

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 "NO_x-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 interesting 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 NO_x sensitive regime to the respective NO_x source, we are arguing that either VOCs, CO, or 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 ($= P_{R1}^i$) can be split up into 3 parts: NO^i reacts with HO_2^i , NO^i reacts with HO_2^j from any other category ($j \neq i$), and HO_2^i reacts with NO^j from any other category ($j \neq i$). Note that at reaction level, the reaction of HO_2^i with NO^j for $i \neq j$ is accounted for by 50% to emission category i and j :

$$P_{R1}^i = k_{R1} \left(\text{NO}^i \text{HO}_2^i + \sum_{j \neq i} \frac{1}{2} \text{NO}^i \text{HO}_2^j + \sum_{j \neq i} \frac{1}{2} \text{NO}^j \text{HO}_2^i \right) \quad (1)$$

$$= k_{R1} \left(\text{NO}^i \text{HO}_2^i + \frac{1}{2} \text{NO}^i (\text{HO}_2 - \text{HO}_2^i) + \frac{1}{2} \text{HO}_2^i (\text{NO} - \text{NO}^i) \right) \quad (2)$$

$$= \frac{1}{2} k_{R1} \left(\frac{\text{NO}^i}{\text{NO}} + \frac{\text{HO}_2^i}{\text{HO}_2} \right). \quad (3)$$

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

$$P_{R1} = k_{R1} \text{NO} \text{HO}_2 \quad (4)$$

$$= k_{R1} \sum_{i=1}^N \text{NO}^i \sum_{j=1}^N \text{HO}_2^j \quad (5)$$

$$= \sum_{i=1}^N \frac{1}{2} k_{R1} \left(\frac{\text{NO}^i}{\text{NO}} + \frac{\text{HO}_2^i}{\text{HO}_2} \right) \quad (6)$$

$$= \sum_{i=1}^N P_{R1}^i. \quad (7)$$

At concentration level, the ODE

$$\frac{d}{dt} O_3^i = P^i - D^i, \quad (8)$$

determines the concentration change of O_3^i and implicitly includes effects wrt. NO_x and VOC saturated regimes (see below). The derived factor of 0.5 describes a basic principle and per se is not including explicitly 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 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 NO_x limited. Now the tagging scheme attributes 50 ppbv ozone to NO_y and 50 ppbv to VOCs, leading to an attribution of 0.625 ppbv O_3 per ppbv NO_y and 33 ppbv O_3 per ppbv-VOC. Increasing the VOC emissions leads to 2 ppmv VOC and to the same ozone concentration, since we have a NO_x -limited/VOC-sensitive regime. Therefore, the NO_y attribution remains unchanged and the VOC attribution is effectively reduced from 33 to 25 ppbv O_3 per ppbv 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-O₃ tagging and by Butler et al., 2012 for the VOC-O₃ tagging.

With the "Perturbation-Method" sensitivities are attributed to sources 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 HO₂, 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 hydrocarbons 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 anthropogenically 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-the-art 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 k_{OH} rate constants for each source category, so that (for example) biogenically tagged VOC will decay more quickly than anthropogenic 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 HO₂.

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.