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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Attribution of ground-level ozone to anthropogenic and natural sources of NO_x and reactive carbon in a global chemical transport model" *by* Tim Butler et al.

Anonymous Referee #1

Received and published: 24 June 2020

Summary: Authors use TOAST in CAM-Chem to attribute ozone to NOx, VOC, or methane separately. Thus, each molecule of ozone is attributed either 100% to NOx, 100% to VOC or 100% to methane. This method likely overstates the role of non-NOx molecules at the global scale because of primarily NOx-limited environments, but because both are showed, this is not a limitation. The results highlight the importance of long-range transport to annual averages, the disproportionate affect of the global shipping sector, and the shipping-methane interactions.

Response: The paper is a nice contribution that is well written with mostly minor recommendations from this reviewer. The comments will primarily be shown in the line by

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Discussion paper

line, but what follows characteristic of my response.

A few scattered recommendations are summarized here. The citations often seem inappropriately recent for well-established phenomenon. There are few qualitative statements without numerical context. The authors focus on selected regions, but provide no specific reason these were chosen nor do they contrast the results with the general case.

The ozone production efficiency metrics and discussion may require more edits. The authors compare OPE between methane and VOC uses table numbers that are in mol/mol, but in the text they say mol/molC. This is particularly problematic because they then highlight the high efficiency of methane. The OPE definition also seems inconsistent in the text compared to how it appears to be calculated. Further detail on the OPE response is in the line-by-line comments.

The authors highlight shipping, yet figures and discussion rarely figures and tables say "Ocean" which according to Table 1includes both natural and anthropogenic sources. This has two major implications for the paper. First, I am assuming that "Ocean NOx" is being implicitly assumed to be all from shipping. This makes sense as an assumption, but should be explicitly stated. For example, the soil NOx emissions from CAMS have an over ocean component which would violate this assumption. Second, ocean is treated as long-range transport and/or extra-regional. Figure 2 suggests that shipping has a low inland penetration that might suggest strongest influences from nearby production. If shipping from state or federal waters is most influential, it may be inappropriate to label it extra-regional or long-range transport. This requires some clarification and perhaps applying more nuanced assignment of "ocean/shipping." Finally, making the connection clear and explicit in your discussion would help readers.

These comments can largely be addressed by textual changes that should mostly be easy to implement.

Line-by-line:

17 - Monks et al. 2015 is a very recent citation for such a well-known phenomenon.

18 - Fleming et al., 2018 is a very recent citation for harm to health. Mills et al. 2018 is a very recent citation for harm to vegetation. There is a long history include protective legislation for decades for both of these.

26 - I think baseline has not yet been defined.

30 to 31 - Consider adding a reference to Cooper et al sonde evaluations or TOAR.

35 - "extremely high" should include a numerical context. What percent of the mean?

59 - Why is NOx from ships having more influence important?

156 - Consider citing a reason for 1760 ppb

159 - How was 2-years estabilished as sufficient? What was the spinup for the methane case?

216 - It is not clear to this reviewer that OPE was calculated based on gross production as described on this line. See comments on lines 284 to 285.

218 - "some source regions" should be enumerated.

271 to 273 - This is a long established phenomenon, which if often expressed as yield of RO2 per mole. This includes books from the 1990s. A 2011 citation seems recent.

284 to 285 - Table 3 reports OPE as mol/mol but mol/molC is in the text. Methane, ocean, and biogenic are dominated by VOC over CO. It appears that OPE is being calculated by converting emissions to molC/yr and burden ozone to mol. For methane, the OPE calcualted this way is identical. For ocean and biogenic, which have some CO, the OPE is nearly identical to your value. This makes me think that the OPE is in mol/molC, not mol/mol. This has consequences for the way results are discussed. For example, assuming that most VOC mass has 4 carbons, the OPEs for NMVOCs increase by 4x. So comparing CH4 to on a mol/molC basis seems odd.

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On the same topic, this method of OPE calculation is different than what this reviewer is used familiar with or as you described on line 216. Your line 216 is more consistent with Kleinman 2002, who cites Liu 1987 and Lin 1988 to define OPE as "the number of molecules of oxidant (O3 + NO2) produced photochemically when a molecule of NOx (NO + NO2) is oxidized." Thus, OPE would be related to gross production not burden. Burden is a net state, which includes both production and loss. Because anthropogenic VOCs react near the surface, they may be subject to higher deposition loss rates and shorter chemical lifetimes. Thus, an OPE based on state rather than production, may weigh in methane's favor.

The indicator you are using, regardless of the name, is clearly useful. The definition and discussion needs to be adjusted to better match what you have done, and to make a better comparison between moles of NMVOC and moles methane.

299 - source attribution includes zero-out/perturbation techniques, while tagging does not. It might be worth using specific language here. While I am not aware of reactive carbon zero-out/perturbation techniques, there is a lot of literature out there.

322 - "natural sources and long-range transport ... [each or together] contribute more to" It was unclear if this was a combined statement.

325 to 326 - This is a complex statement. First, excluding "Ocean" this is not true for NAM. Then, the question is does shipping have a far reaching effect or is it localized. If it is localized and within the regions Exclusive Economic Zone (potentially even within state waters), then is it "intra-regional" or "extra-regional."

337 - A select few regions are shown, but no explanation of why they are shown is provided. Are the typical sites or the sites where transport matters most?

355 to 356 - For China and USA, the minimum contribution is not in winter.

365 - In all regions or in all three regions shown?

366 - The "pronouncement" of the cycle is not clearly stronger in all regions even

though it commonly is.

418 - Did you study fate? loss processes?

428 - Generally associated with PAN discussion (not really line specific). How do you treat the equilibrium reactions that are often artificially defined as "net" forward rates? What implications does that have for tagging approaches to look at PAN?

434 to 464 - Is this mean to help explain PAN or be a separate discussion? The OH reactivity doesn't consider the PAN potential, which is related to the ability to create a peroxy acyl radical. If this is a new thought, perhaps add some sort of transition.

458 - What level of confidence do you have in the Asian VOC? How are VOC speciated differently by region? This could have more general implications in other places in the paper.

480 - Given the NOx-limitation changes due to removing methane, how does assuming linearity in inverting the perturbation?

482 - spinup length for methane?

492 - gross production or net burden?

492 to 496 - I found the relative increases as ambiguous. Increases in total or increases? in methane direct? or increase in net methane contribution? Ultimately, I found the table more clear than the discussion.

499 to 500 - might note this is for annual averages

568 - and stratosphere.

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