We thank Drs. Butler and Evans for their thoughtful and helpful reviews of our paper. Following both of their suggestions, we have reduced the number of figures, showing fewer seasons and altitudes, consolidating the original Figs. 3-9 into 3 figures, and replacing Figs. 13-15 with one new figure (Fig.11).

The full reviews are included below (in *italics*), with our responses interspersed in **bold**. Added or modified text in the revised manuscript is also indicated in **bold**.

Review by M. Evans

This paper describes a method for 'tagging' the O3 produced from the emissions of NO from a variety of sources. It appears to offer a flexible and comprehensive approach to this problem. Given the important of trans-boundary air quality problems and the attribution of O3 related radiative forcing to different emission sources this is a very useful and powerful tool in the armory of diagnostic techniques for atmospheric chemistry models.

The paper should be published, however, there is still in my view, a bit of a mystery as to why the perturbation experiments give a much lower value for the long range transport of O3 than the tagging approach adopted here. My suggestions for the paper would be a little bit more investigation of this problem and a slight reduction in the number of figures.

Overview

The attribution of O3 to different NO emissions sources in a non-trivial activity as the relationship between NOx concentrations and O3 production in non-linear. Previous efforts to target this problem have used either a series of perturbation studies or have tagged the O3 produced over a certain region. Both approaches offer significant limitations. This paper describes an approach that allows the O3 produced from the emissions of NOx to be tagged directly. This is a significant advance in our ability to diagnose models both for science but also for policy activities. The authors present the a generally good description of their approach and show extensive figures of their diagnostics. However, I would suggest they think about whether they can reduce the number of figures, as there appears to be an overwhelming number.

We have reduced the number of figures from 15 to 11 (including 2 new figures to address the reviewers comments).

Major Comments

Non-linearities: The most interesting aspect of this work is the inconsistency between the O3 produced from a certain NO source calculated by this approach and the O3 calculated by the equivalent perturbation study. This difference has significant policy implications. This approach suggests a much more significant fraction of the O3 being due to trans-boundary transport than the perturbation studies suggest. This is a very important result and one that needs to be disseminated to the science and policy community.

Assuming that there is not a bug in the coding, the explanation for this discrepancy is

hard to understand. The authors suggest that this is due to the non-linearity of the chemistry. However, previous literature seems to suggest that may not be the case. Wild et al., [2012] (Modelling future changes in surface ozone: a parameterized approach Fig 3) suggests that the 20% changes should be effectively linear and much larger changes are needed to get a significant non-linear response. It may be that the model used here has a more-significantly non-linear response than the one in the Wild study. The model has a more complex hydrocarbon oxidation scheme but it is not obvious that this would cause this behavior.

The fact that the addition of the individual tracers NOx tracers gives the same result as the case for the simulation without the tagging suggests that there isn't a major problem with the methodology.

We have performed an additional test, where we removed the stratospheric ozone flux to the troposphere, and illustrate that ozone from the tagged NO is identical (within 1ppbv zonal average) to the original untagged ozone. This is shown in a new Fig.1 and discussed in a new Section 3.1 (Test of Method).

A set of perturbations with smaller and larger perturbations (say 1,5,10,50%) would show how non-linear the model response is and would significantly strengthen the author's claims that the non-linearity's are the explanation for the discrepancy. At the moment I don't find this explanation convincing on the evidence presented.

We have performed an additional perturbation case with 5% perturbation and include these results in Fig. 10 (previously Fig. 12). When scaled to give regional attribution the results are almost identical to the 20% perturbation results. So this supports the results of Wild et al. [2012] that different degrees of small perturbations give similar results. However, this does not really address the fundamental non-linearity of ozone chemistry. We have added a new figure (Fig. 11) that quantifies the impact of the changes in OH and HO_2 due to the perturbation in NOx, by plotting the ozone production rate divided by NO concentration, and the ozone loss rate divided by the ozone concentration. These quantities are essentially the reaction rates of $NO+HO_2$ and $NO+RO_2$ for ozone production, and O_3+OH and O_3+HO_2 for the loss.

Whatever the case this work has a significant implication for public policy. I am slightly concerned that it will get lost within a journal that emphasizes model developments rather than more traditional science. The authors should ensure that they have a good strategy for publicizing this result to both the science and policy community as this has significant results for both.

We appreciate Mat's interest in disseminating the results more broadly, but we have used this procedure in previous studies that have been published in JGR and ACP, as we cite in the paper. We hope to include this technique in future HTAP studies.

Description of the methodology: It would be possible for the tagging to be implemented in 2 ways. The 1st would involve running the standard chemistry and the tagged chemistry in parallel with the standard chemistry impacting the tagged chemistry but not vice versa. The 2nd way would involve only having tagged tracers

which interacted with each other and the wider chemistry scheme. As I understand it the methodology uses the 1st approach. A couple of sentences to make this clear would be useful.

Yes, this technique uses the 1st method listed. We explicitly said that in the last paragraph of the Introduction, but have also added it to the beginning of Section 2 where we describe the method.

Minor comment: There appear to be random numbers after each of the references in the reference list.

I'm sure this is a type-setting issue (they are the page numbers where the references appear).

Review by T. Butler

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 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.

We appreciate having this paper brought to our attention. Comparison to this approach has been added in Section 2.

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.

We have added further discussion to Section 2 explaining our choice for tagging NOx instead of VOCs. If all sources are tagged, tagging NOx or VOCs should give the same answer. For the scale of attribution generally investigated with global models, tagging NOx is appropriate since most of the

globe is NOx-limited.

Table 3: Consider the null cycle

R1: NO+O3->NO2+O2

R2: NO2+hv->NO+O

R3: O+O2->O3

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 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.

The tagged NO version of R1 (XNO + O3 -> XNO2 + O3) effectively produces tagged O3, but this should be balanced by NO + O3A -> NO (a loss of tagged O3) so as to preserve the photo-stationary state.

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.

Certainly there are a variety of ways to estimate source attribution, with the most suitable technique depending on the question to be answered. As you say, the production of Ox comes from NO + peroxy radicals. Therefore, tracing sources from NO, or from VOCs to RO2, ultimately reaching the formation of odd oxygen from the photolysis of NO2, should give fundamentally the same answer, when all sources are tagged.

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.

Our tagging scheme preserves the photostationary state for O3 and for O3A, so we do not think there is any need to modify our tagging scheme. The new Fig. 1 illustrates that the tagged mechanism gives the same O3 as untagged in the absence of stratospheric ozone input.

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.

We have kept the original Figs. 3 & 4, but have consolidated previous Figs. 5-9 to the new Figs. 6-7.