainly driven by the reaction (R1). Large positive contributions of shipping to OH and moderate negative contributions to HO_2 are found in region C, resulting from a combination of effects from reaction (R1) and the main OH production resulting from tagged shipping ozone. Whereas in region D moderate positive contributions of shipping to OH and large negative contributions to HO_2 are found. Overall, the contributions from shipping emissions to the OH and HO_2 concentrations show a complex picture, which results from variations in both the background concentrations and shipping concentrations. The impact of an enhanced horizontal resolution is discussed for the same situation in Sec. 5.

Figure 7 shows annual mean contributions of aviation NO_x emissions to OH (left) and HO_2 (right). The air traffic contribution to OH peaks at around 10-20 fmol/mol at the main flight altitude. At the surface, there are other secondary peaks, basically at the locations of the airports. Lee et al. (2010) summarised the work of Grewe et al. (2002) and Köhler et al. (2008) in their Figure 10 and showed

4 atmospheric regions, which are affected differently by air traffic. In the first region (RNOy in their paper), which is mainly the air traffic corridor, the reaction (R1) controls the chemical impact from air traffic emissions. This implies that air traffic largely contributes to OH and negatively contributes to RHO_2 as shown in Figure 7. The region north of RNOy is called RHO2 and the aviation impact is largely controlled by the reaction of O_3 with HO_2 (see Table 3). Hence, this reaction leads to a reduction in HO_2 without affecting the OH concentration in a similar manner. The region RO3 is located in the lower troposphere and away from the major flight corridor. Here, a significant contribution from air traffic to ozone is found, but not so much to NO_y (not shown). The region is controlled by an increase in ozone. Hence it leads to a general increase in HO_x via the reaction of H_2O with $O(^1D)$ (see Table 3). This comparison shows that the OH and HO_2 contributions form aviation, calculated here, are consistent with the chemical regimes identified in previous studies.

A more detailed view on this tagging mechanism is feasible by applying it to a Lagrangian framework (Grewe et al., 2014). Within the EU-Project REACT4C (Reducing Emissions from Aviation by Changing Trajectories for the benefit of Climate), the HO_x tagging mechanism was implemented in the same EMAC model version, including a Lagrangian transport algorithm. Aviation-like pulse emissions of NO_x were released at selected points in the atmosphere, and trajectories with these emissions were tagged so that reactions with the background can be determined in detail. Note that aviation is not emitting CO and NMHCs in our simulation, hence the equations look simplified in Grewe et al. (2014) as the values for CO^{tag} and $NMHC^{tag}$ are zero (see Sec. 3.3). Figure 8 shows the temporal development of several NO_x related species (top and mid) as well as ozone production and loss terms (bottom) for a pulse emission at 45°W, 50°N and 300 hPa. The NO_x emission induces net production of O_3^{tag} (see Eq. 10 in Grewe et al., 2014), mainly via Reaction (R1) and enhanced HO_x^{tag} as calculated via Eqs. (29) and (30). NO_x reacts with OH and forms HNO_3, which eventually leads to washout and a reduction of NO_y^{tag} within a few weeks. When NO_x^{tag} is no longer available for O_3-production, O_3^{tag} is subsequently depleted. We denote the chemical regime, where enough NO_x is available to produce larger amounts of ozone with RegNOx and the following regime as RegO3 (see also Figure8). Regarding the destruction of CH_4^{tag}, these two regimes are also characterising the two different depletion pathways. First, as long as sufficient NO_x^{tag} is available, CH_4^{tag} is reduced because of an increase of OH^{tag} via Reaction (R1) (NO_x driven CH_4 destruction). Second, when NO_x^{tag} is removed, OH^{tag} is mainly produced via photolysis of O_3^{tag} and the subsequent Reaction P_1^{OH} ($H_2O + O^1D \rightarrow 2\ OH$). The tagged OH and HO_2 are far lower in the RegO3 regime compared to the RegNOx regime (Figure 8, mid). And consequently, the gradient in the O_3 driven CH_4 destruction is not as steep. However, due to the longer time period, it dominates the total amount of methane destruction in this case, which can be seen from a budget analysis for the chemical regimes RegNOx (blue bars) and RegO3 (red bars) given in Figure 9. Note that the trajectory is transported into polar night around day 5, which leads to a reduction of OH and HO_2 and a reduction of the photochemical activity. This example shows a reasonable temporal behaviour of the tagged species and it further shows how combining the tagging methodology and a Lagrangian transport algorithm results in a powerful tool, facilitating a detailed analysis of particular processes.

5 Sensitivities

In this Section, we investigate if our tagging scheme responds reasonably to changes in resolution (Sec. 5.1) and emissions (Sec. 5.2). In general, there are no strict verification tests other than checking for plausibility and stability.

5.1 Higher resolution: MECO(n)

By applying the MECO(n) system (Kerkweg and Jöckel, 2012a, b; Hofmann et al., 2012; Mertens et al., 2016), we have increased the horizontal resolution over Europe by roughly a factor of 5, from a resolution of roughly 200 km times 300 km in EMAC to 50 km times 50 km in the nested grid. Figure 10 shows the contributions of the individual emission sectors to the tropospheric ozone column as a mean over Europe for the coarse resolution (top) and the finer resolution (bottom). Clearly, the individual contributions are very similar in terms of mean values and the seasonal cycle. The finer resolution simulation shows finer resolved structures in the horizontal (not shown), which however do not largely affect the large-scale budgets.

As an example of the effects of finer resolution, we present OH and HO_2 contributions from shipping over the Mediterranean Sea, as discussed in Sec. 4.3 and Figure 6. The OH enhancement along shipping routes is much more visible in the finer resolved case (Figure 6, lower left) compared to the lower resolution (upper left). The structures for the OH and HO_2 contributions are again similar: A positive contribution to the OH concentration in the area of shipping emissions (B-D) and a decrease in the contribution to OH and HO_2 where background NO_x is largely enhanced (region A).

The comparison of the coarser and finer resolution clearly shows that the tagging scheme is stable in its behaviour. Naturally, the finer resolution enables more detailed and finer resolved chemical changes due to emissions to be quantified, but basic structures are reproduced in either resolution. This implies that, depending on the underlying research question, either model can be used.

5.2 Emission changes

We performed an additional global simulation with EMAC where we reduced the road traffic emissions by 5%. The simulation set-up hence follows Hoor et al. (2009). This means that the chemical composition and the ozone productivity is different from the base simulation, which leads to roughly 2-3% reduction in the tagged road traffic ozone (not shown). Generally, a reduction of surface NO_x emissions is increasing the ozone productivity (Emmons et al., 2012; Grewe et al., 2012) and consequently a 5% reduction in emissions is expected to lead to significantly less than a 5% reduction in road traffic ozone, which is consistent with our results. Figure 11 shows the relative change in tropospheric ozone induced by the road traffic emission reduction of 5%. The total ozone change of 0.08% (black bar) is a consequence of the reduction of the contribution of road traffic to the tropospheric total ozone by 0.16% and other compensating effects. In total, this leads to a factor of 2 difference between the total ozone change and the road traffic ozone change. The compensating effects are resulting from larger net ozone production rates for the shipping emission sector and other anthropogenic non-traffic emission sectors. This leads to a larger contribution of the anthropogenic non-traffic (dark blue bar) and the (other than road traffic) traffic emission sector (green bar) to total ozone by 0.04% and 0.06%, respectively. Other non-anthropogenic, i.e. natural emission sectors (red bar) reduce this compensation.

The ratio of 2 between the reduction in total ozone and road traffic indicates that a calculation of the road traffic contribution to tropospheric ozone using the perturbation method, i.e. difference between two simulations with changing emissions, underestimates this contribution by exactly this factor of 2. Other studies have shown slightly larger factors, e.g. a factor of 3 for biomass burning NO_x emissions (Emmons et al., 2012) and a factor of 5 for road traffic NO_x emissions. Here, a smaller factor can be expected, since emissions other than NO_x and their impact on ozone are tagged, which reduces the effects from road traffic emission changes. Further, this factor largely depends on the chemical state of the atmosphere, which differ between the simulations. Hence, a direct intercomparison is not possible, however, the results are plausible.

6 Options, limitations, and future perspectives

The primary goal for developping this TAGGING submodel is to diagnose the impact of many individual emission sectors on radiatively active species such as ozone and methane (via OH as the main methane loss process) in multi-decadal simulations of the atmospheric composition. While this represents a major improvement in comparison to many available tagging mechanisms, it also has its limitations. Such a mechanism requires to be fast enough and to have a limited memory demand. It is a trade-off between complexity, accuracy, and even correctness. The approach presented in Section 2 is an accurate and self-consistent decomposition of concentrations with respect to processes, considered. In order to limit the memory demand, we have mapped the complex chemistry scheme to a family concept, which reduces the number of required additional tracers to a minimum. Obviously, this mapping represents a loss in accuracy and in some cases unwanted and unphysical effects may occur. While the effect of mixing of tags through PAN processing is to some extend wanted (see discussion in Section 4.3), this also causes some unwanted effects. For example, during the degradation of methane, hydrocarbons are produced, which are classified as NMHC family. In reality, they are not contributing to PAN formation, whereas in the tagging scheme, they are grouped in the NMHC category and thereby falsely contribute to PAN formation. Hence, the information on the type of hydrocarbons is lost in the family concept and represents an unphysical side-effect. We might overcome these effects, at least to some extend, by structuring the families in more detail. Such as different NMHC categories according to their number of C-atoms. The coupling of families may represent a major problem, since tags are mixed unwantedly between the families for fast exchange rates. Here, we concentrate on effective exchanges, only. Hence, the introduction of PAN buffers, PAN-NHMC and PAN-NO_y, together with a PAN lifetime may reduce this artefact. NO_y from one emission source which forms PAN will be accounted first in a buffer, which will decompose totally back to the original NO_y emission source. Only, for long life-times of the formed PAN a mxing of tags could be allowed.

We presented for the first time a HO_x tagging mechanism, which provides reasonable information on how individual emission sources contribute to OH concentrations. Here, we also have mapped the HO_x chemistry to a reduced HO_x-scheme. This leads to inaccuracies in the OH contributions, which are normally less than 10-20%. First results show that an accuracy of less than 1% can be achieved if the complete mechanism is taken into account (V. Rieger, pers. comm.), which will be presented in a forthcoming paper. However, the respective changes on NO_y and ozone are marginal.

7 Conclusions

We present a submodel for the Earth-System Model EMAC, which diagnoses online the contributions of individual source categories (mainly emission sectors) to the concentrations of various trace species. For the first time, we take into account the competition of nitrogen oxides, carbon monoxide and non-methane hydrocarbons for the production and destruction of ozone. We concentrated on 10 source categories and 7 species and families, which are tagged. As a result, we introduced 70 new tracers. The physical and chemical tendencies for these tracers are obtained from other submodels of EMAC, such as the chemistry (MECCA), scavenging (SCAV), etc. The tagging mechanism is distributing the calculated physical and chemical tendencies into the tagged tracer fields. Therefore, the computing time increase by the TAGGING submodel is small, around 10%.

We performed a present-day simulation and showed that the TAGGING submodel provides contributions of individual emission sectors to the concentration of ozone, which roughly agree with previous estimates. A detailed analysis of the calculated contribution of aviation and shipping to OH and HO_2 shows reasonable results in different chemical regimes. Changes in the model's resolution shows a stable performance of the TAGGING submodel. Changes in the strength of road traffic emissions yields a decrease in ozone, which is partly compensated for by an increase in ozone from other source categories, since the ozone production efficiency increases, which is in agreement with earlier findings (Grewe et al., 2012; Emmons et al., 2012).

The advantage of this specific tagging scheme is that (1) the effect of ten source categories on ozone and other trace species can be monitored online in one simulation, (2) the competition between ozone precursors is included, (3) no linearisation is required, and (4) the scheme is applicable for long-term simulations, e.g. over a century. On the other hand, the disadvantage is that (1) the family concept is not flexible and fixed in this specific way, and consequently (2) any change in the set of chemical species requires an adaptation of the TAGGING scheme, and (3) due to memory limitations, a restriction to the main chemical species and families is required.

To summarise, the TAGGING submodel provides a powerful tool to identify the contribution of individual emission sectors to main atmospheric constituents at every grid point and timestep of the simulation and can be further used to derive, for instance, radiative forcings or contribution to air quality information for individual emission sectors.

8 Code availability

The Modular Earth Submodel System (MESSy) is continuously further developed and applied by a consortium of institutions. The usage of MESSy and access to the source code is licensed to all affiliates of institutions which are members of the MESSy Consortium. Institutions can become a member of the MESSy Consortium by signing the MESSy Memorandum of Understanding. More information can be found on the MESSy Consortium Website (http://www.messy-interface.org).

Acknowledgements. This study has been conducted in the framework of the DLR projects VEU, VEU2 and WeCare. We gratefully acknowledge the computational resources provided by the Leibniz Supercomputing Centre (LRZ) in Garching and the German Climate Computing Centre (DKRZ) in Hamburg. We are thankful to Roland Eichinger, DLR, for a detailed internal review.

References

Butler, T.M., Lawrence, M.G., Taraborrelli, D., Lelieveld, J., Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach, Atmos. Environm. 45, 4082-4090, DOI: 10.1016/j.atmosenv.2011.03.040, 2012.

Crutzen, P.J. and Schmaizl, U.: Chemical budgets of the stratosphere, Planer. Space Sci. 31, 1009-1032, 1983.

Dahlmann, K, Grewe, V., Ponater, M., Matthes, S., Quantifying The Contributions Of Individual NOx Sources To The Trend In Ozone Radiative Forcing , Atmos. Environm. 45, 2860-2868, DOI: 10.1016/j.atmosenv.2011.02.071, 2011.

Deckert, R., Jöckel, P., Grewe, V., Gottschaldt, K.-D., and Hoor, P.: A quasi chemistry-transport model mode for EMAC, Geosci. Model Dev., 4, 195-206, doi:10.5194/gmd-4-195-2011, 2011.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hòlm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Quarterly Journal of the Royal Meteorological Society, 137, 553–597, doi:10.1002/qj.828, 2011.

Dunker, A.M., Yarwood, G., Ortmann, J.P., Wilson, G.M., Comparison of Source Apportionment and Source Sensitivity of Ozone in a Three-Dimensional Air Quality Model, Environm. Sci. Tech. 36, 2953-2964, DOI: 10.1021/es011418f, 2002.

Emmons, L. K., Hess, P. G., Lamarque, J.-F., and Pfister, G. G.: Tagged ozone mechanism for MOZART-4, CAM-chem and other chemical transport models, Geosci. Model Dev., 5, 1531-1542, doi:10.5194/gmd-5-1531-2012, 2012.

Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., van der Gon, H. D., Frost, G., Heil, A., Kaiser, J., Kinne, S., Klimont, Z., Kloster, S., Lamarque, J.-F., Liousse, C., Masui, T., Meleux, F., Mieville, A., Ohara, T., Raut, J.-C., Riahi, K., Schultz, M., Smith, S., Thompson, A., Aardenne, J., Werf, G. and Vuuren, D. Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980 - 2010 period, Climatic Change, 109, 163-190, doi:10.1007/s10584-011-0154-1, 2011.

Grewe, V., Brunner, D., Dameris, M., Grenfell, J.L., Hein, R., Shindell, D., and Staehelin, J., Origin and variability of upper tropospheric nitrogen oxides and ozone at northern mid-latitudes, Atmos. Environm. 35, 3421-3433, 2001.

Grewe, V., Dameris, M., Fichter, C., Lee, D., Impact of aircraft NO_x emissions. Part 2: Effects of lowering the flight altitude, Meteorol. Z. 3, 197-205, 2002.

Grewe, V.: Technical Note: A diagnostic for ozone contributions of various NO_x emissions in multi-decadal chemistry-climate model simulations, Atmos. Chem. Phys., 4, 729–736, doi:10.5194/acp-4-729-2004, 2004.

Grewe, V.: Impact of climate variability on tropospheric ozone, Sci. Total Environ., 374, 167–81, 2007.

Grewe, V., Stenke, A., Ponater, M., Sausen, R., Pitari, G., Iachetti, D., Rogers, H., Dessens, O., Pyle, J., Isaksen, I.S.A., Gulstad, L., Søvde, O.A., Marizy, C., and Pascuillo, E., Climate impact of supersonic air traffic: an approach to optimize a potential future supersonic fleet - results from the EU-project SCENIC, Atmos. Chem. Phys. 7, 5129-5145, 2007.

Grewe, V., Tsati, E., Hoor, P., On the attribution of contributions of atmospheric trace gases to emissions in atmospheric model applications, Geosci. Model Dev., 3, 487–499, doi:10.5194/gmdd-3-819-2010, 2010.

Grewe V., Dahlmann, K., Matthes, S., Steinbrecht, W., Attributing ozone to NO_x emissions: Implications for climate mitigation measures, Atmos. Environm., 59, 102-107, 2012.

Grewe, V., A new method to diagnose the contribution of anthropogenic activities to temperature: temperature tagging, Geosci. Model Dev., 6, 2013a.

Grewe, V., A generalized tagging method, Geosc. Mod. Dev. 6, 247-253, 2013b.

Grewe, V., Frömming, C., Matthes, S., Brinkop, S., Ponater, M., Dietmüller, S., Jöckel, P., Garny, H., Dahlmann, K., Tsati, E., Søvde, O. A., Fuglestvedt, J., Berntsen, T. K., Shine, K. P., Irvine, E. A., Champougny, T., and Hullah, P.: Aircraft routing with minimal climate impact: The REACT4C climate cost function modelling approach (V1.0), Geosci. Model Dev. 7, 175-201, doi:10.5194/gmd-7-175-2014, 2014.

Gromov, S., Jöckel, P., Sander, R., and Brenninkmeijer, C. A. M.: A kinetic chemistry tagging technique and its application to modelling the stable isotopic composition of atmospheric trace gases, Geosci. Model Dev. Discuss., 3, 201–272, doi:10.5194/gmdd-3-201-2010, 2010.

Guenther, A., Hewitt, C., E., D., Fall, R. G., C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W., Pierce, T., S., B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmermann, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.

Hofmann, C., Kerkweg, A., Wernli, H., and Jöckel, P.: The 1-way on-line coupled atmospheric chemistry model system MECO(n) - Part 3: Meteorological evaluation of the on-line coupled system, Geosci. Model Dev., 5, 129-147, doi:10.5194/gmd-5-129-2012, 2012.

Hoor, P., Borken-Kleefeld, J., Caro, D., Dessens, O., Endresen, O., Gauss, M., Grewe, V., Hauglustaine, D., Isaksen, I. S. A., Jöckel, P., Lelieveld, J., Myhre, G., Meijer, E., Olivie, D., Prather, M., Schnadt Poberaj, C., Shine, K. P., Staehelin, J., Tang, Q., van Aardenne, J., van Velthoven, P., and Sausen, R.: The impact of traffic emissions on atmospheric ozone and OH: results from QUANTIFY, Atmos. Chem. Phys., 9, 3113–3136, doi:10.5194/acp-9-3113-2009, 2009.

Horowitz, L. and Jacob, D., Global impact of fossil fuel combustion on atmospheric NOx, J. Geophys. Res., 104, D19, doi:10.1029/1999JD900205, 1999.

Jöckel, P., Sander, R., Tost, H., and Lelieveld, J.: Technical Note: The Modular Earth Submodel System (MESSy) - a new approach towards Earth System Modeling , Atmos. Chem. Phys., 5, 433-444, doi:10.5194/acp-5-433-2005, 2005.

Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerkweg, A., Lawrence, M. G., Sander, R., Steil, B., Stiller, G., Tanarhte, M., Taraborrelli, D., van Aardenne, J., and Lelieveld, J.: The atmospheric chemistry general circulation model ECHAM5/MESSy1: consistent simulation of ozone from the surface to the mesosphere, Atmos. Chem. Phys., 6, 5067-5104, doi:10.5194/acp-6-5067-2006, 2006.

Jöckel, P., Kerkweg, A., Buchholz-Dietsch, J., Tost, H., Sander, R., and Pozzer, A: Technical Note: Coupling of chemical processes with the Modular Earth Submodel System (MESSy) submodel TRACER , Atmos. Chem. Phys., 8, 1677-1687, doi:10.5194/acp-8-1677-2008, 2008.

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), Geosci. Model Dev., 3, 717-752, doi:10.5194/gmd-3-717-2010, 2010.

Jöckel, P., Tost, H., Pozzer, A., Kunze, M., Kirner, O., Brenninkmeijer, C. A. M., Brinkop, S., Cai, D. S., Dyroff, C., Eckstein, J., Frank, F., Garny, H., Gottschaldt, K.-D., Graf, P., Grewe, V., Kerkweg, A., Kern, B., Matthes, S., Mertens, M., Meul, S., Neumaier, M., Nützel, M., Oberländer-Hayn, S., Ruhnke, R., Runde, T., Sander, R., Scharffe, D., and Zahn, A.: Earth System Chemistry Integrated Modelling (ESCiMo) with the Modular Earth Submodel System (MESSy, version 2.51), Geosci. Model Dev. 9, 1153-1200, doi:10.5194/gmd-9-1153-2016, 2016.

Kerkweg, A., Buchholz, J., Ganzeveld, L., Pozzer, A., Tost, H., and Jöckeli, P. Technical note: An implementation of the dry removal processes dry deposition and sedimentation in the modular earth submodel system (messy). Atmospheric Chemistry and Physics 6, 4617-4632, 2006a.

Kerkweg, A., Sander, R., Tost, H., and Jöckel, P. Technical note: Implementation of prescribed (OFFLEM), calculated (ONLEM), and pseudo-emissions (TNUDGE) of chemical species in the Modular Earth Submodel System (MESSy), Atmos. Chem. Phys., 6, 3603–3609, doi:10.5194/acp-6-3603-2006, 2006b.

Kerkweg, A. and Jöckel, P.: The 1-way on-line coupled atmospheric chemistry model system MECO(n) - Part 1: Description of the limited-area atmospheric chemistry model COSMO/MESSy, Geosci. Model Dev., 5, 87-110, doi:10.5194/gmd-5-87-2012, 2012a.

Kerkweg, A. and Jöckel, P.: The 1-way on-line coupled atmospheric chemistry model system MECO(n) - Part 2: On-line coupling with the Multi-Model-Driver (MMD), Geosci. Model Dev., 5, 111-128, doi:10.5194/gmd-5-111-2012, 2012b.

Köhler, M.O., Rädel, G., Dessens, O., Shine, K.P., Rogers, H.L., Wild, O., Pyle, J.A., Impact of perturbations to nitrogen oxide emissions from global aviation. J. Geophys. Res. 113, D11305. doi:10.1029/2007JD009140, 2008.

Lamarque, J.-F., Hess, P., Emmons, L., Buja, L., Washington, W., Granier, C. Tropospheric ozone evolution between 1890 and 1990. J. Geophys. Res.,110:D08304, doi:10.1029/2004JD005537, 2005.

Landgraf and P. J. Crutzen. An etcient method for online calculations of photolysis and heating rates. J. Atmos. Sci. 55, 863-878, 1998.

Lee, D. S., Pitari, G., Grewe, V., Gierens, K., Penner, J. E., Petzold, A., Prather, M. J., Schumann, U., Bais, A., Berntsen, T., Iachetti, D., Lim, L. L., and Sausen, R.: Transport impacts on atmosphere and climate: Aviation, Atmos. Environm. 44, 4678-4734, 2010.

Lelieveld, J. and Dentener, F.J.: What conrols tropospheric chemistry, J. Geophys. Res., 105, 3531-3551, 2000.

Meijer, E., van Velthoven, P., Thompson, A., Pfister, L., Schlager, H., Schulte, P., and Kelder, H.: Model calculations of the impact of NOx from air traffic, lightning, and surface emissions, compared withmeasurements, J. Geophys. Res., 105, 3833–3850, 2000.

Mertens, M., Kerkweg, A., Jöckel, P., Tost, H., and Hofmann, C.: The 1-way on-line coupled model system MECO(n) - Part 4: Chemical evaluation (based on MESSy v2.52), Geosci. Model Dev., 9, 3545-3567, doi:10.5194/gmd-9-3545-2016, 2016.

Price, C., and Rind, D., A simple lightning parameterization for calculating global lightning distributions, J. Geophys. Res., 97(D9), 9919-9933 doi:10.1029/92JD00719, 1992.

Roberts, J. M.: PAN and related compounds, in: Volatile Organic Compounds in the Atmosphere, Ed. Koopmann,R., Blackwell Publishing Ltd, 221-268, 2007.

Roeckner, E., Bäuml, G., Bonaventura, L., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kirchner, I.,Kornblueh, L., Manzini, E., Rhodin, A., Schlese, U., Schulzweida, U., and Tompkins, A.: The atmospheric general circulation model ECHAM5. PART I: Model description, Tech. rep., Max Planck Institute for Meteorology, MPI-Report 349, http://www.mpimet.mpg.de/fileadmin/publikationen/Reports/ max_scirep_349.pdf, 2003.

Sander, R., Baumgaertner, A., Gromov, S., Harder, H., Jöckel, P., Kerkweg, A., Kubistin, D., Regelin, E., Riede, H., Sandu, A., Taraborrelli, D., Tost, H., and Xie, Z.-Q.: The atmospheric chemistry box model CAABA/MECCA-3.0, Geosci. Model Dev., 4, 373-380, doi:10.5194/gmd-4-373-2011, 2011.

Sillman, S. The use of NOy, H2O2 and HNO3 a for O3-NOx-VOC sensitivity in urban locations. J. Geophys. Res. 100, 14,175-14,188, 1995.

Tost, H., Jöckel, P., and Lelieveld, J.: Influence of different convection parameterisations in a GCM, Atmos. Chem. Phys., 6, 5475–5493, doi:10.5194/acp-6-5475-2006, 2006a.

Tost, H., Jöckel, P., Kerkweg, A., Sander, R., and Lelieveld, J., Technical note: A new comprehensive scavenging submodel for global atmospheric chemistry modelling. Atmospheric Chemistry and Physics, 6, 565-574, 2006b.

Tost, H., Jöckel, P., and Lelieveld, J.: Lightning and convection parameterisations - uncertainties in global modelling, Atmos. Chem. Phys. 7, 4553-4568, doi:10.5194/acp-7-4553-2007, http://www.atmos-chem-phys.net/7/4553/2007/, 2007.

Tsati, E.-E., Investigation of the impacts of emissions on the trace gas budgets in the troposphere by using global climate chemistry model simulations. Dissertation, Ludwig-Maximilians-Universität München, Fakultät für Physik, http://nbn-resolving.de/urn:nbn:de:bvb:19-175246, 2014.

Yienger, J. J. and Levy II, H. L.: Global inventory of soil-biogenic NOx emissions, J. Geophys. Res. 100, 11,447–11,464, 1995.

Table 4. Comparison of different studies with respect to the contribution (%) of stratospheric ozone to the tropospheric ozone concentration. Numbers are rough estimates, only, as taken from published figures. Note that values for L05 are surface values only and percentage values from E12 are estimated from mixing ratios, however a mean value of 17% is given therein. See text for more explanations. SH and NH abbreviates Southern and Northern Hemisphere, respectively.

Reference	SH	Tropics	NH
LD00	40	10	25
L05	20	$<$10	10
G07	5-10	10	15
E12	20	$<$5	15
This work	10-15	5-10	10-20

Table 5. Qualitative characterisation of four different regions (A-D) in the Mediterranean Sea. A: Southern France; B: Strait of Gibraltar; C: Central Mediterranean Sea; D: Tunesian Coast. See Figure 6 (top row) for the location of the regions. The signs '++', '+', '○', and '-' indicate a qualitative estimate of the respective characteristics, 'very strong/very large', 'strong/large', 'moderate', 'negative'.

	A	B	C	D
Region has polluted background	++	+	○	○
Region is impacted by shipping NO_x	++	+	+	++
Region is impacted by shipping ozone	+	+	+	++
Shipping emissions are converting HO_2 into OH via $NO+HO_2 \longrightarrow OH + NO_2$	++	++	+	+
Shipping ozone produces OH via $O_3 \longrightarrow O(^1D) \xrightarrow{H_2O} OH$	+	+	+	++
Contribution of shipping emissions to OH	-	+	++	+
Contribution of shipping emissions to HO_2	-	-	○	-

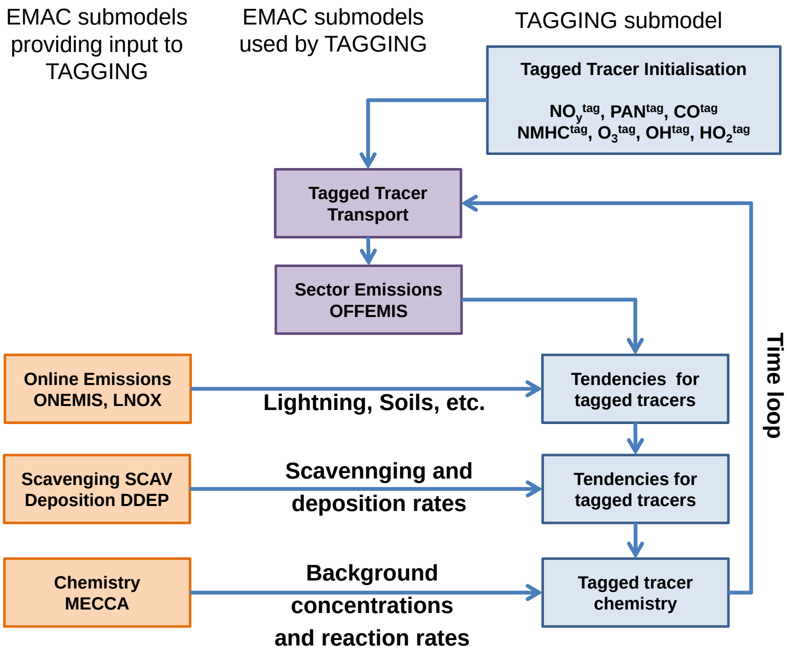

Figure 1. Sketch of the tagging algorithm.

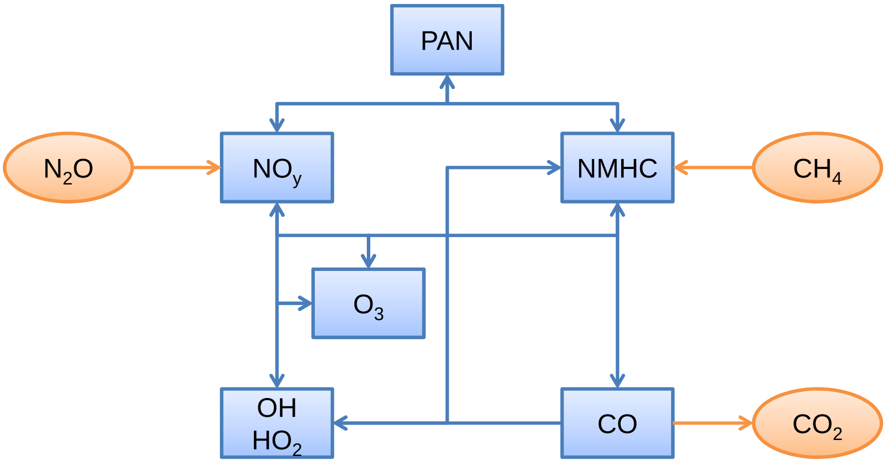

Figure 2. Sketch of the chemistry of tagged species (blue) and key relations to other species (orange). Note that stratospheric ozone is not included here. For HO$_x$ chemistry see also Figure 3

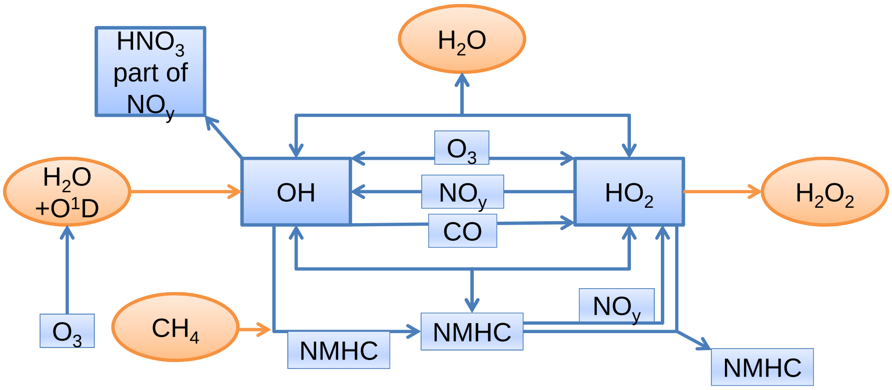

Figure 3. Atmospheric HO_x chemistry used in the TAGGING scheme. Blue boxes indicate tagged species and families and orange circles non-tagged species. Arrows indicate reactions.

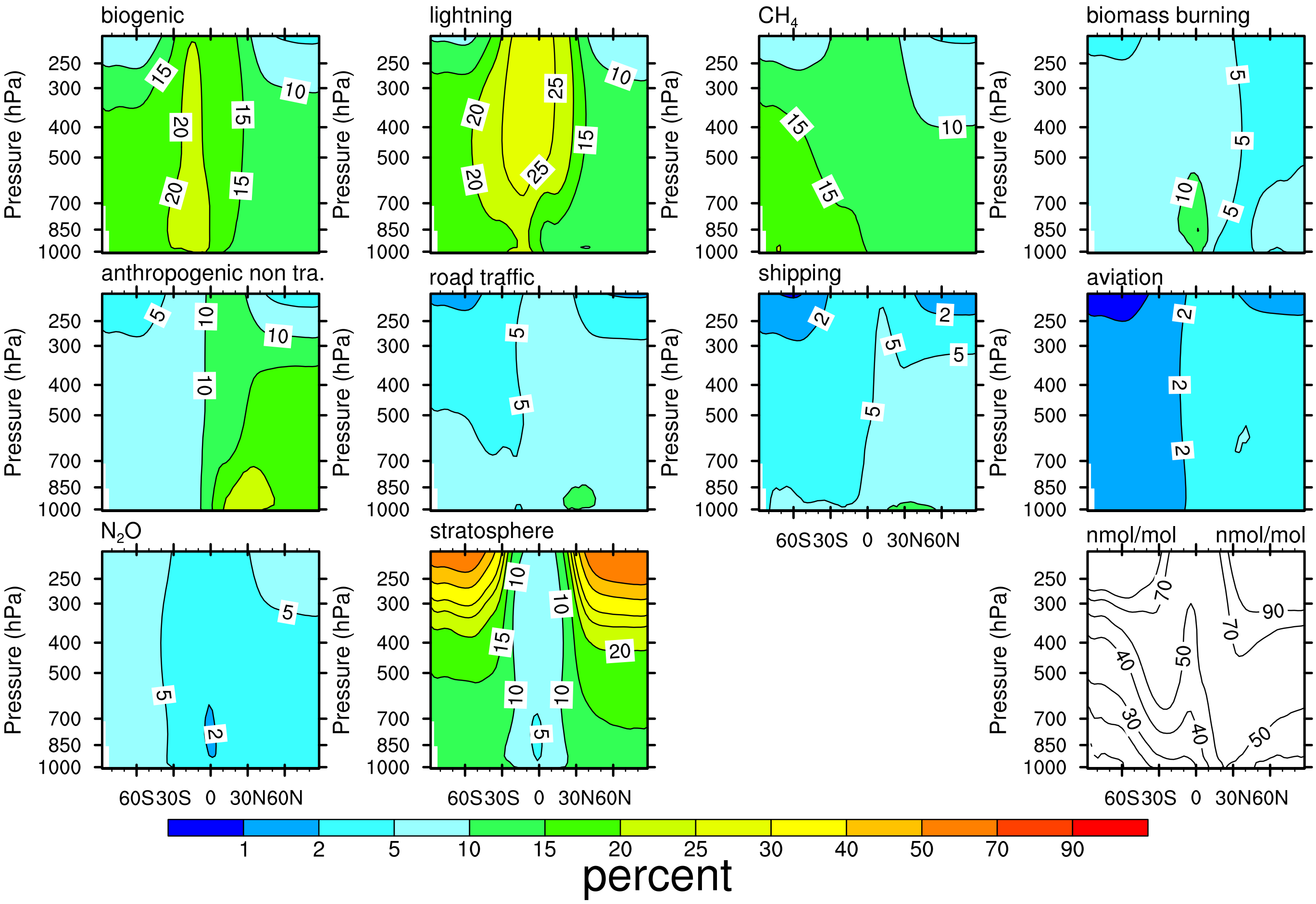

Figure 4. Annual mean contributions [%] of 10 emission sectors to the simulated ozone volume mixing ratios. The simulated ozone volume mixing ratio is shown in the lower right panel.

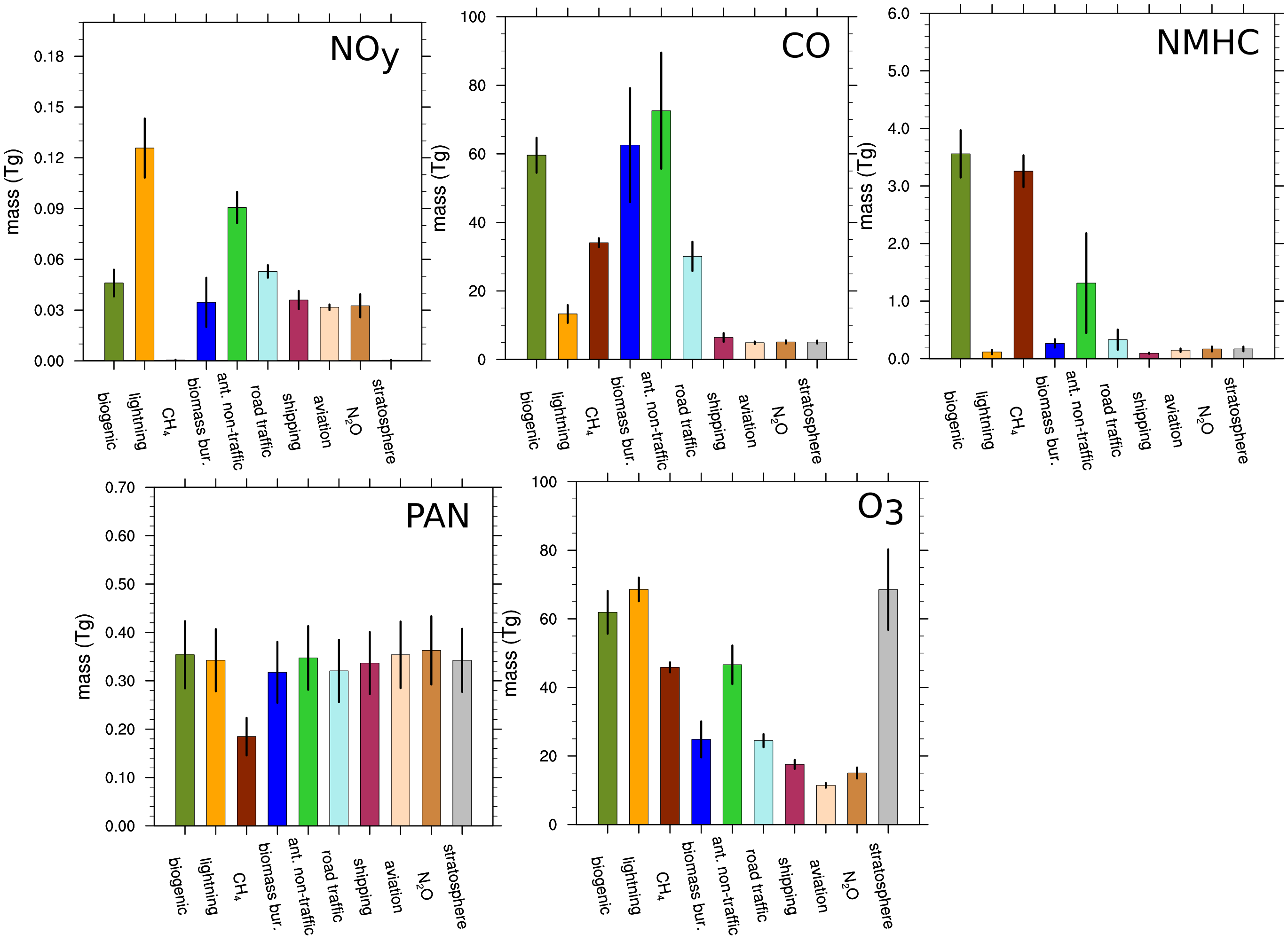

Figure 5. Contributions to the annual mean tropospheric budgets [Tg] of 10 emission sectors. Top row: NO_y, CO, and NMHCs; Bottom row: PAN and O_3. Errorbars indicate the interannual variability.

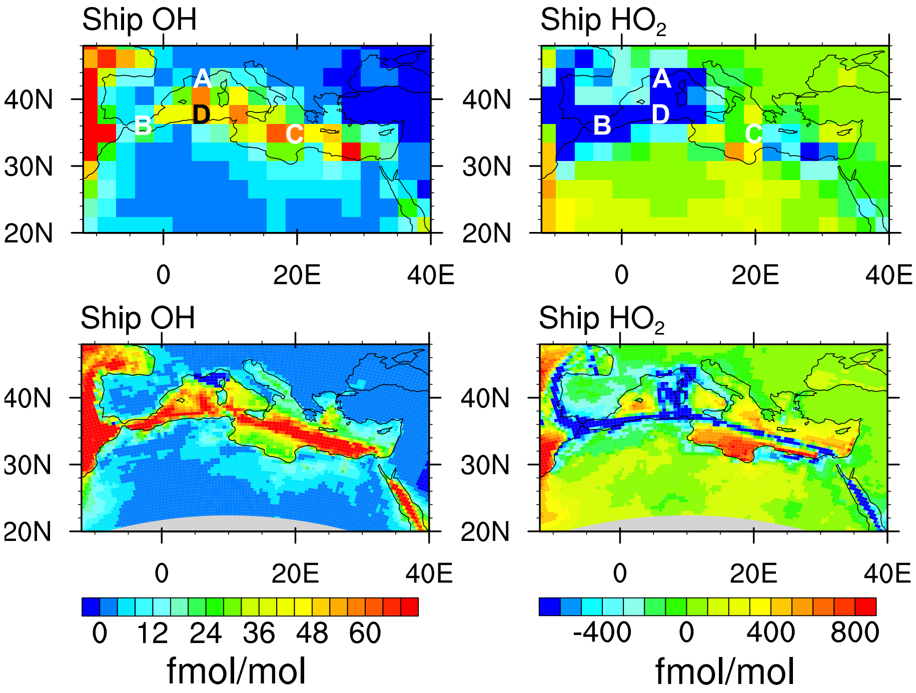

Figure 6. Absolute contribution of shipping to the simulated OH (left) and HO_2 (right) volume mixing ratios (in fmol/mol) for August 2007. Top row: EMAC; Bottom row: MECO(n). Regions A-D are characterised by different chemical situations. A: Southern France; B: Strait of Gibraltar; C: Central Mediterranean Sea; D: Tunesian Coast; See text for more details.

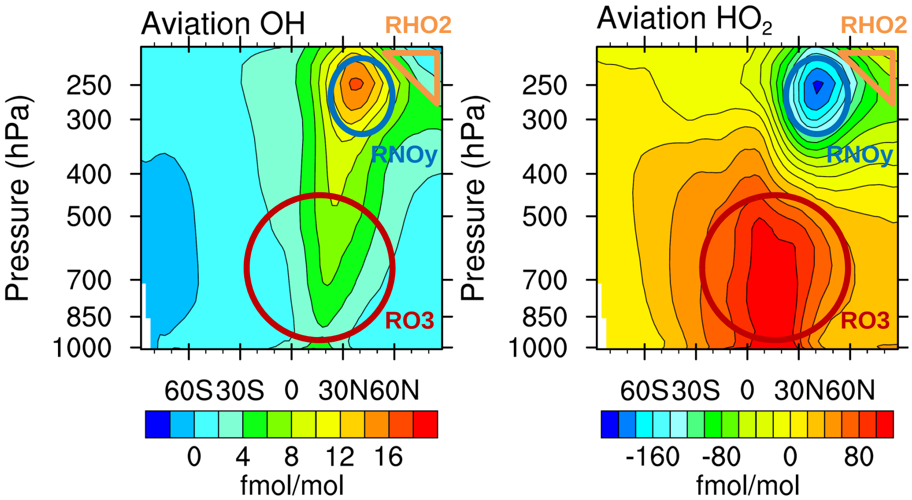

Figure 7. Annual mean absolute contribution [fmol/mol] of aviation to the simulated OH (left) and HO_2 (right) volume mixing ratios. The regions RO3, RNOy, and RHO2 are characterised by distinct different chemical response to aviation emissions as described by Grewe et al. (2002) (see text for further details).

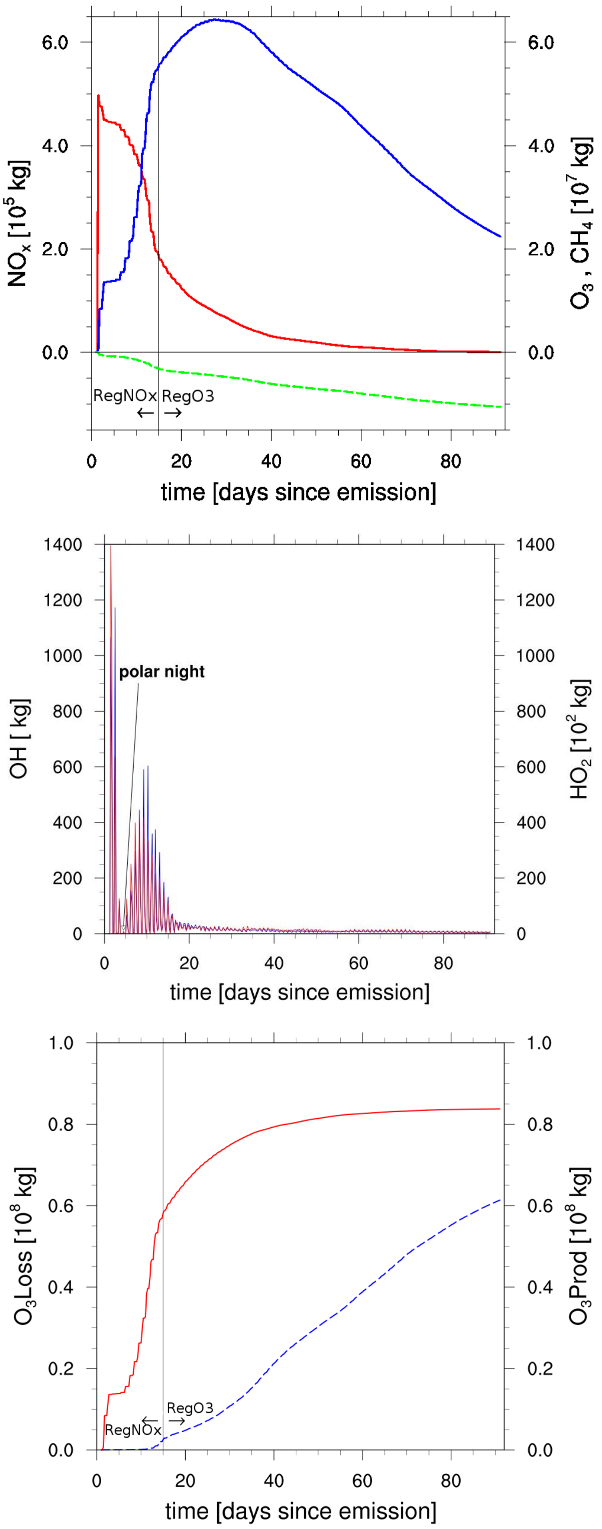

Figure 8. Temporal development of NO_x related species (top: NO_x (red), O_3 (blue), CH_4 (green), mid: OH (blue), HO_2 (red)) and production or loss terms (bottom: cumulative O_3-loss (blue) and cumulative O_3-production (red)) induced by a pulse emission at 45°W, 50°N and 300 hPa on December, 23, 2000. The discrimination between the regimes RegNOx and RegO3 refers to the NO_x dominated (days 1-15 after emission) and the O_3 dominated regime (days 16-90 after emission), respectively.

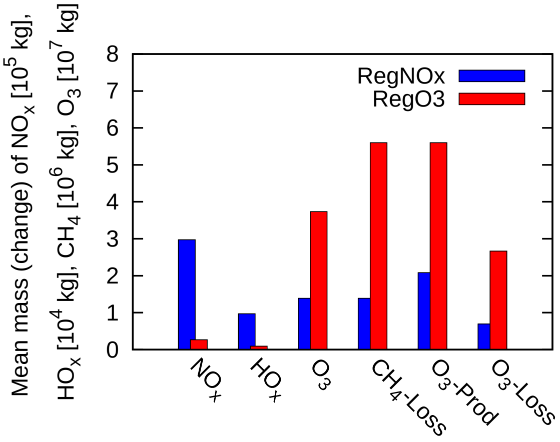

Figure 9. Mean contributions to NO_x related species and production or loss terms for the RegNOx regime (NO_x dominated, blue) and RegO3 regime (O_3 dominated, red), respectively. Values are given as temporal means over the two time periods.

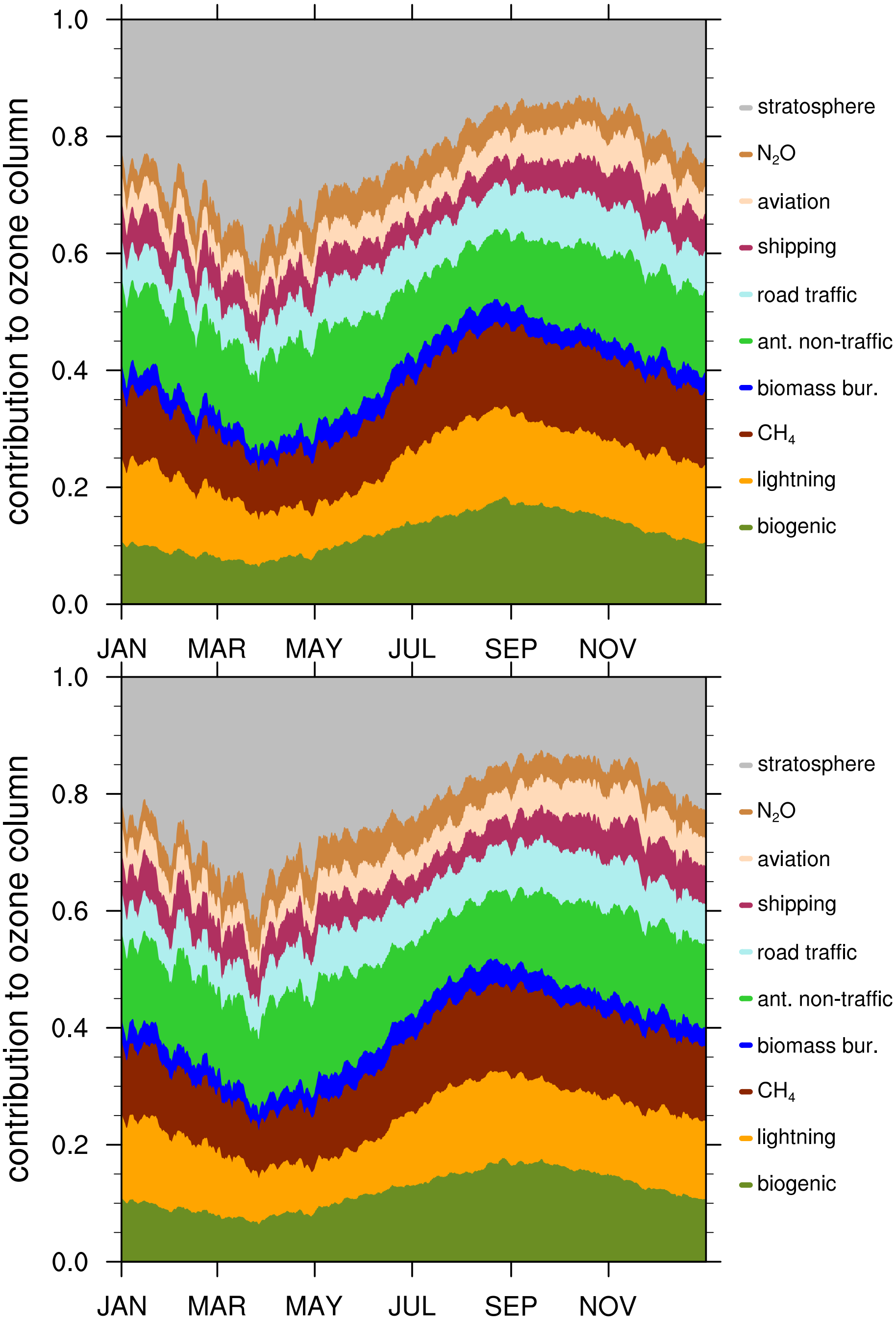

Figure 10. Contributions (fraction) of individual emission sectors to the European tropospheric ozone concentration for a coarser resolution simulation with EMAC (top) and a finer resolution with MECO(n) (bottom) for the year 2008.

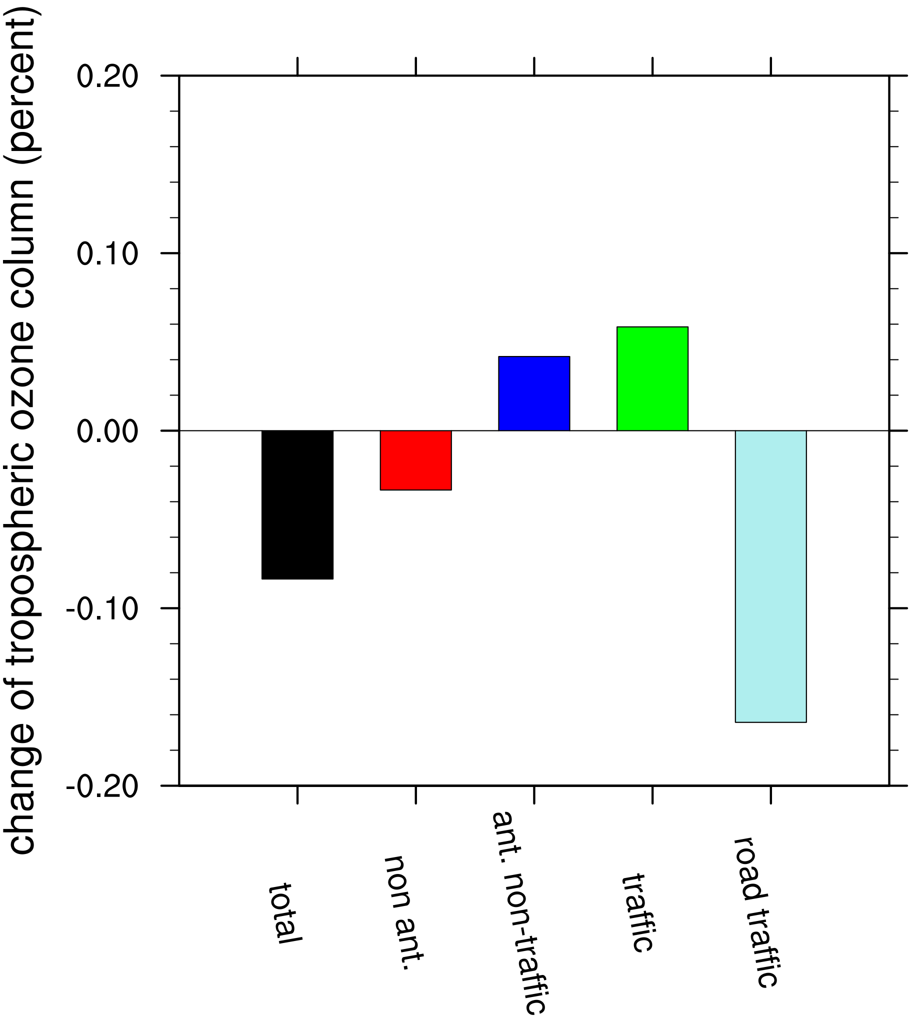

Figure 11. Changes in the global tropospheric ozone budget [%] resulting from a 5% reduction in the road traffic emissions.