**Geoscientific
Model Development
Discussions**

Interactive comment on "Tagged ozone mechanism for MOZART-4, CAM-chem, and other chemical transport models" *by* L. K. Emmons et al.

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Emmons et al. describe a method for attributing all chemical production of ozone in the troposphere to various sources of NOx through the use of additional tracers added to the chemical mechanism. All ozone which is not attributed to chemical production in this way is assumed to have originated in the stratosphere. The application of the method is described using the MOZART-4 chemical transport model, although in principle it could be readily applied to any model for which the chemical mechanism can be easily altered.

This tagging technique has been applied in several previously published studies, but has not been fully documented in these studies. Its documentation in this GMD paper provides a valuable service to the community. I find the paper to be clearly and

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concisely written, although the number of figures could be reduced. I also have some reservations about the method itself which I think the authors should address in a revised version of the manuscript.

I would like to draw the authors' attention to the work of Butler et al. (2011), Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach, Atmospheric Environment. In this paper, we describe a method for attributing the chemical production of ozone to emissions of VOC, rather than NOx, as Emmons et al. have done in their GMDD manuscript. The authors could consider briefly comparing their approach with ours.

Page 1952, lines 17-19: Focusing on the role of NOx in ozone production rather than peroxy radicals seems reasonable in the context of a global CTM where most of the domain is likely to be NOx-limited rather than VOC-limited, but it would be nice if the authors could briefly justify this choice here.

Table 3: Consider the null cycle

R1: $NO + O_3 \rightarrow NO_2 + O_2$

R2: $NO_2 + h\nu \rightarrow NO + O$

R3: $O + O_2 \rightarrow O_3$

In the tagged versions of R1, as described in Table 3 of Emmons et al., tagging information is preserved when tagged NO reacts with O3, but when tagged O3 reacts with NO, the tagging information appears to be lost.

This would appear to be a potential "sink" for tagged O3. Such tagged O3 reacting with untagged NO would lead to the production of untagged NO2, which can then be rapidly photolysed (at least during daytime) yielding untagged O3.

Assuming all NO is tagged, then the cycle R1-R2-R3 will result in the original O3 tag being replaced with the tag held by the NO molecule. This would tend to shift the

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attribution of transported ozone towards local sources of NOx. In the case of untagged O3 (ie. ozone from the stratosphere), the cycle R1-R2-R3 will result in this stratospheric ozone being tagged with the identity of the NO source.

This provides an explanation as to why the stratospheric contribution to surface ozone is found to be extremely low using this tagging method. What it is in fact showing is the number of ozone molecules which have managed to dodge all of the NO molecules in the troposphere on their way down from the stratosphere to the surface. This could also explain some of the apparent discrepancy between the tagging and perturbation methods of ozone attribution; the attributed ozone from the tagging method is the sum of the ozone produced by the reactions of tagged NO with peroxy radicals, and ozone of stratospheric origin which has been through the R1-R2-R3 cycle involving the tagged NO.

In Butler et al. (2011), our tagging approach does not directly track production of O3. Instead we examine the production of Ox, or "odd oxygen", a chemical family which includes O3, O, and NO2. Rapid null cycles such as R1-R2-R3 have no net effect on the total amount of Ox, and our analysis focuses on production of Ox, which overwhelmingly occurs in the troposphere by reaction of NO with peroxy radicals. By tagging the peroxy radicals from different VOC sources we were able to attribute ozone production to those VOC. We compared our calculated VOC reactivites with a perturbation method (the MOIR, Maximum Ozone Incremental Reactivity, Carter et al. (1994), Development of ozone reactivity scales for volatile organic compounds, Journal of the Air and Waste Management Association) and found a very good correspondence between the tagged and perturbation approaches. By using a chemical box model, we were able to tune the chemical regime of our simulation so that it corresponded exactly to the conditions of maximum ozone production. In a 3D model containing a range of chemical regimes from NOx-limited to NOx-saturated, such a good agreement between our tagging method any one particular perturbation method would not be expected. The applicability of tagging schemes to different chemical regimes remains a topic of active

investigation.

The revised version of Emmons et al. should contain some discussion of the effects of the R1-R2-R3 reaction cycle on the attribution of ozone production. The authors should state the degree to which they expect their method to be influenced by this reaction cycle, and if they believe that their method is affected by this reaction cycle, they could include some future perspectives on how to deal with this in subsequent versions of the tagging scheme.

The paper has a very large number of figures. Many of these could be cut without seriously affecting the quality of the paper. Fewer figures would in fact improve the readability of the paper, and the removed figures could still be included as an online supplement.

Fig. 3 (tagged O3 zonal average Jan) could be replaced with an annual average, allowing Fig. 4 to be cut. The seasonal variation could be described in the text.

Fig. 7 and 8 are barely discussed in the text and could be cut. Fig. 9 is interesting due to the discrepancy between tagged and total HNO3 and could be left in the main text for this reason.

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