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Interactive comment on "Contribution of emissions to concentrations: The TAGGING 1.0 submodel based on the Modular Earth Submodel System (MESSy 2.52)" *by* Volker Grewe et al.

Anonymous Referee #1

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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 ulti-

mately 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.

One of the most interesting aspects of the TAGGING approach is that it considers both NOx 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 NOx 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 NOx precursors by using a combinatorial approach that effectively gives equal weight to NOx 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). Earlier work described by Dunker et al. (2002) uses a technique for attributing ozone production to either NOx 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 NOx and VOC precursors of ozone fits with the previous work of Emmons et al (2012), Butler et al. (2011) and Dunker et al. (2002).

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 NOx, 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

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like to see the authors acknowledge this result as being unphysical, and being due to the blending of NOx and VOC precursor tags during the production of tagged PAN (and subsequently produced NOx 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 NOx precursors" and "PAN from VOC precursors", and thus reducing these particular unphysical results. 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 NOx-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 NOy 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.

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

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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-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 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.

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.

Line 40: NOx 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 NOx in their model as a chemical family?

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.

Line 96: Ozone production also depends on RO2.

Line 102: Please provide a forward reference to where tagging of HO2 is described.

Line 184: A table listing the members of the NOy and VOC families would be useful.

Line 217: Please also list the members of this "effective ozone" family.

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?

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.

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 NOy, H2O2, and HNO3 as indicators for ozone-NOx- hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100, 14175-14188, 1995.

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