Response to referee comments on acp-2020-436

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We thank Volker Grewe and the Anonymous Referee for their comments on our manuscript. Our responses are given below. In each case we reproduce the referee comments in boldface, and provide our responses in standard script. Where we have made changes to the original manuscript in response to the referee comments, these changes are described together with our response. Both referees noted that the manuscript is well written. In our modifications to the manuscript we have tried to balance preservation of as much of the original text as possible, with what we hope are changes that satisfy the comments of the referees. We believe that the revised version of the manuscript has improved compared to the original, and thank the referees again for their comments. In our responses we refer to line numbers in the original manuscript. We append a revised manuscript here with the changes mentioned in our responses marked up.

Response to Anonymous Referee #1

> **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.**

We would like to correct an apparent misunderstanding by the referee here. Our source attribution method does not perform a 100% attribution of ozone to methane. Rather, methane is treated as just one form of the many forms of “reactive carbon”, to which we do perform a 100% attribution (in addition to the 100% attribution to NO_x). While we do give a definition of reactive carbon in the paragraph beginning on line 67, we have also added text to the first paragraph of the introduction section to make it even clearer that reactive carbon includes methane.

> **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 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.

We have taken note of these general comments, and provide our responses as appropriate after the line-by-line comments from the referee where the relevant specific comments are made. In response to the point about the “Ocean” region, we have added a sentence to the paragaph discussing Table 1 to make it clear that all NO_x from this region is due to shipping, and that the predominant source of reactive carbon is biogenic DMS. We have also modified the relevant footnote in Table 1 to repeat this point.

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

The referee is correct. We have generally tried to provide recent references in order to direct interested readers to relatively new work, which itself usually contains further references, but we acknowledge that also including older references here can provide a fuller context. In this case, we have added the citation of Crutzen (1973) to the statement in question, and in the same spirit, added a citation of Atkinson (2000) later in the same paragraph.

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.

Again, we agree. We have added references to Haagen-Smit (1952) and Reich and Amundson (1985), which are both examples of important early work that are still well-cited today.

26 - I think baseline has not yet been defined.

Here we are actually already defining baseline to mean the long-range transported component of ozone. We have added a sentence to make this clearer, and given references to Parrish et al. (2017) and Derwent et al. (2018) which both use the term this way.

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

We have discussed TOAR (and used data from the project) later in the manuscript. In the text in question here, the point we are making is about recent trends in two specific regions, which we think is already adequately made with the references we have included, so we prefer to leave the manuscript unchanged here.

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

We show this spread in our Figure 1, and comment on its magnitude. To respond to the this comment, we have added some text to the discussion of Figure 1 at the beginning of Section 3 noting that the spread in the model estimates is of a similar order to the Northern Hemisphere annual mean surface ozone itself, and also added a forward to reference to this section to the part of the introduction mentioned by the referee.

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

This statement about earlier results is included to indicate that our study is not the first to point out that ship NO_x has more influence on surface ozone than aircraft NO_x, despite the latter being more efficient at producing ozone. We feel that this is worth keeping in the manuscript.

156 - Consider citing a reason for 1760 ppb

This value comes from the model setup that we adapted from Tilmes et al. (2015) for this work. We have clarified this in the manuscript text.

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

As mentioned in our earlier response to this referee, there is no “methane case” in this manuscript. We hope that our earlier response has clarified that. The model spinup for the NO_x and reactive cases is described in more detail in Butler et al. (2018), which is referenced twice in the paragraph in question. In order to respond to this comment, we added some extra text in response to this comment, noting that the model was deemed to be spun up when the maximum difference in December mean surface ozone attributable to any tagged source was less than 1% in any two subsequent years of simulation.

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.

We agree with the referee that our definition of OPE is unclear. We have clarified our definition of this quantity in the manuscript text to indicate that we define this as the contribution of each emission source to the tropospheric ozone burden, with units of moles of ozone per mole of N or C emitted.

> **218 - "some source regions" should be enumerated.**

We have added that specifically South East Asia, Northern Africa, the Middle East, Middle America, and Central Asia are included with the "Rest of the World" in Figure 2 in order to enable better comparison Figure 3.

> **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.**

We have added references to Bowman and Seinfeld (1994) and Atkinson (2000).

> **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.**

We have updated Table 3 to clarify that the OPE of reactive carbon is reported in mol/mol(C), and we have made some small changes to the paragraph beginning on line 284 to consistently report the OPE in its correct units, and to reinforce that the OPE is "per unit of reactive carbon". Additional related changes were also made elsewhere in the manuscript based on an earlier comment by this referee.

We believe that the normalisation of the contribution of each VOC molecule to the tropospheric ozone burden by its carbon content does make sense in a global model, in which emitted species have the time to be completely broken down by photochemical and other loss processes. More carbon per molecule means more chemical bonds, and potentially more opportunity for a large molecule to generate the peroxy radicals which can go on to form ozone, even if these processes all take a lot more time than the ozone production over regional scales, where the molar emissions and the OH rate constant are more important at determining the ozone proudction. By removing this effect, we are able to discuss the OPE of reactive carbon in terms of the amount of detail in the model chemical mecanism and the co-emission of $\mathrm{NO_x}$. After careful consideration we do not see any need to modify our discussion of OPE any further.

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.

We stand by our statement, and note that neither referee has provided any references to earlier work which actually does perform a complete attribution of tropospheric ozone to reactive carbon precursors alone. Furthermore, we note that the recent review by Heald and Kroll (2020) cites only the work of Butler et al. (2018) as the source of data for its Figure 1, in which the contribution of reactive carbon to tropospheric ozone is shown.

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

Yes, this is intended to be a combined statement. We have added the word “together” to make this clearer.

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."

The question of the geographical extent of the effect of shipping emissions on surface ozone remains open. We have added some extra text to the paragraph beginning on line 389 (original manuscript) indicating that future work should also include more refined attribution of ozone to shipping emissions from coastal regions and the high seas.

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?

We have added a sentence immediately following this which gives some reasons for the selection of these regions.

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

We are not sure what we originally intended to communicate with this sentence. We have simply deleted it, and do not believe that this detracts from the discussion of our results in any meaningful way.

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

This feature is seen in all regions, we have made this more explict.

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

We have deleted “but more pronounced”.

418 - Did you study fate? loss processes?

We address this issue in our response to the review by Volker Grewe.

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?

In our system, the forwards and backwards reactions are modelled explicitly. Butler et al. (2018) provides a complete description of the chemical mechanism and how it is tagged. We consider the implementation of our tagging scheme in additional chemical mechanisms as an open research area.

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.

The text in question is indeed distinct from the disussion of PAN, so we have added a new sub-section heading to aid the 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.

VOC speciation remains a challenge for emission inventories. The emission inventory used here is described by (Janssens-Maenhout et al., 2015) and specifies NMVOC as a total rather than with a speciation.

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

The responses in receptor regions to reduction perturbations are often shown inverted (HTAP, 2010; Jonson et al., 2018, eg.). We believe that this makes the results easier to follow.

482 - spinup length for methane?

As noted in our response to an earlier comment from the referee, there is no separate attribution of ozone to methane. We hope that our earlier response has clarified this.

492 - gross production or net burden?

The previous sentence already states clearly that we are referring to the net burden of ozone.

> **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.**

We agree that the text here was unclear. We have tried to make it clearer when we are referring to the ozone attributable to methane using the tagging system, and when we are referring to the change in the ozone burden as a response to the change in methane. We also switched to using the absolute change in ozone burden to introduce the point that the ozone increase due to rising methane is partialy offset by less ozone production from other VOC. We hope that these modifications have helped to improve the readability of this paragraph.

> **499 to 500 - might note this is for annual averages**

We have clarified this statement so that it refers to annual average ozone.

> **568 - and stratosphere.**

We have added a mention of the stratospheric contribution to springtime ozone to the beginning of this paragraph.

Response to Volker Grewe

> **Butler et al. present an analysis of modelled surface ozone concentrations with respect to the chemical production via either NOx or VOCs. The paper is well written and offers important insights in the relation between regional emissions and ozone surface mixing ratios. However, I think some more comments on**
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> - **Interpretation of the diagnostics and**
> - **Uncertainties**
>
> **should be given.**
>
> **Interpretation:**
>
> **a) Loss processes As far as I understood the ozone production terms are taken into account in the tagging scheme for ozone. How is the ozone destruction treated? Increase in the NOx emissions and hence NOx concentrations affect not only ozone production, but also the lifetime of ozone (e.g. Stevenson et al. 2006). Hence also the individual sources contribute differently to the ozone destruction. How would your results change, if you take this effect into account?**

It is not clear exactly which loss processes the referee is referring to here. One well-known effect of NO_x emissions in polluted regions is the temporary removal of ozone often referred to as “titration”. This loss of ozone is temporary, since the NO_2 it produces can rapidly photolyse, ultimately yielding ozone again. Our tagging scheme accounts for this by tracking not just ozone, but all members of the "odd oxygen" family, as described in Butler et al. (2018).

More generally, tagged ozone (and other odd oxygen species) are lost at the same rate as the corresponding non-tagged species in the model. The tagging scheme thus delivers information on the contribution of different precursors to the modelled odd oxygen species (including ozone) at any given model time step. In this sense the method is similar to the method described by Grewe et al. (2017). Further details are given in Butler et al. (2018), which is referenced extensively from the current manuscript.

In cases where changing emissions might cause secondary effects in the lifetime of ozone or other odd oxygen species, these effects could be investigated using perturbation runs to explore the sensitivity of ozone to changes in the chemical environment. We have added some text to the introductory paragraph in which the tagging and perturbation approaches are compared to acknowledge this effect.

> **b) Ambiguity While the separation of the ozone production wrt NOx and VOC is very helpful in understanding the driving mechanisms, it may also appear as ambiguous. E.g. Figure 4 indicates that European ozone is largely dominated by NOx from ozone (top) or methane (bottom). That sounds like a contradiction. Shouldn't it be in the end one ozone bar having all contributions included, instead of two (top and bottom figure)? I think it would be helpful to add some discussions here.**

Actually we believe that by separating the attribution of ozone into its two chemically distinct precursors, our method actually removes a lot of the ambiguity which could be caused if this were not done. For example, there are both anthropogenic and biogenic sources of both NO_x and reactive carbon, but much more ozone is produced by the interaction of anthropogenic NO_x with biogenic reactive carbon than the other way around. Without the separation of NO_x and reactive carbon in the attribution scheme, this detail risks being lost. As an example of this, the recent study of Mertens et al. (2020) (mentioned by this referee below) did not distinguish between biogenic NO_x and reactive carbon emissions, thus introducing ambiguity about the exact nature of the biogenic influence on ozone in their results.

Fundamentally, each ozone molecule produced chemically in the troposphere has two precursors, one NO_x, and one reactive carbon. Any source attribution system which does not distinguish between these two distinct types of precursors in some way must necessarily lose information about the origin of ozone. We don't see how we could possibly make this point any more clearly. It features prominently in the abstract, the first paragraph of the introduction, and in the structure of the manuscript itself.

> **Uncertainty:**
>
> **a) Resolution: The plume processes for ships are mentioned, which I think is an important process to be considered. But what is about model resolution in general? Does this affect city or harbour plumes as well?**

Yes, this process certainly does apply more generally than just to ship plumes. We have added a reference to Wild and Prather (2006) in the discussion of plume chemistry in order to bring this point out more.

b) Quality of emission data How sensitive are the results to uncertainties from emission data. Biogenic emissions, etc. ?

Uncertainties in emissions are a major issue in atmospheric chemistry modelling. Most emission inventories do not include uncertainty estimates, the inventory used in this study (Janssens-Maenhout et al., 2015) being no exception. The focus of our study is not the exploration of the sensitivity to uncertainties in emissions, but rather the application of our still relatively new tagging method to understand ozone source/receptor relationships using a well-established emission inventory. Specifically with regard to emissions, our study highlights the role of shipping, and of NMVOC emissions from East Asia as potentially important for further investigation in future work. This is one of the strengths of the tagging approach in general, which has already been pointed out by Grewe et al. (2010).

Minor Comments:

page 2 / line 53/54 Dahlmann et al. calculated explicitly the ozone production efficiency and showed that lightning and aviation NOx emissions are most efficient, in case you want to quantify the number of ozone molecules per emitted NOx.

We have added a reference to Dahlmann et al. (2011).

page 4 / line 108 Grewe (2013) provided a theoretical framework for taking into account these competing effects and compared that in a simple framework in Grewe et al (2010) and in a chemistry-climate model in Grewe et al. (2017). Please rephrase that this is NOT common to all tagging schemes.

We have replaced the word “problem” here with “challenge”, in order to avoid creating the impression that other tagging schemes are somehow deficient or incorrect. But we stand by the fundamental point that tropospheric ozone is primarily produced through interaction of two chemically distinct types of precursors, and that this does indeed create a challenge for ozone source attribution. Different methods make different choices about how they meet this challenge, which is why they can produce different results. A thorough review is beyond the scope of the present manuscript, but a reference is given to Butler et al. (2018), where such a review is presented.

line 115: There is also a nice table in recently published work by Mertens et al. (2020) (https://doi.org/10.5194/acp-20-7843-2020) discussing in detail the characteristics of these two methods, which might be helpful here.

Table 1 from Mertens et al. (2020) does make a nice contribution to the discussion of the complementary nature of tagging and perturbation approaches. We have added a reference.

line 115: Perhaps you want to adapt the naming consistently throughout the manuscript? contribution/share for tagging approaches changes/impact for perturbation? E.g. line 56 Hoor et al used perturbation approaches. The wording "contribution" in this respect might be misguiding.

We agree that the use of consistent language is important. As well as the discussion of Hoor et al. (2009) in the introduction, we have also modified the discussion of Jonson et al. (2020) in Section 3.2.2 to avoid using the term "contribution" to describe results obtained with perturbation approaches.

> **line 126: This statement might be misunderstood. The Butler et al tagging scheme is the only one, which separately analyses attribution of tropospheric ozone to its NOx and reactive carbon precursors, whereas the Grewe et al scheme is the only, which analysis attribution of tropospheric ozone to both together, NOx and reactive carbon precursors, taking competing effects into account.**

This comment is related to an earlier comment by the same referee regarding the nature of ozone source attribution. In addition to our earlier response, we have added another sentence to the manuscript here as well to re-emphasise the point that there are different approaches to ozone source attribution. We also note that the original manuscript already contains a reference to Grewe et al. (2017) as an example of ozone source attribution with tagging.
Since the referee has opened the discussion on different tagging approaches, we take the opportunity here to also comment on the recent work of Bates and Jacob (2020). Given the diversity of tagging approaches, for ozone we believe that an inter-comparison of these different approaches could be informative. We have added some text mentioning this to the paragraph in question, as well as to the end of Section 3.1.2, where we had already called for the widespread implementation of tagging techniques into models for use in model inter-comparisons.

> **line 159: Is there any reason why the spin-up differs?**

Yes, the reason for the longer spinup in the reactive carbon run is because the tag representing ozone produced from methane takes longer to spin up than any of the ozone tags in the NO_x run, consistent with the longer lifetime of methane. The other referee also asked for more detail about the spinup, and we have expanded the discussion here accordingly.

> **line 233: also Dahlmann et al. 2011.**

We have added the reference.

> **line 401: Please elaborate a little bit more on this comparison in terms of quantitative values. I guess we should expect a difference in the strength of the contribution vs perturbation? If so, can that be explained by the difference in the method?**

We do not believe that it is currently possible to perform an apples-to-apples comparison of contributions to surface ozone derived from perturbation studies as reported in the literature, with the contributions calculated here through tagging. We agree with previous work from the referee that these approaches can often yield different results (Grewe et al., 2010; Mertens et al., 2018). Given the other differences between our work and the previous literature on perturbation studies (different models, different emissions, different years, etc…) we tend to believe that any quantitative comparison could be misleading, so we prefer to stick with our cautious, qualitative comparisons.

The authors believe that the best way forward here is to carefully design future studies so that the source attribution methods themselves can be compared, rather than any other confounding factors which may be present. The work by Mertens et al. (2018) is a good example of a study which combines both perturbation and tagging in a consistent framework. We also believe that our own methane perturbation work in the present manuscript is also useful in this respect.

line 550: RF and human health effects are not calculated. Please re-phrase that this is a potential important impact based on literature and not your findings

We have modified the text to indicate that this is prior knowledge.

Figure 4: Please adapt the text in the figure to explicitly state that surface ozone is presented. Caption: Please include some more details, e.g. "Source-receptor relationships between annual averaged surface ozone volume mixing ratio and NOx and VOC emission type and region.", in order to clarify that with region the NOx emission and not the ozone production is meant.

We agree that the key word “surface” was missing from our caption, so we have included this. We find the referee’s suggested rewording of the caption somewhat awkward, so we have attempted to rewrite the caption along the lines suggested by referee.

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Attribution of ground-level ozone to anthropogenic and natural sources of NO_x and reactive carbon in a global chemical transport model

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Abstract. We perform a source attribution for tropospheric and ground-level ozone using a novel technique which accounts separately for the contributions of the two chemically distinct emitted precursors (reactive carbon and oxides of nitrogen) to the chemical production of ozone in the troposphere. By tagging anthropogenic emissions of these precursors according to the geographical region from which they are emitted, we determine source/receptor relationships for ground-level ozone. Our methodology reproduces earlier results obtained through other techniques for ozone source attribution, and also delivers additional information about the modelled processes responsible for intercontinental transport of ozone, which is especially strong during the spring months. The current generation of chemical transport models used to support international negotiations aimed at reducing the intercontinental transport of ozone show especially strong inter-model differences in simulated springtime ozone. Current models also simulate a large range of different responses of surface ozone to methane, one of the major precursors of ground-level ozone. Using our novel source attribution technique, we show that emissions of NO_x from international shipping over the high seas play a disproportionately strong role in our model system to the hemispheric-scale response of surface ozone to changes in methane, as well as to the springtime maximum in intercontinental transport of ozone and its precursors. We recommend a renewed focus on improvement of the representation of the chemistry of ship NO_x emissions in current-generation models. We demonstrate the utility of ozone source attribution as a powerful model diagnostic tool, and recommend that similar source attribution techniques become a standard part of future model inter-comparison studies.

1 Introduction

Tropospheric ozone plays a central role in the chemistry and self-cleansing capacity of the troposphere ~~(Monks et al., 2015)~~ (Crutzen, 1973; Monks et al., 2015), but at high concentrations close to the ground, it is harmful to human health ~~(Fleming et al., 2018) and vegetation (Mills et al., 2018)~~(Haagen-Smit, 1952; Fleming et al., 2018) and vegetation (Reich and Amundson, 1985; Mills et al., 201 . As well as being transported into the troposphere through exchange with the stratosphere, ozone can be formed through chemical reactions in the troposphere involving two chemically distinct precursors: oxides of nitrogen (collectively NO_x); and reactive carbon species~~(Crutzen, 1973)~~, including carbon monixide, methane, and volatile organic compounds (Crutzen, 1973; Atkinson, 2000) . Increases in tropospheric ozone since preindustrial times have been attributed primarily to increases in anthropogenic emissions of NO_x and methane, the most abundant reactive carbon species in the atmosphere (Wang and Jacob, 1998; Stevenson et al., 2013).

Ozone is long-lived enough in the troposphere to circumnavigate the Northern Hemisphere along the prevailing westerly winds (Jacob et al., 1999). Emissions of NO_x or reactive carbon in any Northern Hemisphere source region can thus contribute to the ~~baseline~~ ozone mixing ratio in any other region of the Northern Hemisphere. This long-range contribution to the ozone mixing ratio is often referred to as "baseline" ozone (Parrish et al., 2017; Derwent et al., 2018). Due to seasonal variation in the lifetime of ozone, this effect is strongest in spring and weakest in summer (Fiore et al., 2009). The ambient ozone mixing ratio at any location is a combination of ozone transported from the hemispheric background, and in-situ photochemical production. Recent analyses of long-term trends in baseline ozone in western regions of North America (Parrish et al., 2017) and Europe (Derwent et al., 2018) have shown increasing trends since reliable measurements began in the 1980s until approximately 2000-2010, and indicate that these trends may be beginning to reverse.

Chemical Transport Models (CTMs) are commonly used to interpret observations of ozone, and synthesise understanding of the fundamental processes controlling its origin and fate in the atmosphere in order to project future trends (eg. Young et al., 2018). The range in values of surface ozone mixing ratio over the Northern Hemisphere simulated by contemporary CTMs is extremely high (see for example our Figure 1 in Section 3), requiring the use of a large ensemble of models (eg. HTAP, 2010; Young et al., 2018). When compared with available measurements of ozone for the Northern Hemisphere (eg. Schultz et al., 2017), ensembles of global CTMs are generally able to simulate the spatial distribution and seasonal cycles of surface ozone, but are consistently biased high in the Northern Hemisphere, and have difficulty in simulating long-term trends (Young et al., 2018). Potential sources of uncertainty in CTMs include uncertainties in their chemical mechanisms (the representations of the relevant chemical reactions and their rates), their representation of atmospheric transport processes, as well as exchange processes between the atmosphere and the surface of the Earth, including emissions of the ozone precursors NO_x and reactive carbon.

The most important class of reactions for the formation of ozone in the troposphere is the reaction of NO (nitric oxide) with a peroxy radical, which is itself formed during the oxidation of reactive carbon (Atkinson, 2000). During this process, the NO is converted to NO_2 (nitrogen dioxide), which can be rapidly photolysed, ultimately forming ozone and recycling NO. The ozone production efficiency of NO_x (the combined concentration of NO and NO_2) can vary significantly depending on the location and timing of the NO_x emissions. In the polluted boundary layer, NO_x is rapidly removed from the atmosphere through the reaction of NO_2 with OH, forming HNO_3, which is subsequently lost via dry or wet deposition. Under less polluted conditions, NO_2 photolysis competes more effectively with HNO_3 production, allowing each unit of NO_x to react with a higher number of peroxy radicals before eventually being scavenged by OH, thus leading to higher ozone production efficiency per unit of NO_x. When NO_x is lofted into the free troposphere, its ozone productivity increases substantially (Jacob et al., 1996). Emissions of NO_x in the tropics are thus especially effective at producing tropospheric ozone due to being transported aloft due to deep convection (Zhang et al., 2016). NO_x emissions from both aircraft and lightning are also highly efficient at producing tropospheric ozone ~~(Beck et al., 1992)~~(Beck et al., 1992; Dahlmann et al., 2011). Combustion of fossil fuels is the largest source of NO_x in the atmosphere (Galloway et al., 2008).

Lawrence and Crutzen (1999) first pointed out that international shipping can have a disproportionately high influence on tropospheric ozone due to the disperse nature of NO_x emissions from this source. Hoor et al. (2009) quantified the ~~contribution to tropospheric ozone of~~ sensitivity of tropospheric ozone to NO_x emissions from different modes of transport (land, sea, and air), finding that aircraft emissions were most efficient at producing ozone (per molecule of NO_x emitted), followed by ships and then land transport. For near-surface ozone however, NO_x emissions from ships were shown to have a higher influence than NO_x emissions from aircraft. Ozone production from ship NO_x is however highly uncertain in current CTMs. Kasibhatla et al. (2000) and von Glasow et al. (2003) showed that global CTMs, due to their coarse resolution (usually in the hundreds of km) do not resolve the chemistry of ship exhaust plumes, which tends to remove NO_x from the atmosphere more quickly than simulated by the global CTMs, which effectively instantly dilute these emissions into very large volumes. Wild and Prather (2006) also showed that this effect applies more generally to other concentrated emission sources such as urban areas. Vinken et al. (2011) introduced a method for parameterising ship exhaust plume chemistry using lookup tables in their global CTM, but this method has not been widely adopted by the modelling community. Modelling of ship NO_x and its effects on the atmosphere remains a challenge for global CTMs.

The term “reactive carbon” encompasses a very wide range of atmospheric constituents (eg. Chameides et al., 1992; Goldstein and Galbally, 2007; Heald and Kroll, 2020). In contrast to NO_x, most of the reactive carbon emitted to the atmosphere is not of anthropogenic origin, but rather emitted from the biosphere. In this study we restrict our definition to molecules which yield peroxy radicals (either hydroperoxy radicals HO_2 or organic peroxy radicals RO_2) during their gas phase oxidation, and thus contribute to ozone formation by potentially converting NO to NO_2. This definition thus includes carbon monoxide (CO) and the large family of molecules known as Volatile Organic Compounds (VOC). The simplest VOC is methane, which is often considered separately from Non-Methane Volatile Organic Compounds (NMVOC) due to its very long lifetime in the troposphere. The ozone production potential of reactive carbon depends on the rate at which it is oxidised in the atmosphere, usually through reaction with the OH radical (Carter, 1994), as well as the subsequent chemistry of its oxidation products (Butler et al., 2011; Derwent, 2020). Most reactive carbon species have relatively short lifetimes in the troposphere due to their reaction with OH radicals. Methane, due to its exceptionally low reactivity is well-mixed in the troposphere. In contrast to other forms of reactive carbon, emissions of methane can contribute to ozone formation at any location in the troposphere where photochemical conditions are favourable (Fiore et al., 2008). Despite its low reactivity in comparison to other types of reactive carbon, methane is highly abundant, and has been shown to make a large contribution to tropospheric ozone (Wang and Jacob, 1998; Fiore et al., 2008; Stevenson et al., 2013; Butler et al., 2018).

PAN (Peroxyacetyl Nitrate) is an important reservoir species for both peroxy radicals and for NO_x (Fischer et al., 2014). Peroxyacetyl radicals are formed during the oxidation of a wide range of different types of NMVOC from a wide range of different sources. PAN is formed through reaction of peroxyacetyl radicals with NO_2, primarily in the polluted boundary layer where both are abundant (Atkinson, 2000). The lifetime of PAN is strongly temperature dependent. At colder temperatures higher in the troposphere, PAN can be transported over long distances, and act as a source of NO_2 and peroxyacetyl radicals in remote regions upon subsidence and thermal decomposition (Fischer et al., 2014). The chemical mechanisms and reaction rate constants involved in the formation and decomposition of PAN vary widely between CTMs (Emmerson and Evans, 2009;

Knote et al., 2015), leading to large inter-model differences in simulated PAN (Emmons et al., 2015). Fiore et al. (2018) has suggested that measurements of PAN at northern midlatitude mountaintop sites in spring could provide a useful constraint on CTMs, although the number of observations available is limited.

With careful interpretation, the results of ensembles of CTMs can be used to diagnose long-range transboundary transport of ozone, and to develop intercontinental source-receptor relationships, relating the effects of precursor emissions from different regions of the Northern Hemisphere to mixing ratios of ground-level ozone in other regions of the Northern Hemisphere. An example is the activity of the Task Force on Hemispheric Transport of Air Pollution (HTAP, 2010), which reports to the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and thus informs international policymaking for the mitigation of air pollution. The TF-HTAP studies used a “perturbation” approach, in which a control simulation was compared with sensitivity simulations in which emissions of particular ozone precursors were reduced by 20%. Combined 20% reductions of global average methane and remote anthropogenic emissions of $\mathrm{NO_x}$, CO, and NMVOC were shown to have an approximately equal effect on annual average ozone as 20% reduction of local precursor emissions, indicating the strong role of long-range transport in influencing surface ozone in the Northern Hemisphere. Results derived from the phase one of the TF-HTAP exercise (and the phase two exercise described by Galmarini et al., 2017) are discussed in more detail by Fiore et al. (2009); Reidmiller et al. (2009); Huang et al. (2017); Jonson et al. (2018).

An alternative approach to the perturbation technique for source attribution is “tagging” ~~(eg. Wang et al., 1998; Dunker et al., 2002; Grew~~
(eg. Wang et al., 1998; Dunker et al., 2002; Grewe et al., 2010; Emmons et al., 2012; Derwent et al., 2015; Grewe et al., 2017; Butler et al
. When applied to ozone source attribution in a CTM, this technique involves labelling (or “tagging”) modelled ozone with the identity of either the geographical region in which it is chemically produced, or with the identity of the emitted precursor(s) which ultimately led to its production. A common ~~problem~~ challenge faced by all tagging approaches is that the production of one molecule of ozone in the troposphere requires two precursors: one molecule of NO; and one peroxy radical (produced during reactive carbon oxidation). Should the ozone molecule inherit its tag from the emitted $\mathrm{NO_x}$, the emitted reactive carbon, or in some other way? Butler et al. (2018) provides a detailed review of the different approaches to answering this question, including the trade-offs made in each case. Butler et al. (2018) also describe a novel and unique tagging methodology which allows separate attribution of tropospheric ozone to both its $\mathrm{NO_x}$ and its reactive carbon precursor, at the cost of extra computational expense compared with other tagging methodologies. Recent work from Bates and Jacob (2020) takes the approach of defining an extended odd oxygen family including peroxy radicals, which effectively shifts the production of odd oxygen purely to photolysis reactions. Further comparison of different tagging approaches is beyond the scope of this manuscript, but remains an interesting topic for future work.

Tagging and perturbation approaches are complementary to each other ~~(Clappier et al., 2017; Thunis et al., 2019)~~(Clappier et al., 2017; T
. While tagging delivers information about the contribution of different emission sources to a pollutant of interest, perturbation studies deliver information about the sensitivity of pollutants to changes in emissions, including changes in the chemical lifetimes of pollutants in response to changes in emissions. In the absence of nonlinear chemical interactions, these two different approaches ultimately yield the same results, but for tropospheric ozone, which can under some circumstances show highly nonlinear interactions between its $\mathrm{NO_x}$ and reactive carbon precursors, these approaches can sometimes yield very

different results (Grewe et al., 2010; Mertens et al., 2018). Since air pollution mitigation strategies must involve some change in emissions, perturbation studies will always be necessary for policy-relevant modelling of atmospheric chemistry. However, tagging studies on their own can play a role in helping to identify which emissions to mitigate (Grewe et al., 2010). When combined with perturbation studies, tagging can reveal how the contribution of unmitigated sources to ozone changes in response to mitigation measures (Mertens et al., 2018). Butler et al. (2018) have also noted that tagging studies provide useful diagnostic information about model processes, and argued for their inclusion in model inter-comparison exercises. The method described by Butler et al. (2018) is currently the only available approach which provides separate attribution of tropospheric ozone to its NO_x and reactive carbon precursors. Other schemes take different approaches to the attribution of ozone to these two chemically distinct precursors. A thorough review of several different approaches is presented in Butler et al. (2018).

In this study we use the ozone tagging methodology previously described by Butler et al. (2018) to perform a source attribution for ground-level ozone to both NO_x and reactive carbon. This work builds on the work of Butler et al. (2018) by tagging anthropogenic emissions of NO_x and reactive carbon by their geographical source region, and examining the seasonal cycle of the surface ozone attribution in receptor regions as defined in the HTAP Phase 2 exercise. By performing separate attribution of ground-level ozone to both NO_x and reactive carbon (including methane), we hope to provide more useful information to inform emission mitigation scenarios. We also show how our tagging methodology can be used as a model diagnostic tool to understand the atmospheric budgets of ozone and PAN in more detail than previously possible, potentially informing efforts to reduce the currently high level of inter-model uncertainty. Furthermore, we examine the changing contributions of the different sources of NO_x and reactive carbon to a perturbation of the global methane burden, showing how the contribution of emissions from unmitigated sectors would respond to mitigation of methane emissions.

The tagging approach and model setup is described in Section 2. In Section 3 we evaluate our simulations against observations from TOAR and the ensemble of simulations from HTAP Phase 2, show the intercontinental source attribution for ozone and its precursors, and examine the response of this source attribution to a 20% perturbation in the global methane burden. Conclusions are drawn in Section 4.

2 Experiment design

Simulations are performed with CAM4-chem (Community Atmosphere Model version 4 with chemistry), a component of the CESM (the Community Earth System Model) version 1.2.2 (Tilmes et al., 2015; Lamarque et al., 2012) using the same model configuration as Butler et al. (2018). The model is run at a horizontal resolution of 1.9×2.5 degrees, with 56 vertical levels using specified dynamics for the year 2010 from the MERRA reanalysis (Rienecker et al., 2011). As in Butler et al. (2018), we have replaced the default chemical mechanism with a tagged mechanism based on an earlier version of the MOZART-4 mechanism Emmons et al. (2012). Our tagging system allows the attribution of tropospheric ozone to chemical production by either NO_x or reactive carbon precursors (as well as transport from the stratosphere). A complete attribution of tropospheric ozone to both kinds of precursors requires two model runs: one with NO_x emissions tagged; and another with reactive carbon emissions tagged. Chemical production of ozone in the stratosphere (primarily through photolysis of molecular oxygen), and other minor production pathways for tropospheric ozone are also tagged, as described in Butler et al. (2018). For both NO_x tagging and VOC tagging, the sum of the tagged ozone tracers is equal to the total ozone as simulated by the model.

As in Butler et al. (2018), anthropogenic emissions of NO_x, CO, and NMVOC for 2010 are taken from the EDGAR-HTAPv2 emission inventory (Janssens-Maenhout et al., 2015), biomass burning emissions are from GFEDv3 (van der Werf et al., 2010), and methane is held fixed at the surface to a global average value of 1760 ppb, as in Tilmes et al. (2015). Two simulations (base runs) are performed with this model setup: one in which all sources of NO_x are tagged as described below (the "NO_x-tagged" run); and one in which all sources of reactive carbon are tagged as described below (the "VOC-tagged" run). As in Butler et al. (2018), the length of the spinup period was one year for the NO_x-tagged run, and two years for the VOC-tagged run. The model was deemed to be spun up when the maximum difference between the simulated December mean surface ozone attributable to any tagged source was less than 1% in any two subsequent years of simulation.

With the exception of surface-based anthropogenic emissions of NO_x, CO, and NMVOC, the tag identities used in this study are identical to those used in Butler et al. (2018). In this study, all surface-based anthropogenic emissions are tagged with a label representing the geographical location at which the emissions occur. This approach allows attribution of simulated ozone to anthropogenic precursor emissions from specific locations. Specifically, anthropogenic emissions of NO_x and reactive carbon are tagged according to their Tier 1 Source Region as defined for the HTAP phase 2 multi-model ensemble experiment, which is described in more detail in (Galmarini et al., 2017). Due to computational constraints, not all of the HTAP Tier 1 regions are tagged in this study. Since the primary focus of this study is on the attribution of ground-level ozone in the Northern Hemisphere, only the major anthropogenic Northern Hemisphere source regions are tagged, while other anthropogenic sources are tagged with the label "Rest of the World". A full list of the tags used in the NO_x- and VOC-tagged runs is given in Table 1. The explicitly tagged source regions differ between the NO_x-tagged and VOC-tagged runs because VOC tagging is computationally more expensive than the NO_x-tagging (Butler et al., 2018). One important difference between this study and Butler et al. (2018) is that anthropogenic emissions of CO for each source region are tagged together with emissions of NMVOC in this study in order to save computational resources. For the emissions tagged as "Oceanic emissions" (Table 1) we note that the only source of NO_x from this region in our simulations is from shipping, and that the major source of reactive carbon is biogenic emissions of dimethyl sulphide (DMS).

In addition to the NO_x- and VOC-tagged base runs described above, we also perform two additional runs in order to investigate the response of tropospheric ozone to a perturbation in the tropospheric burden of methane: one with NO_x tagging; and another with VOC tagging. In each of these methane perturbation runs, the initial atmospheric methane burden and the methane mixing ratio imposed at the surface as a boundary condition are reduced by 20%. This translates to a surface methane mixing ratio of 1410 ppb in these methane perturbation runs. In these methane perturbation runs, all other sources of NO_x and reactive carbon are left unchanged. The methane perturbation runs also require two years of spinup for the model to arrive at steady state.

CAM4-chem in version 1.2.2 of the CESM has previously been evaluated by Tilmes et al. (2015), and the modified version used in this study has also been discussed thoroughly by Butler et al. (2018). In Section 3, we describe the key differences in methane and tropospheric ozone between our base simulation and the CAM4-chem simulation reported by Tilmes et al. (2015), and compare our simulated surface ozone with observations from TOAR (Schultz et al., 2017) as well as with the ensemble of CTM simulations from the HTAP phase 2 multi-model study (Galmarini et al., 2017). The full set of CTMs participating in the HTAP phase 2 multi-model ensemble is given in Table 3 of Galmarini et al. (2017). In this study we compare surface ozone from our base simulation with results from a subset of twelve CTMs: CAM-chem (simulations performed by NCAR); CHASER_re1; CHASER_t106; C-IFS; C-IFS_v2; EMEP_rv4.5; EMEP_rv48; GEMMACH; GEOS-Chem-ADJOINT; GEOS-Chem; OsloCTM3.v2; RAQMS. Details of the configurations used by each of these models in the HTAP phase 2 ensemble can be found in Galmarini et al. (2017), and references therein.

3 Results and discussion

All results presented in this study are based on the definition of the troposphere as the model grid cells below the level of 150 ppb of ozone. By design, the ozone simulated in our base model runs is identical with the simulation reported in Butler et al. (2018). Our simulation for 2010 produces a tropospheric ozone burden of 319 $\mathrm{Tg(O_3)}$, which is within one standard deviation of the multi-model mean reported by Young et al. (2013) for the year 2000 (337 ± 23 $\mathrm{Tg(O_3)}$). Our simulated tropospheric ozone burden is slightly higher than the burden reported by Tilmes et al. (2015) using a similar model setup (309 $\mathrm{Tg(O_3)}$), which could be due to the use of different emissions datasets. Our simulated tropospheric methane burden (4150 $\mathrm{Tg(CH_4)}$ is the same as reported by Tilmes et al. (2015), but our methane lifetime (due to oxidation in the troposphere by OH), at 7.59 years, is shorter than the 8.82 years reported by Tilmes et al. (2015), likely also due to the use of different emission datasets. Our methane lifetime is towards the lower end of the range (7.1 – 10.6 years) simulated in CTMs, as reported by Saunois et al. (2016).

In Figure 1 we compare our simulated monthly mean surface ozone mixing ratio for 2010 with data from TOAR and with the other models in the HTAP phase 2 CTM ensemble. Results are shown averaged over HTAP Tier 2 receptor regions, and only include grid cells for which TOAR observations are available. In general, most of the HTAP models overestimate the monthly mean surface ozone mixing ratio in regions for which observations are available, consistent with the high model bias reported by Young et al. (2018). Also apparent from Figure 1 is the large range in simulated surface ozone between members of the HTAP model ensemble, which is especially high in the northern spring, approaching a spread of approximately 30 ppb between the lowest and highest ensemble members, which is of a similar order to the northern hemisphere annual mean surface ozone itself. Our modelled monthly average surface ozone mixing ratio in the HTAP Tier 2 receptor regions is generally close to the HTAP ensemble mean, and usually within one standard deviation of the ensemble mean.

3.1 Source attribution of tropospheric ozone

The attribution of annual average tropospheric ozone to emissions of $\mathrm{NO_x}$ and reactive carbon precursors based on the source tags from Table 1 is shown in Figures 2 and 3 and quantified in Tables 2 and 3. Figures showing the attribution of monthly mean ozone are available in the Supplementary Material. For each tagged source, Tables 2 and 3 include the emissions of $\mathrm{NO_x}$ and reactive carbon (respectively, and where applicable), the contribution of each source to the 2010 average tropospheric ozone burden, the contribution to the Northern Hemisphere 2010 annual average surface mixing ratio, and (where applicable) the ozone production efficiency of each emission source (~~in~~ defined here as the contribution of each emission source to the tropospheric ozone burden, with units of moles of ozone ~~produced~~ per mole of N or C emitted). Figures 2 and 3 show the spatial distribution of the annual average surface ozone as attributed to each source of NO_x and reactive carbon, respectively. In Figure 2, ozone attributable to anthropogenic NO_x emissions in some source regions (specifically South East Asia, Northern Africa, the Middle East, Middle America, and Central Asia) has been added to the "Rest of the world" total in order to unify the definition of this source region with the definition of this region in the VOC-tagged run. The difference in the stratospheric contribution between the NO_x- and VOC-tagged runs is due to the role of NO_x produced in the stratosphere from dissociation of N_2O. Ozone produced in reactions involving this stratospheric source of NO_x are counted in our source attribution as stratospheric ozone, as described in Butler et al. (2018).

3.1.1 Attribution to NO_x emissions

Anthropogenic NO_x emissions from the three major high-latitude source regions (Europe, East Asia, and North America) contribute to high modelled ozone concentrations both locally and in the Northern Hemisphere background. Lightning NO_x, soil NO_x, and ozone input from the stratosphere all contribute additionally to modelled global background ozone. Emissions of NO_x from shipping contribute significantly to ozone over the major northern hemisphere ocean basins, which is also transported over continental regions. South Asia stands out in comparison with the other major Northern Hemisphere source regions, in that ozone produced from NO_x emitted in South Asia is relatively localised to the South Asian region itself, and not transported into the hemispheric background to the same extent as ozone produced from NO_x emissions in the other major Northern Hemisphere source regions.

Table 2 shows that NO_x emissions from lightning and aircraft are especially efficient at producing ozone in the free troposphere, consistent with previous work ~~(eg. Beck et al., 1992; Jacob et al., 1996)~~(eg. Beck et al., 1992; Jacob et al., 1996; Dahlmann et al., 2
. Similarly, surface emissions of NO_x from regions closer to the tropics (eg. South East Asia and Middle America) produce ozone more effectively due to rapid convective transport of emitted NO_x into the free troposphere, consistent with Zhang et al. (2016). Of the major Northern Hemisphere source regions, NO_x emissions from South Asia are the most efficient at producing ozone, consistent with a stronger role of vertical transport over this region. In contrast, NO_x emissions from the major anthropogenic source regions in the high northern latitudes (Europe, East Asia, and North America) are among the least productive of all global NO_x emissions, consistent with a relatively small amount of convective transport, leading to higher rates of NO_x removal. Despite their low ozone production efficiency, emissions of NO_x in the high northern latitudes contribute significantly to surface ozone across the northern hemisphere (Figure 2 and Table 2).

Table 2 also shows that NO_x emissions from shipping are also relatively efficient at producing ozone, which is also consistent with previous work (eg. Lawrence and Crutzen, 1999; Hoor et al., 2009). The high ozone production efficiency of ship emissions is due to their location in relatively pristine regions with few other sources of NO_x. Due to the high ozone productivity of ship emissions, and being emitted at relatively high latitudes, they contribute significantly to the Northern Hemispheric background (Figure 2 and Table 2). As noted above, the ozone production from ship NO_x is likely to be overestimated due to the artificial dilution of emissions into relatively coarse model grid cells.

Mertens et al. (2018) report a contribution of shipping to the tropospheric ozone burden of 18 Tg(O_3) using their tagging technique, and based on a model simulation with ship NO_x emissions of 6 Tg(N)yr^{-}1. In our study, we calculate a contribution of ship NO_x to tropospheric ozone of 19.9 Tg(O_3) based on ship NO_x emissions of 4.28 Tg(N)yr^{-}1, implying a much higher ozone production efficiency for ship NO_x in our study. Since the tagging technique used by Mertens et al. (2018) is based on the technique described by Grewe et al. (2017), which combines the effects of tagged NO_x and reactive carbon precursors into a single tagged ozone molecule during ozone production, we do not expect our results to be directly comparable. Since shipping emits significantly more NO_x than reactive carbon, we would expect the combinatorial tagging approach of Mertens et al. (2018) to attribute less ozone to shipping than our method, as the ozone produced from ship NO_x would also be partially attributed to the reactive carbon precursor involved in the ozone production. Indeed, Mertens et al. (2018) report maximum contributions of shipping to surface ozone of about 10 ppb in summer over major Northern Hemisphere ocean basins. In our study, surface ozone attributable to shipping over these regions can exceed 20 ppb (see the Supplementary Material).

3.1.2 Attribution to reactive carbon emissions

Methane and biogenic emissions clearly stand out as major reactive carbon precursors to tropospheric ozone, contributing 35% and 24% respectively to the tropospheric ozone burden in our simulation. Anthropogenic emissions of reactive carbon (excluding biomass burning) together contribute about 14 % to the tropospheric ozone burden. The relatively low influence of anthropogenic reactive carbon emissions on ground-level ozone has been noted elsewhere (eg. HTAP, 2010; Butler et al., 2018), but despite this low overall ozone productivity, anthropogenic reactive carbon emissions from source regions in higher northern latitudes still contribute disproportionately highly to surface ozone in the Northern Hemisphere (Table 3).

Due to the emissions of CO being tagged together with emitted VOC in this study, the contribution of each tagged source to the tropospheric ozone burden (and therefore also the ozone production efficiency of each tagged source) is a mixture of ozone production due to emitted CO and emitted NMVOC. The ozone attributed to methane oxidation in Table 3 is due do all stages of methane oxidation in the MOZART-4 chemical mechanism, including the final step in which CO from earlier stages of methane oxidation is itself oxidised to CO_2. The oxidation of CO can produce at maximum one peroxy radical (HO_2). The maximum ozone production potential of CO is therefore 1 mole of ozone per mole of emitted CO. VOC (including methane) can produce significantly more ozone per mole emitted carbon, when taking into account the subsequent oxidation of the initial oxidation products ~~(Butler et al., 2011)~~(Bowman and Seinfeld, 1994; Atkinson, 2000; Butler et al., 2011). Future studies using this tagging methodology should consider tagging CO emissions separately from NMVOC emissions if they aim to determine the ozone production efficiency of anthropogenic NMVOC emissions from different world regions. Butler et al. (2018) did tag NMVOC emissions separately from CO emissions, but did not tag anthropogenic emissions separately according to their geographical region. We reexamined the output of the otherwise identical VOC-tagged run described by Butler et al. (2018) in order to determine the ozone production efficiency of NMVOC emissions from anthropogenic, biomass burning, and biogenic sources. Respectively, these are 0.0580, 0.0354, and 0.0268 (mol(O_3)/mol(C)). The ozone production efficiency of biogenic NMVOC recalculated from Butler et al. (2018) is not significantly different from the value reported here in Table 3, reflecting the relative minor contribution of CO to the total amount of emitted biogenic reactive carbon. For biomass burning and anthropogenic sources however, the ozone production efficiency of NMVOC emitted from these sources is greater than the corresponding value from Table 3, reflecting the fact that the numbers from Table 3 also include emissions of CO.

~~Interestingly, we~~ We note that methane has a higher ozone production efficiency per unit of reactive carbon (0.0689 mol ~~mol^{-1}~~/mol(C), Table 3) than any of the NMVOC in our runs. The low ozone production efficiency of biogenic NMVOC is consistent with large amounts of isoprene being emitted in remote regions under low-NO_x conditions, where loss of peroxy radicals through reaction with other peroxy radicals could be expected to dominate (Atkinson, 2000). It might however be expected that anthropogenic NMVOC would have a higher ozone production efficiency, due to their being co-emitted with anthropogenic NO_x, favouring the conversion of NO to NO_2 through reaction with peroxy radicals, and thus the production of ozone. The relatively low production efficiency of anthropogenic NMVOC in our model runs could be due to the relatively simple chemistry of methane oxidation being well-described in the version of the MOZART-4 chemical mechanism used here, in which the relatively complex chemistry of the higher NMVOC has been simplified. Coates and Butler (2015) noted that the ozone production potential of NMVOC in simplified chemical mechanisms tended to be lower than the more comprehensive Master Chemical Mechanism (Saunders et al., 2003). Utembe et al. (2010) previously noted increased tropospheric ozone in a CTM when using a more explicit oxidation mechanism for NMVOC. The extremely low ozone production efficiency of reactive carbon from oceanic sources in Table 3 is due to the lack of any ozone forming pathways in the oxidation of dimethyl sulphide (DMS) in the MOZART-4 chemical mechanism as used in this study. DMS is the dominant source of reactive carbon over the oceans in our model simulations.

To our knowledge, the only other study to perform source attribution of global tropospheric ozone specifically to reactive carbon precursors is Butler et al. (2018), on which the present study builds. Here, we attribute 113 Tg of ozone to methane oxidation (Table 3). Grewe et al. (2017) attribute 45 Tg of ozone to methane using their tagging approach, which combines the effects of tagged NO_x and reactive carbon precursors into a single tagged ozone molecule during ozone production. Ozone production due to methane oxidation under their combinatorial tagging approach would be expected to also include attribution to the source of NO_x involved in the ozone production. We would thus expect Grewe et al. (2017) to attribute approximately half of the amount of ozone to methane as we would. Doubling the value reported by Grewe et al. (2017) yields 90 Tg of ozone attributable to methane oxidation, which is much closer to our value of 113 Tg.

Widespread implementation of tagging techniques for separated tagging of NO_x and reactive carbon emissions in other CTMs, along with systematic inter-comparisons of their results could help to understand differences in the simulated budgets of tropospheric ozone. Due to the variety of approaches taken by different tagging techniques (summarised in Butler et al., 2018) , an inter-comparison of a range of different tagging techniques with other methods for ozone source attribution could be informative.

3.2 Source-receptor relationships for ozone

3.2.1 Annual average surface ozone

Figure 4 shows the modelled annual average surface ozone concentration in the five major HTAP Tier 1 regions in the northern hemisphere (Europe, Russia/Belarus/Ukraine, South Asia, East Asia, and North America), including a full attribution of ozone in each of these regions to all sources, including transport from the stratosphere and emitted precursors of both $\mathrm{NO_x}$ and reactive carbon. Annual average ozone in most of the regions shown in Figure 4 is close to the Northern Hemisphere annual average of 30 ppb (Table 2), except in South Asia and East Asia, where the annual average surface ozone mixing ratio is closer to 40 ppb. The difference in each case is primarily due to a larger source of ozone produced from locally emitted precursors. Transport from the stratosphere contributes approximately 2–4 ppb to annual average surface ozone depending on the receptor region, consistent with the 2.91 ppb contribution of stratospheric ozone to the annual average surface ozone in the Northern Hemisphere average surface ozone (Table 3). As already shown in the previous section, anthropogenic sources of $\mathrm{NO_x}$ dominate other $\mathrm{NO_x}$ sources as ozone precursors, while the major reactive carbon precursors are methane and BVOC.

In each of the five regions shown in Figure 4, natural sources and long-range transport of ozone produced from extra-regional anthropogenic precursors together contribute more to the annual average surface ozone than anthropogenic emissions within the region itself. In each region, the local anthropogenic $\mathrm{NO_x}$ emissions produce more ozone than can be attributed to anthropogenic $\mathrm{NO_x}$ emissions in any other Tier 1 regions, but with only one exception (South Asia), the combined contribution of external anthropogenic $\mathrm{NO_x}$ emissions to annual average surface ozone is greater than the local contribution. The importance of long-range transboundary transport of ozone has been noted elsewhere (HTAP, 2010).

While anthropogenic precursor emissions from South Asia contribute significantly to surface ozone within the South Asia region, they contribute relatively little to surface ozone in the other four regions shown in Figure 4. This is also consistent with the surface ozone maps in Figure 2, and the higher ozone productivity of $\mathrm{NO_x}$ emissions from South Asia when compared with the other major Northern Hemisphere source regions (Table 2). Emissions of ozone precursors (particularly $\mathrm{NO_x}$) from South Asia are transported efficiently into the free troposphere, where they contribute disproportionately to the global tropospheric ozone burden (as also noted by Zhang et al., 2016), but the contribution of South Asian emissions to surface ozone in other parts of the Northern Hemisphere is disproportionately smaller than emissions from the other HTAP Tier 1 regions.

3.2.2 Seasonal cycles of surface ozone

Figures 5, 6, and 7 show the seasonal cycles of surface ozone in the three selected Tier 2 regions “North West Europe”, ”North East China”, and “North West United States” respectively. These regions are selected in order to compare two regions on the western side of their respective continents (where long-range transport is expected to be important) with a region on the eastern side of its continent that is also a major source region. A set of figures for other HTAP Tier 2 regions, with a complete attribution of surface ozone to all tagged HTAP Tier 1 source regions is available in the Supplementary Material. In each of Figures 5, 6, and 7, results are shown for both $\mathrm{NO_x}$- and VOC-tagging. In each receptor region, the contribution of long-range transport due to extra-regional anthropogenic emissions from HTAP Tier 1 regions is shown both in aggregate (top panels) and by individual Tier 1 source region (bottom panels). The definition of the “Rest of the world” ozone tracer has been harmonised between the NO_x- and VOC-tagged runs in these figures. Consistent with the annual averages from Figure 4, anthropogenic NO_x sources also dominate the seasonal cycle of modelled ozone, while the major reactive carbon precursors of ozone are methane and BVOC.

All three receptor regions show a seasonal cycle of ozone with a spring-summer ozone maximum superimposed on a year-round ozone baseline. The summertime maximum in ozone is clearly due to local photochemical production from the combination of locally-emitted anthropogenic NO_x and biogenic VOC. The strong role of locally-emitted precursors in the production of ozone in summer is consistent with earlier work (eg. Reidmiller et al., 2009; Huang et al., 2017; Jonson et al., 2018; Han et al., 2019), while the importance of biogenic VOC emissions, especially isoprene, for ozone production in summer has also been noted elsewhere (eg. Chameides et al., 1992; Andersson and Engardt, 2010; Han et al., 2019). Biogenic emissions of NO_x (from soils) also contribute to this summertime maximum in local photochemical ozone production in all three of the regions shown in Figures 5, 6, and 7, but to a much smaller extent than anthropogenic NO_x emissions.

The year-round baseline ozone in our model simulations in all three receptor regions can be primarily explained by slower photochemistry involving methane as the reactive carbon precursor, in combination with extra-regional anthropogenic NO_x (Figures 5, 6, and 7). ~~Both show a minimum contribution in winter of about 10 ppb in all three receptor regions.~~ The contribution of methane to surface ozone is slightly larger in summer, coinciding with the peak in local anthropogenic NO_x emissions, consistent with local photochemical ozone production from enhanced local methane oxidation. The contribution of extra-regional anthropogenic NO_x to surface ozone is largest in spring, coinciding with the peak in the contribution of extra-regional anthropogenic reactive carbon, consistent with long-range transboundary transport of ozone produced elsewhere.

Maxima in springtime ozone have previously been linked to long-range transboundary transport in all major receptor regions (HTAP, 2010; Lin et al., 2012; Jonson et al., 2018; Ni et al., 2018). This transported ozone can be attributed to input from the stratosphere, as well as extra-regional anthropogenic emissions of NO_x and reactive carbon. In our simulations, the contribution of stratospheric ozone peaks around March, while the contribution of extra-regional anthropogenic emissions tends to peak around April, when it contributes more strongly to monthly average surface ozone in each region than local anthropogenic NO_x (Figures 5, 6, and 7). In all Northern Hemisphere regions, the springtime peak in the contribution of extra-regional anthropogenic reactive carbon is smaller ~~, but more pronounced~~ than the corresponding springtime peak in the contribution of extra-regional anthropogenic NO_x. Previous work has identified uncertainties in the treatment of ozone production from NMVOC oxidation as a potential source of inter-model differences (eg. Emmerson and Evans, 2009; Utembe et al., 2010; Coates and Butler, 2015). The relatively large influence of anthropogenic NMVOC on springtime ozone (compared with its influence during other time of the year) could be a contributing factor to the large spread in springtime ozone simulated by current generation CTMs (Figure 1).

NO_x from shipping is the largest single contributor to springtime transboundary ozone transport in all three receptor regions shown here. We note however that the coarse resolution of our model (2 degrees) would be expected to exaggerate the effects of ship NO_x on ozone production due to rapid dilution of the emissions (von Glasow et al., 2003), as well as exaggerate the transport of NO_x and ozone near coastlines due to unrealistically high diffusion between adjacent land and ocean grid cells. The contribution of shipping emissions to surface ozone in our simulations should thus be considered an upper bound, especially in coastal regions. The high contribution of ship NO_x to summertime ozone in Europe (Figure 5) may be an artefact of coarse model resolution, combined with high shipping volume near coasts in the Eastern North Atlantic Ocean as well as the North Sea. Early work by Lawrence and Crutzen (1999) showed a stronger influence of ship NO_x on surface ozone in North West Europe than on any other continental region. Jonson et al. (2018) show that the only other CTM in the HTAP phase 2 ensemble to report the results of a perturbation of shipping emissions (the EMEP_rv48 CTM with a resolution of 0.5 × 0.5 degrees) shows a similar magnitude for the influence of ship NO_x on summertime ozone in Europe as for springtime ozone. Lupaşcu and Butler (2019), using a regional model at 50×50 km resolution and a similar ozone tagging system as used in the present study, showed that the contribution of ship NO_x to ozone in coastal regions of Europe reaches a maximum level in summer. Jonson et al. (2020), using a global model with a resolution of 0.5 × 0.5 degrees showed that shipping near coastal ~~regions contributes significantly to~~ strongly influences ozone over North West Europe in both spring and summer, while NO_x emissions from shipping on the high seas ~~makes a stronger contribution to~~ have a stronger influence on European ozone in spring than in summer. In contrast, the study of Aksoyoglu et al. (2016), using a higher-resolution regional model (20 ×20 km) for Europe, does not indicate such a strong role for ship NO_x on summertime ozone over Europe.

In other receptor regions, the influence of ship NO_x emissions on surface ozone is largest in spring (Figures 6 and 7), suggesting a stronger influence of NO_x emissions over the high seas on springtime ozone in our simulations in these regions. Model-dependent inconsistencies in the treatment of ship NO_x emissions may play a role in the large spread of simulated ozone between models in springtime (Figure 1). Future work should examine the contribution of ship NO_x emissions to ozone in both spring and summer, using model systems which include both better representations of plume dilution over the major shipping routes, ~~and~~ more refined attribution to shipping emissions from coastal regions and the high seas, as well as higher resolution over receptor regions.

Previous work has indicated a strong influence of anthropogenic emissions from both North America and East Asia on springtime ozone in Europe (Jonson et al., 2018), a strong influence of East Asian emissions on springtime ozone in North America (Lin et al., 2012), and a diverse range of intercontinental influences on springtime ozone in East Asia (Ni et al., 2018). Direct numerical comparison of our results with these previous studies is difficult due to the different methodologies used. These previous studies all employed the perturbation technique to determine the influence of all anthropogenic emissions (both NO_x and reactive carbon) from each source region, while this work uses a tagging approach which separately attributes ozone to emitted NO_x and reactive carbon. Qualitatively, our results as shown in Figures 5, 6, and 7 do however appear consistent with this earlier work. Comparison of the NO_x-tagged and VOC-tagged results in these Figures shows that anthropogenic NO_x emissions from most source regions have a stronger influence on springtime ozone in any given receptor region than anthropogenic emissions of reactive carbon. The only exception to this is East Asia, where reactive carbon emissions are substantially higher than in other HTAP Tier 1 source regions (Table 3). Reactive carbon emissions from East Asia contribute approximately equally to springtime ozone in North America as East Asian NO_x emissions, and in Europe, East Asian reactive carbon contributes more to springtime ozone than East Asian NO_x.

3.3 Long-range transport of ozone precursors

Fiore et al. (2018) has suggested that measurements of the abundance of PAN at mountaintop sites in spring may be useful as an indicator of intercontinental transport of ozone and its precursors, as well as being a diagnostic for uncertainties in CTM simulations, which show large inter-model differences in simulated PAN (Emmons et al., 2015). The column integrated density of PAN in the lower troposphere (defined here as the model layers between 500 and 800 hPa) in the three HTAP Tier 2 receptor regions “North West Europe”, ”North East China”, and “North West United States” are shown in Figures 8, 9, 10. A set of figures for other HTAP Tier 2 regions, with a complete attribution of surface ozone to all tagged HTAP Tier 1 source regions is available in the Supplementary Material. Simulated PAN is highest in late winter to early spring, consistent with earlier work (Fischer et al., 2014; Fiore et al., 2018). The extra-regional contribution to PAN is also highest in spring, and this is due primarily to anthropogenic NMVOC, also consistent with Fischer et al. (2014).

Our model simulations with NO_x- and VOC tagging provide a unique opportunity to examine the origin and fate of PAN as simulated in our model, since this allows simultaneous attribution of simulated PAN to both is NO_x precursor and its reactive carbon precursor. Comparison of the bottom two panels in each of Figures 8, 9, 10 shows consistently that for any given land-based HTAP Tier 1 source region, the anthropogenic NMVOC emissions contribute more to PAN formation than the anthropogenic NO_x emissions from that region to the PAN modelled in all HTAP Tier 2 receptor regions. The balance of extra-regional PAN in all cases is due to NO_x emissions from shipping. In our simulations, significant amounts of PAN are formed downwind of the regions in which the anthropogenic NMVOC precursors are emitted, often through reaction with NO_x emitted from shipping. A strong influence of anthropogenic NO_x emissions on PAN in the northern mid-latitudes is consistent with the results shown by Fischer et al. (2014) (their Figure 7, which does not distinguish between different sources of anthropogenic NO_x).

Figures 8, 9, and 10 also show that the reactive carbon component of PAN is generally more persistent than the NO_x component. For example, the contribution of anthropogenic NMVOC from North America to springtime PAN over East Asia is only slightly lower than its contribution to springtime PAN over Europe, which is much closer to North America considering the prevailing westerly winds (bottom right panels of Figures 8 and 9). In contrast, the contribution of anthropogenic NO_x from North America to springtime PAN in East Asia is substantially less than its contribution to springtime PAN over Europe (bottom left panels of Figures 8 and 9).

3.4 Attribution of Northern Hemisphere total organic reactivity

We examine the Northern Hemisphere budget of reactive carbon in more detail in Figure 11. This figure shows the seasonal cycle of the Northern Hemisphere column-integrated total reactivity with respect to the OH radical of all reactive carbon containing species in our simulation, attributed to their emission source. The total OH reactivity of reactive carbon species of an airmass is often linked to its ozone production potential (Chameides et al., 1992; Kleinman et al., 2002). The OH reactivities shown in Figure 11 include in each case the OH reactivity of the primary emitted species, as well as the OH reactivity of each carbon-containing oxidation product. These were calculated using monthly averaged output of the modelled concentration of each carbon-containing species (including its associated tags), and the temperature- and pressure-dependent rate coefficients for their reaction with the OH radical, then averaged over all Northern Hemisphere grid cells, weighted by air density.

The total Northern Hemisphere OH reactivity of reactive carbon remains fairly constant year-round at about $0.6 – 0.7\ \mathrm{s}^{-1}$, but the seasonal cycles of the OH reactivity attributable to different reactive carbon sources show more variability. Methane (and its oxidation products) contribute about $0.2 – 0.3\ \mathrm{s}^{-1}$ (almost half of the total hemispheric reactivity), with a slight maximum in the summer, consistent with enhanced oxidation (and thus enhanced availability of more reactive methane oxidation products) due to higher OH in summer. The contributions of anthropogenic and biogenic reactive carbon sources to total hemispheric reactivity are similar, ranging between about $0.1 – 0.3\ \mathrm{s}^{-1}$, but with distinct seasonal cycles. The reactivity of biogenic carbon is highest in summer-autumn (consistent with the Northern Hemisphere growing season), while reactivity of anthropogenic carbon is highest in winter-spring (consistent with constant year-round anthropogenic emissions, and a build-up of reactive carbon over winter due to lower hemispheric OH). The build-up of anthropogenic reactive carbon throughout the Northern Hemisphere over winter, combined with the resumption of OH chemistry in spring is consistent with the disproportionate effect of extra-regional anthropogenic reactive carbon on springtime ozone seen in Figures 5, 6, and 7. Uncertainties in the model chemical mechanisms associated with the oxidation of anthropogenic NMVOC (eg. Emmerson and Evans, 2009; Utembe et al., 2010; Coates and Butler, 2015) may thus also contribute to the large spread in simulated ozone seen in the HTAP ensemble during spring (Figure 1).

Figure 11 also shows the geographical origin of Northern Hemisphere anthropogenic carbon reactivity. Emissions of reactive carbon from East Asia stand out as the single major source of enhanced anthropogenic carbon reactivity in winter and spring in our simulations. This is consistent with the high emissions of reactive carbon from this region in 2010 noted earlier (Table 3). Growth in NMVOC emissions from East Asia may have continued since this time (Li et al., 2019), while $\mathrm{NO_x}$ emissions have been decreasing (Liu et al., 2017). Increasing trends in local production of ozone during summer over East Asia (eg. Li et al., 2018) should be associated with increased oxidation of reactive carbon, and thus potentially less export of reactive carbon into the Northern Hemisphere background during summer. We expect, however, that increasing emissions of reactive carbon in East Asia should lead to an increased build-up of East Asian reactive carbon in the Northern Hemisphere over winter, and thus also to increased East Asian contribution to extra-regional springtime ozone in other parts of the Northern Hemisphere.

Our tagging technique is currently the only one we know of which is capable of examining the budget of reactive carbon in the level of detail presented in this study. The separate tracking of the carbon-containing and nitrogen-containing components of PAN is particularly informative, suggesting that significant amounts of PAN are formed downwind of source regions in our model, especially during winter and spring, due to a build-up of anthropogenic reactive carbon over winter when photochemistry is relatively slow. Given the large variety in model representations of NMVOC chemistry, including PAN formation and decomposition processes (Emmerson and Evans, 2009; Knote et al., 2015) and the large inter-model differences in simulated PAN (Emmons et al., 2015), the widespread implementation of similar tagging diagnostics in other CTMs may help to provide additional information about the origin and fate of simulated PAN, and more generally about the influence of reactive carbon on atmospheric composition. In combination with routine mountaintop observations of springtime PAN, this may aid understanding of the global PAN budget (Fiore et al., 2018) and other processes responsible for intercontinental transport of air pollution. Better constraints on these chemical and transport processes should also help to reduce inter-model differences in simulated springtime ozone (Figure 1).

3.5 Tropospheric ozone sensitivity to methane

We performed an additional set of model runs with both NO_x- and VOC-tagging with the methane surface boundary condition reduced from 1760 ppb to 1410 ppb, a reduction of 350 ppb, or 20%. This perturbation can also be expressed as an increase of 25%. Here we interpret the methane perturbation run in terms of the atmospheric response to a 25% increase in the methane surface mixing ratio at steady state.

In response to the 25% increase in the imposed surface mixing ratio of methane, the total tropospheric burden increased by 776 Tg(CH_4), an increase of 23%. The strength of the annual tropospheric chemical sink of methane due to OH increased by 72.5 Tg(CH_4), or 15.2%. The corresponding increase in the methane lifetime was 0.48 years, or 6.75%. The relatively small growth in the chemical methane sink compared with the magnitude of the perturbation in methane itself is consistent with the feedback of methane on its own lifetime due to depletion of OH (Prather, 1996). Table 4 shows the response of the tropospheric ozone burden (and the contributions of different reactive carbon precursors) to the 25% increase in the imposed surface mixing ratio of methane. The 1 ppb simulated increase in Northern Hemisphere surface ozone in response to a 25% increase in methane burden is consistent with previous work (HTAP, 2010). The 9.22 Tg increase in tropospheric ozone burden is also consistent with the review of Fiore et al. (2008), who derived a sensitivity of 0.11–0.16 Tg(O_3) per Tg(CH_4)yr^{-1} emitted based on an analysis of the literature. We calculate 0.13 Tg(O_3) per Tg(CH_4)yr^{-1} based on our results.

The relative increase in tropospheric ozone ~~due~~ attributed by our tagging scheme to methane (13.0%) is comparable to, but slightly smaller than the increase in the magnitude of the chemical methane sink due to OH (15.2%), consistent with the troposphere as a whole becoming slightly more NO_x-limited with increasing methane. The ~~relative~~ absolute increase in the total ozone burden (~~2.98%)~~9.22 Tg(O_3)) is, however, significantly lower than the increase in the ~~ozone produced from methane oxidation~~burden of ozone attributed by our tagging scheme to methane (13.0 Tg(O_3). When the methane burden is increased, the contribution of every other reactive carbon source to the tropospheric ozone burden decreases (each by approximately 1 – 2%) to partially offset the increased ozone production from methane oxidation. This is also consistent with a slightly more NO_x-limited atmosphere with increasing methane. In a future with an increased methane burden, control of NMVOC emissions could be expected to be less effective at large-scale reduction in annual average ground-level ozone.

Table 5 shows the change in the contributions of different NO_x sources to tropospheric ozone in response to the 25% increase in methane burden. As expected, all NO_x sources become more productive when the total atmospheric burden of reactive carbon is increased (consistent with the troposphere as a whole becoming more NO_x-limited). The increase in the productivity of the different NO_x sources under an increased burden of methane is however not uniform. Ozone production due to NO_x from shipping stands out as highly sensitive to the global methane burden in our simulations. Ship NO_x accounts for almost 30% of the 1 ppb increase in Northern Hemisphere average surface ozone when the methane burden is increased by 25% (Table 5), despite being a much smaller percentage of total global NO_x emissions (Table 2).

The spatial distribution of the increase in annual average surface ozone from ship $\mathrm{NO_x}$ in response to the 25% increase in methane is similar to the spatial distribution of surface ozone due to ship $\mathrm{NO_x}$ in our base run (Figure 2). Figures showing the response of attributed surface ozone are available in the Supplementary Material. The response is largest over the major Northern Hemisphere ocean basins, but also extends over continental regions. The seasonal cycle of the increase in annual average surface ozone from ship $\mathrm{NO_x}$ in the three HTAP Tier 2 regions examined here in response to the 25% increase in methane is similar to the seasonal cycle of surface ozone due to ship $\mathrm{NO_x}$ in our base run (Figures 5, 6, and 7). The maximum response of surface ozone from ship $\mathrm{NO_x}$ to rising methane is simulated over the major Northern Hemisphere ocean basins in summer (which in our simulations influences surface ozone in North West Europe, Figure 5), while the influence of this response over most Northern Hemisphere continental regions is generally higher in winter-spring (as seen in North East China, Figure 6).

Previous work (Lawrence and Crutzen, 1999) has noted the disproportionate influence of ship $\mathrm{NO_x}$ on tropospheric ozone due to the diffuse and widespread nature of this source over regions which would otherwise have very low mixing ratios of $\mathrm{NO_x}$. Fiore et al. (2008) noted that the response of surface ozone to increased methane was especially strong in ship tracks. Myhre et al. (2011) also showed that ship $\mathrm{NO_x}$ emissions reduce the global methane lifetime much more than terrestrial $\mathrm{NO_x}$ emissions. We note again that the contribution of ship $\mathrm{NO_x}$ to ozone in our simulations (as in most current-generation CTMs) is likely to be an overestimate due to the unrealistic dilution of these emissions into coarse model grid cells (von Glasow et al., 2003), and the lack of explicit plume chemistry (Vinken et al., 2011). We do expect however, that the interaction between ship $\mathrm{NO_x}$ and methane for ozone production would persist in our model even with a more realistic treatment of ship emissions, since this interaction is likely due to the location, rather than the magnitude of ship emissions. We are not aware of any previous work linking the combined influence of these two sources to a potentially disproportionate influence on background ozone in the Northern Hemisphere, and on modelled surface ozone air quality in inhabited regions of the Northern Hemisphere, especially in spring. Given the current uncertainty in attribution of recent trends in methane (Turner et al., 2019) and the potential for future increases in methane emissions, combined with slower reductions in $\mathrm{NO_x}$ emissions from international shipping than from other sectors (eg. the SSP5 future emission scenario Rao et al., 2017), we expect that model simulations of future background ozone in the Northern Hemisphere, especially during spring, may come to be increasingly influenced by ozone produced through the interaction of methane and ship $\mathrm{NO_x}$. Future work should investigate the ozone production through interaction of these two sources in more detail.

4 Conclusions

We have performed a source attribution for tropospheric ozone in a chemical transport model using a novel technique which separately accounts for the influence of both the emitted $\mathrm{NO_x}$ and the emitted reactive carbon precursors on simulated tropospheric ozone. By tagging anthropogenic emissions of $\mathrm{NO_x}$ and reactive carbon according to their geographical region we have calculated source/receptor relationships for the Northern Hemisphere. The results of our study are consistent with previous work, and provide a number of important new insights of relevance to both the mitigation of intercontinental transboundary air pollution and ongoing efforts to reduce the uncertainty in the current generation of chemical transport models.

Consistent with previous work, annual average ground-level ozone in all major Northern Hemisphere regions is primarily influenced by extra-regional emissions of both NO_x and reactive carbon. In all cases, local anthropogenic emissions of ozone precursors have a smaller influence on annual average ozone than the combined effect of precursor emissions from the rest of the world. As a reactive carbon precursor, methane contributes 35% of the tropospheric ozone burden, and 41% of the Northern Hemisphere annual average surface mixing ratio, more than any other source of reactive carbon. Our novel tagging methodology also reproduces the well-known dependence of summer ozone maxima on local emissions of anthropogenic NO_x and biogenic reactive carbon, and the enhanced importance of intercontinental transport of ozone from remote anthropogenic sources in spring. Consistent with previous work, we find that emissions of NO_x at low latitudes produce free-tropospheric ozone more effectively due to more efficient vertical transport. We show, however, that NO_x sources at higher northern latitudes have a stronger influence on ground-level ozone, which ~~has~~ is known to have a lower radiative forcing but a higher influence human health and ecosystems.

The current generation of chemical transport models has particular difficulty in simulating the intercontinental transport of ozone, as shown by the large spread in ensemble simulations of ground-level ozone during the spring months. We show that our tagging methodology can deliver detailed diagnostic information about the origin and budget of springtime ozone in our model, along with information about the springtime budget of peroxyacetyl nitrate (PAN), which is also associated with springtime long-range transport and ozone production. We show that a substantial proportion of the free-tropospheric PAN simulated by our model in spring is not produced in the polluted boundary layer over the major anthropogenic source regions, but is rather produced in our model downwind of these regions through the interaction of transported anthropogenic reactive carbon and NO_x emitted from international shipping. Reactive carbon of anthropogenic origin (and its oxidation products, including PAN) builds up in our model across the entire Northern Hemisphere during the winter months, and then contributes in our simulations to a short burst of hemispheric-scale ozone production during spring. In all but the most polluted source regions, anthropogenic NMVOC do not make a significant contribution to simulated ground level ozone in any other season but spring.

We showed here that export of anthropogenic reactive carbon from East Asia may be playing a dominant role in contributing to the build up of reactive carbon in the Northern Hemisphere over winter, and thus to the hemispheric-scale production of ground-level ozone in spring. Given the likely lack of recent mitigation in reactive carbon emissions from East Asia, we expect this effect to be ongoing, and recommend that future work continue investigation of this possibility using updated emission inventories.

~~The~~ In addition to a contribution from the stratosphere, the springtime peak in transported ozone in our model is influenced by the interaction of two processes known to be especially poorly represented in current models: the chemistry of the intermediate oxidation products of NMVOC; and the emissions of NO_x from international shipping. Furthermore, the response of ground-level ozone to changes in methane also appears highly sensitive to the treatment of ship NO_x, especially in spring. We believe that our tagging technique could deliver useful information about the large differences in simulated springtime ozone between current generation models, if implemented in a larger number of models and used systematically in model inter-comparison exercises. This could potentially point the way to improved representations of the processes responsible for intercontinental transport of ozone.

Improved global chemical transport models are required to inform effective policies aimed at reducing intercontinental transport of ground-level ozone, a problem which is most urgent in the springtime. In particular, we recommend that developers of emission inventories and CTMs revisit their representations of anthropogenic NMVOC emissions and associated oxidation chemistry in order to reduce the uncertainties in modelled springtime ozone. Additionally, more explicit representations of the $\mathrm{NO_x}$ chemistry of ship exhaust plumes should be prioritised in order to improve the suitability of current models for simulating both intercontinental transport of ozone as well as the response of ozone to changing atmospheric methane.

Code availability. The CESM is maintained by NCAR, and is provided free to the community. The specific modifications made to the model to enable tagging of ozone production have been described by Butler et al. (2018) and are available in the online supplement to that work, which is archived and accessible through the following DOI: 10.5194/gmd-11-2825-2018

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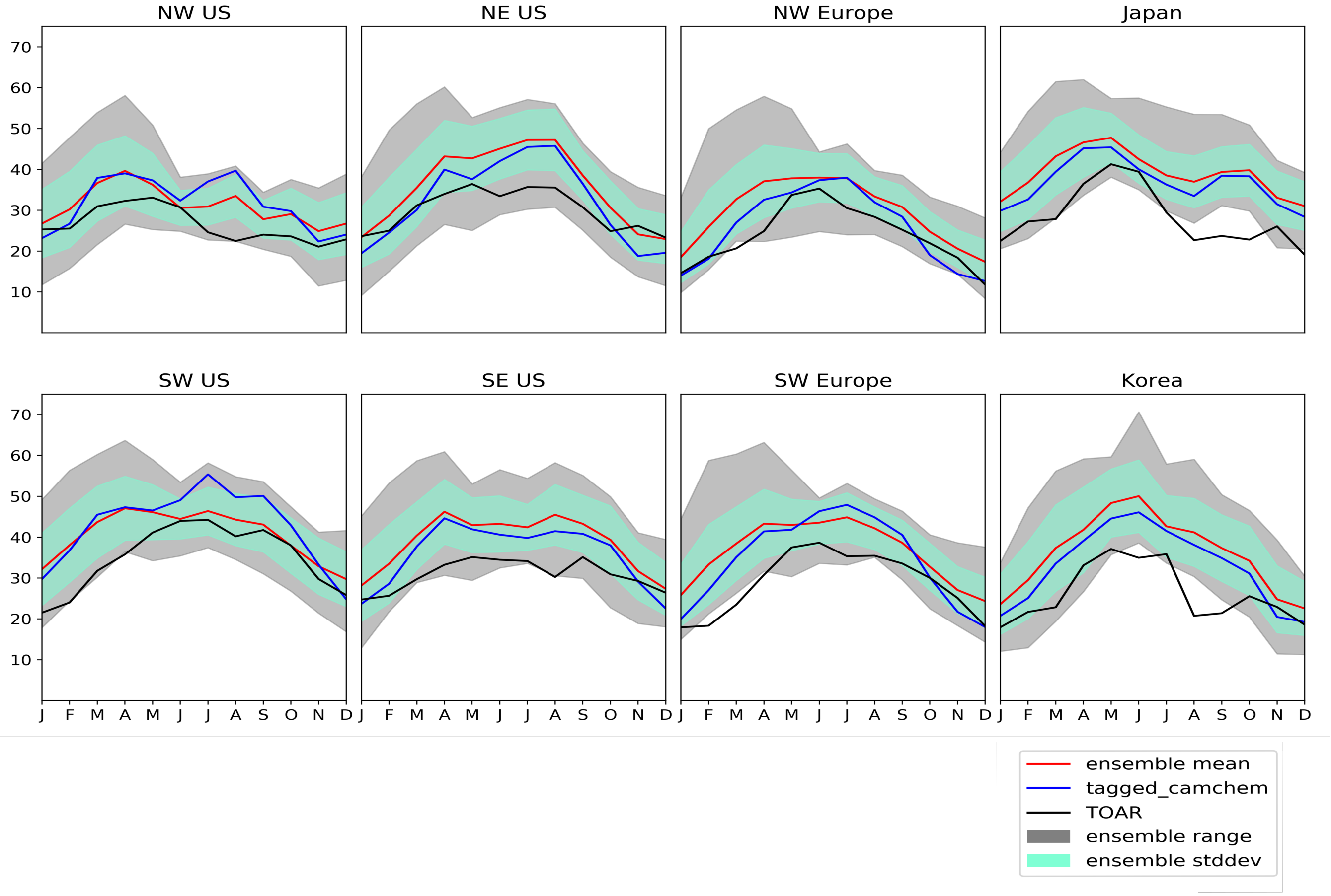

Figure 1. Seasonal cycle of monthly mean surface ozone (ppb) in HTAP Tier 2 regions from our base model run (blue line), compared with with observations from TOAR (black line), and other models from the HTAP ensemble of global models: ensemble mean (red line); ensemble standard deviation (green shaded area); and ensemble range (grey shaded area). Only grid cells containing TOAR observations have been used.

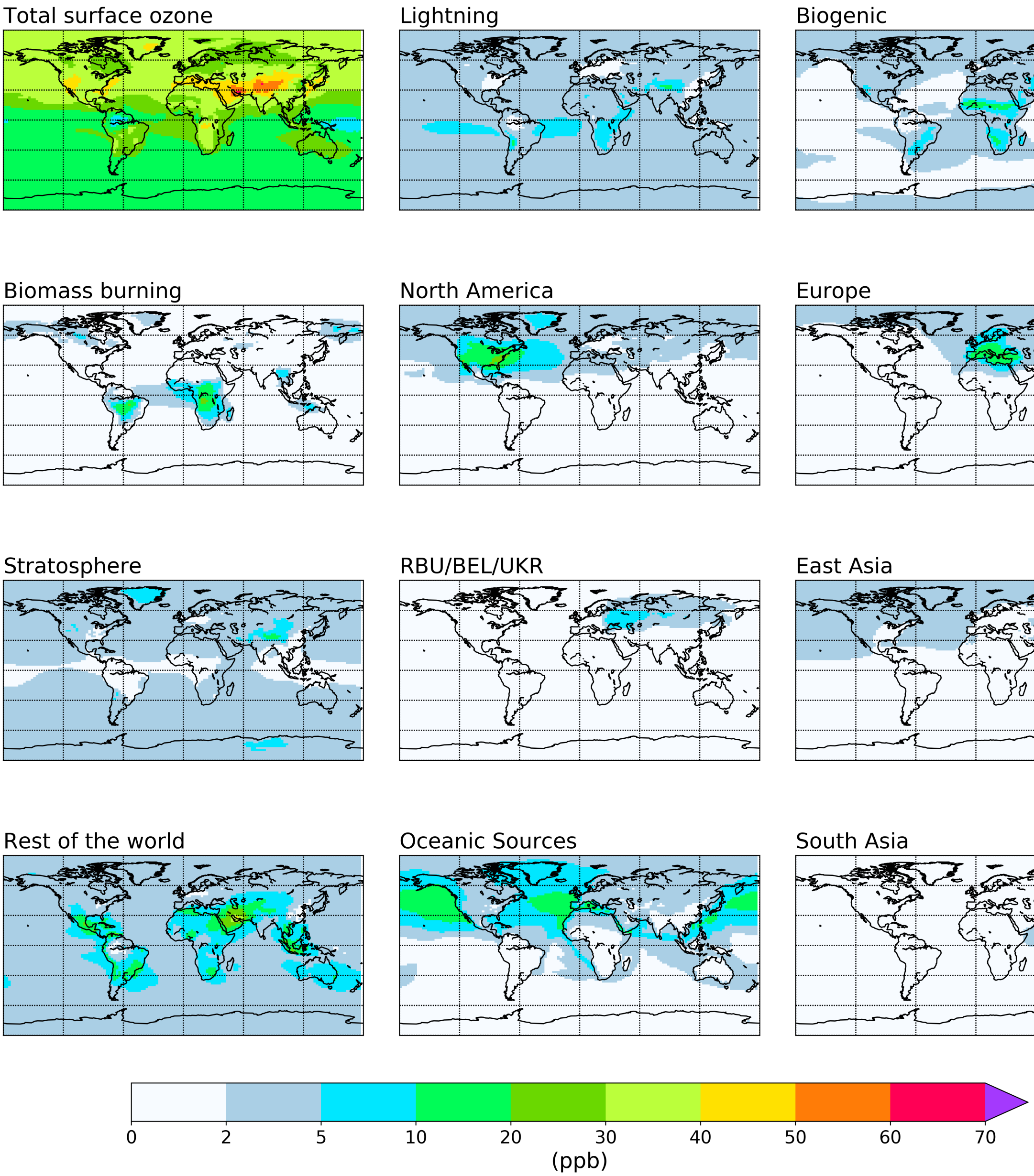

Figure 2. Annual mean surface ozone (ppb) from the NO_x-tagged base run. Total ozone is shown in the top left panel. Tagged ozone tracers are shown in other panels.

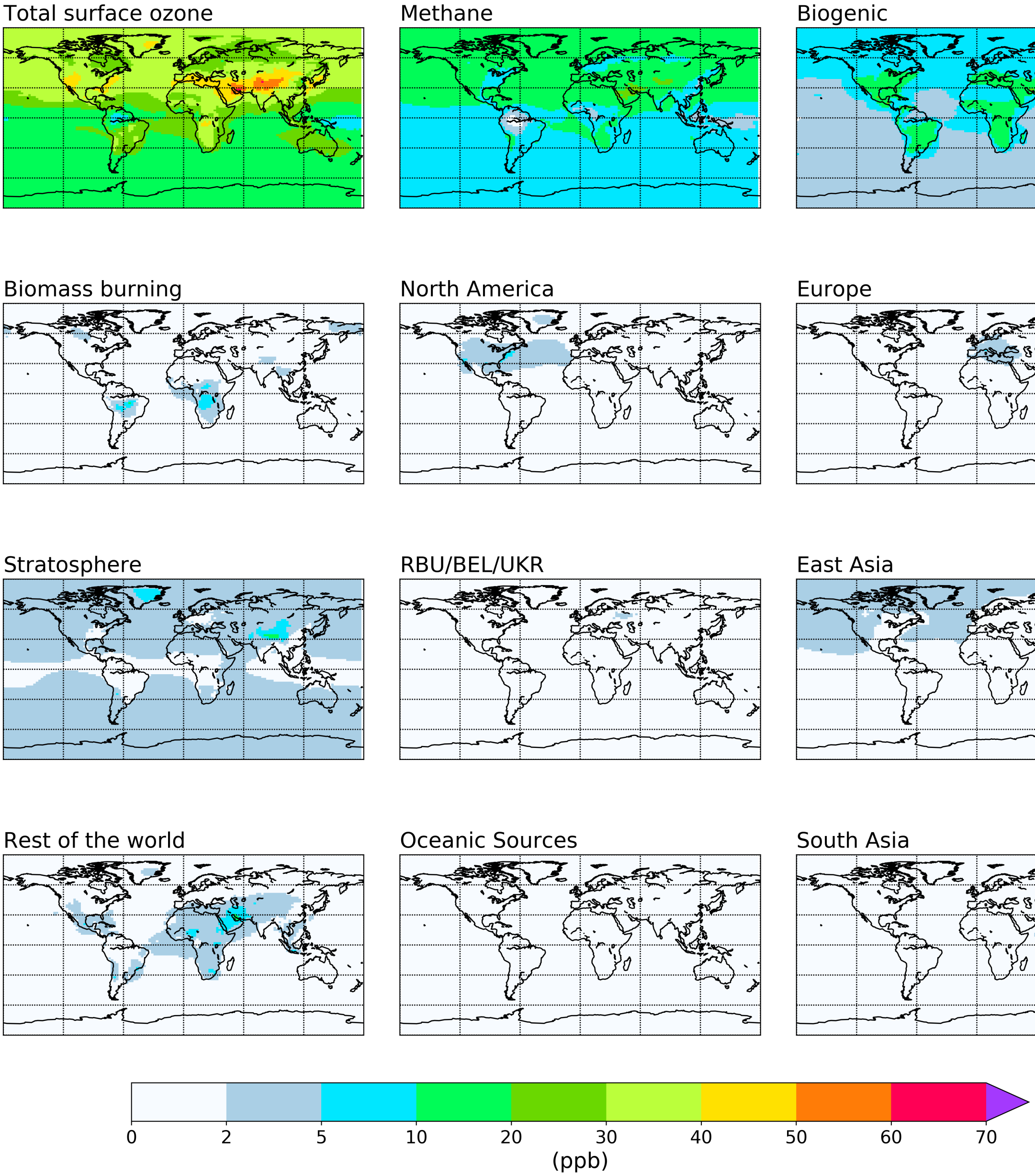

Figure 3. Annual mean surface ozone (ppb) from the VOC-tagged base run. Total ozone is shown in the top left panel. Tagged ozone tracers are shown in other panels.

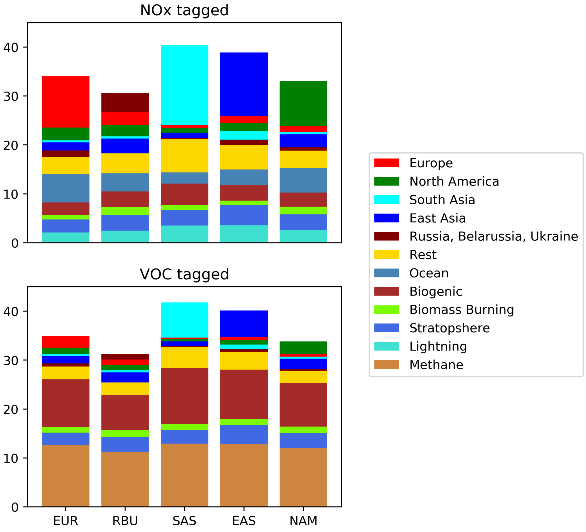

Figure 4. Source-receptor relationships for annual average surface ozone (ppb) in major Northern Hemisphere Tier 1 regions EUR (Europe); RBU (Russia, Belarus, and Ukraine); SAS (South Asia); EAS (East Asia); and NAM (North America). ~~Annual~~ The attribution relates the annual average surface ozone ~~(ppb) is shown for~~ modelled in each region ~~with attribution~~ to the emitted precursors NO_x ~~emissions~~ (top panel) and reactive carbon ~~emissions~~ (bottom panel) from all ~~other~~ HTAP Tier 1 regions.

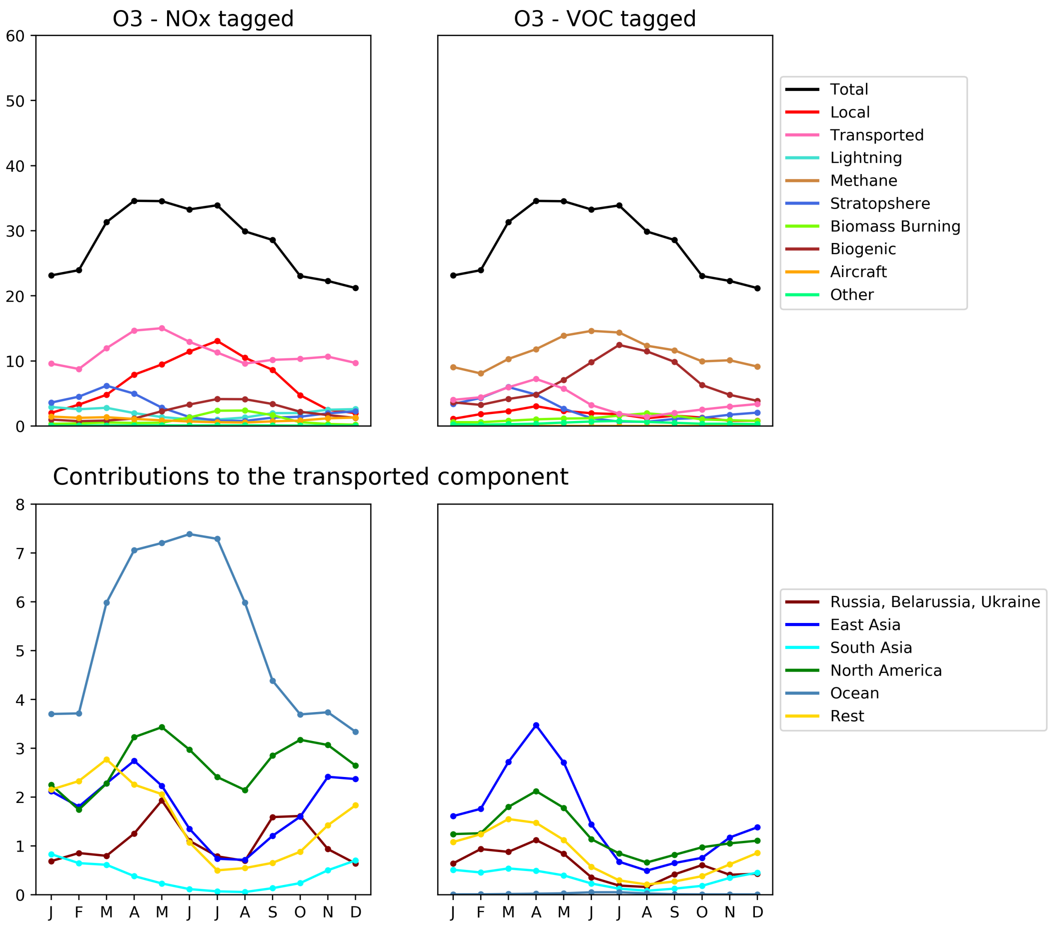

Figure 5. Seasonal cycle of surface ozone (ppb) in the HTAP Tier 2 receptor region "North West Europe". NO_x-tagging is shown in the left panels, and reactive carbon tagging in the right panels. Top panels show total monthly mean ozone (black line) as well as the local anthropogenic component, long-range transported anthropogenic component, and natural components. Bottom panels show the individual Tier 1 source regions responsible for the long-range transported component of ozone.

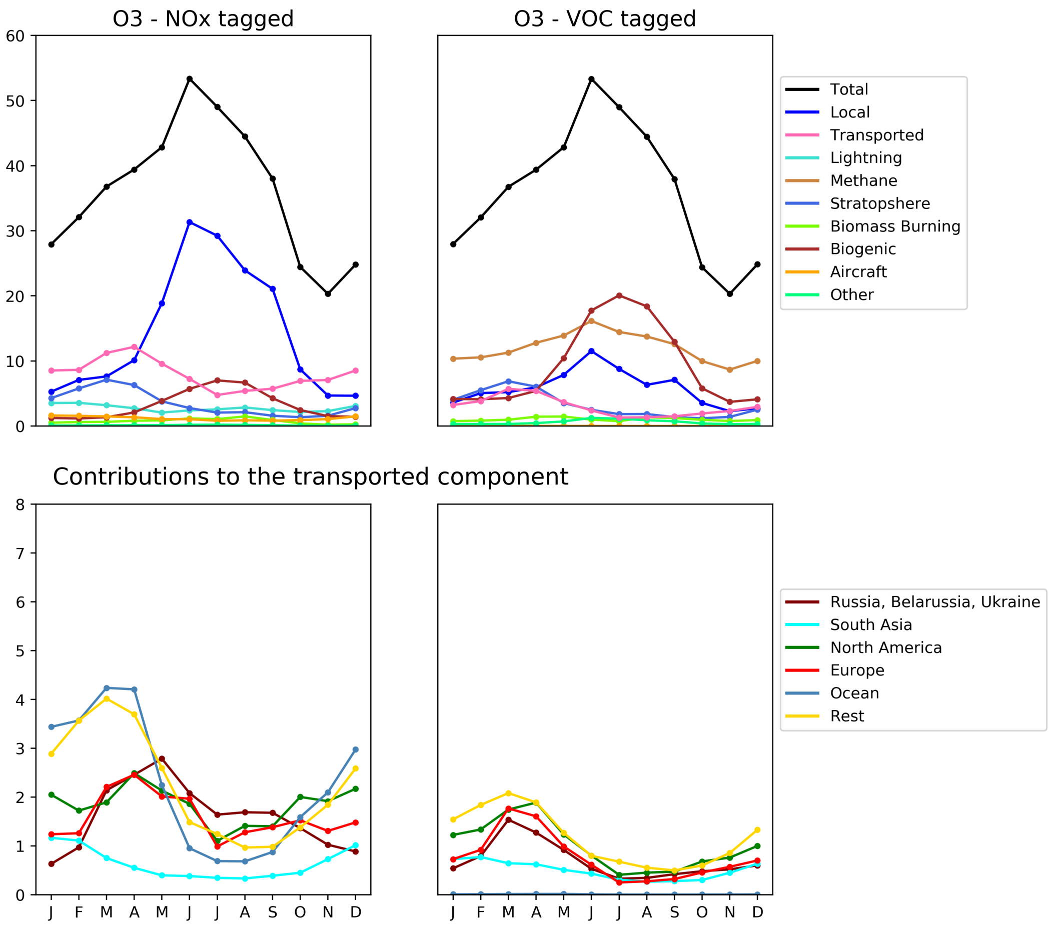

Figure 6. Seasonal cycle of surface ozone (ppb) in the HTAP Tier 2 receptor region "North East China". NO_x-tagging is shown in the left panels, and reactive carbon tagging in the right panels. Top panels show total monthly mean ozone (black line) as well as the local anthropogenic component, long-range transported anthropogenic component, and natural components. Bottom panels show the individual Tier 1 source regions responsible for the long-range transported component of ozone.

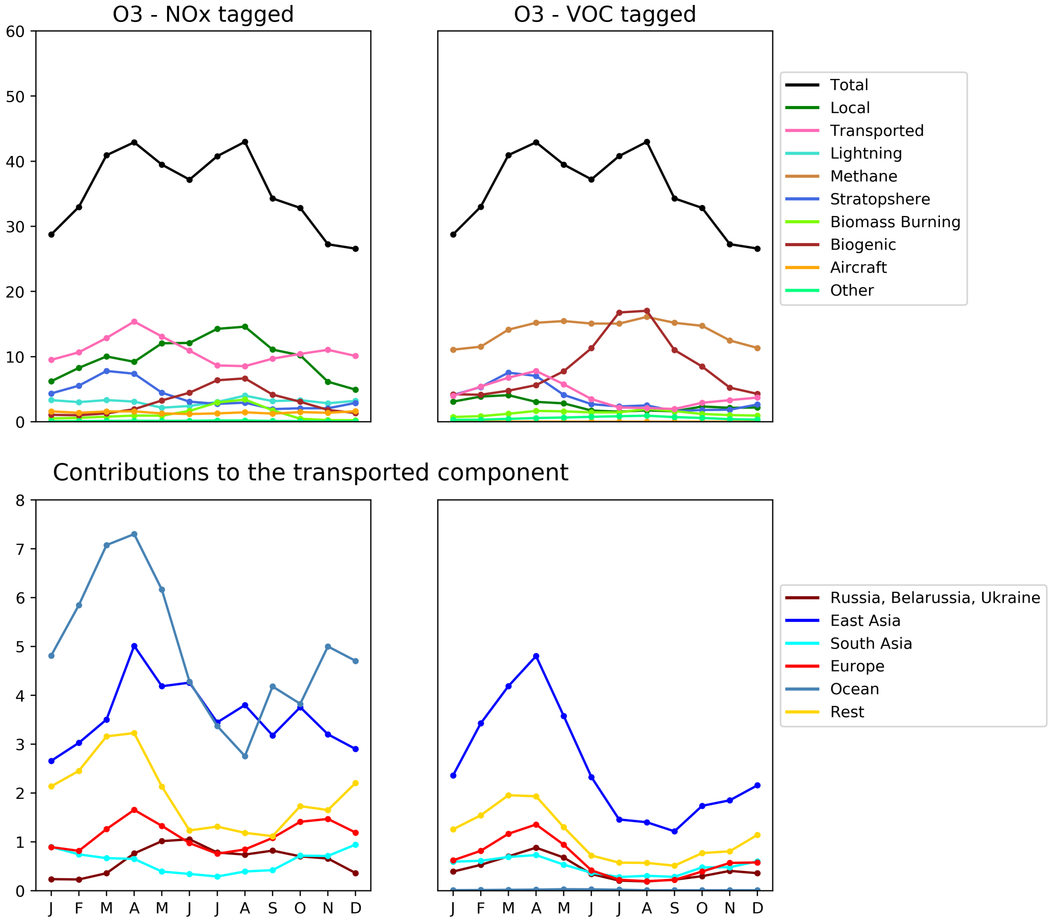

Figure 7. Seasonal cycle of surface ozone (ppb) in the HTAP Tier 2 receptor region "North West United States". NO_x-tagging is shown in the left panels, and reactive carbon tagging in the right panels. Top panels show total monthly mean ozone (black line) as well as the local anthropogenic component, long-range transported anthropogenic component, and natural components. Bottom panels show the individual Tier 1 source regions responsible for the long-range transported component of ozone.

Figure 8. Seasonal cycle of column-integrated lower tropospheric PAN (10^{-15} molec cm^{-2}) in the HTAP Tier 2 receptor region "North West Europe". The lower troposphere is defined here as all model levels between 800 and 500 hPa. NO$_x$-tagging is shown in the left panels, and reactive carbon tagging in the right panels. Top panels show total monthly mean PAN (black line) as well as the local anthropogenic component, long-range transported anthropogenic component, and natural components. Bottom panels show the individual Tier 1 source regions responsible for the long-range transported component of PAN.

Figure 9. Seasonal cycle of column-integrated lower tropospheric PAN (10^{-15} molec cm^{-2}) in the HTAP Tier 2 receptor region "North East China". The lower troposphere is defined here as all model levels between 800 and 500 hPa. $\mathrm{NO_x}$-tagging is shown in the left panels, and reactive carbon tagging in the right panels. Top panels show total monthly mean PAN (black line) as well as the local anthropogenic component, long-range transported anthropogenic component, and natural components. Bottom panels show the individual Tier 1 source regions responsible for the long-range transported component of PAN.

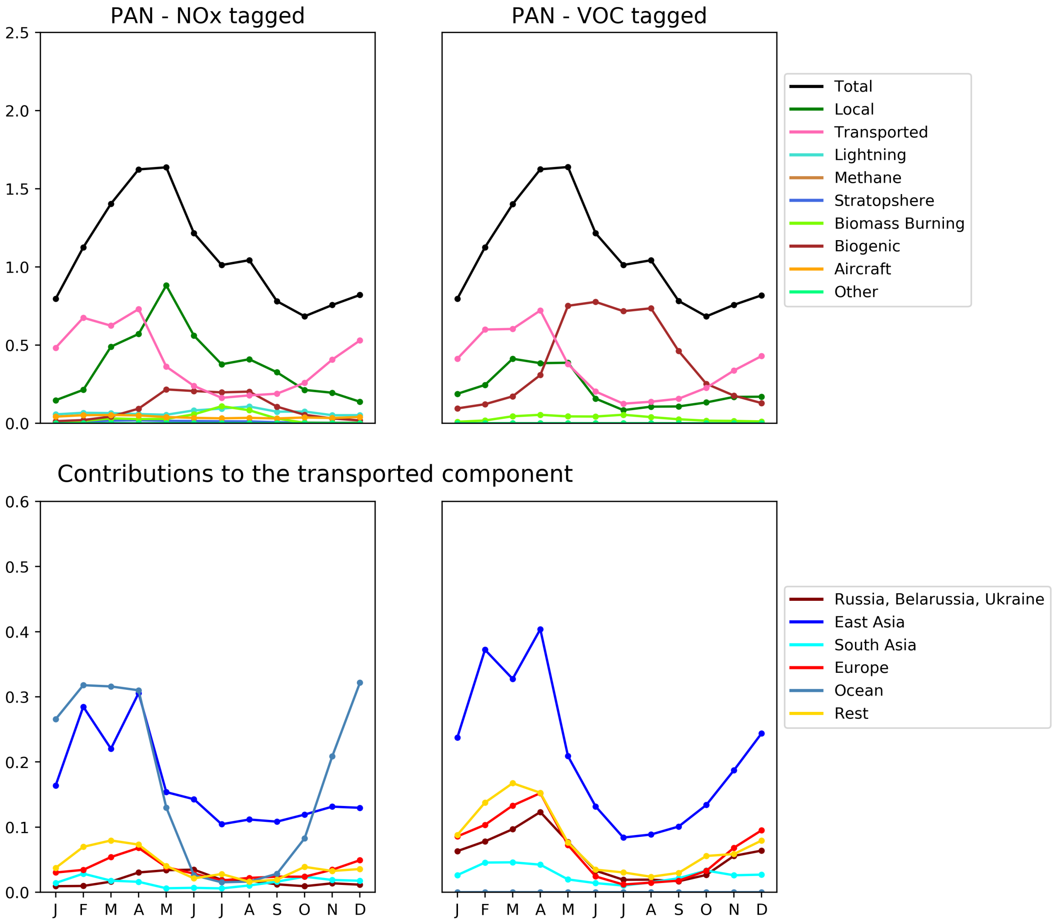

Figure 10. Seasonal cycle of column-integrated lower tropospheric PAN (10^{-15} molec cm^{-2}) in the HTAP Tier 2 receptor region "North West United States". The lower troposphere is defined here as all model levels between 800 and 500 hPa. NO$_x$-tagging is shown in the left panels, and reactive carbon tagging in the right panels. Top panels show total monthly mean PAN (black line) as well as the local anthropogenic component, long-range transported anthropogenic component, and natural components. Bottom panels show the individual Tier 1 source regions responsible for the long-range transported component of PAN.

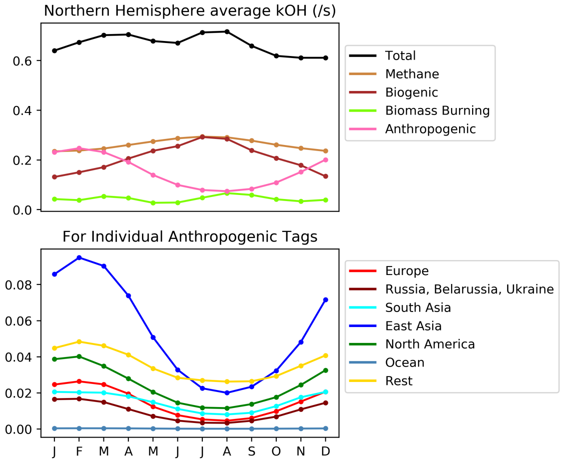

Figure 11. Seasonal cycle of northern hemispheric tropospheric column-integrated OH reactivity (s^{-1}) due to reactive carbon from the VOC-tagged run. The complete attribution is shown in the top panel, and the detailed attribution to anthropogenic emissions from HTAP Tier 1 source regions is shown in the bottom panel.

Table 1. List of tags used for attribution of tropospheric ozone in the NO_x- and VOC-tagged runs. Anthropogenic emissions of NO_x and reactive carbon are tagged based on their HTAP Tier 1 region. Other tags are as in Butler et al. (2018).

Tag name	NO_x-tagging	VOC-tagging
HTAP Tier 1 regions		
Oceans[1]	Explicit	Explicit
North America	Explicit	Explicit
Europe	Explicit	Explicit
South Asia	Explicit	Explicit
East Asia	Explicit	Explicit
Russia, Belarus, Ukraine	Explicit	Explicit
South East Asia	Explicit	RoW
Northern Africa	Explicit	RoW
Middle East	Explicit	RoW
Middle America	Explicit	RoW
Central Asia	Explicit	RoW
Pacific, Australia, New Zealand	RoW	RoW
Southern Africa	RoW	RoW
South America	RoW	RoW
Arctic	RoW	RoW
Antarctic	RoW	RoW
Other tags		
Stratosphere	Global[2]	Global
Aircraft	Global	Global
Biogenic	Global	Global
Biomass burning	Global	Global
Lightning	Global	N/A
Methane	N/A	Global
Extra production	Global[3]	Global[4]

[1] NO_x from "Oceans" is exclusively from shipping, while reactive carbon from this region is predominantly biogenic.

[2] For NO_x tagging, the stratosphere tag is applied directly to ozone produced in the stratosphere (as for VOC tagging) and also to NO produced from dissociation of N_2O.

[3] For NO_x tagging, "extra production" of ozone is due to the self reaction of OH radicals and reactions between HO_2 and organic peroxy radicals.

[4] For VOC tagging, "extra production" of ozone is due to the self reaction of OH radicals and reaction of OH with H_2O_2.

Table 2. Attribution of ozone to tagged sources of $\mathrm{NO_x}$. Also shown is the contribution of the stratosphere, and the contribution of minor chemical production pathways in the troposphere. Contributions of each tagged source are shown to both the 2010 annual average tropospheric burden and to the annual average Northern Hemisphere surface mixing ratio. Where applicable, the Ozone Production Efficiency (OPE) of $\mathrm{NO_x}$ emissions from each tagged source is also given.

$\mathrm{NO_x}$ Source	Emissions (Tg(N)/yr)	Ozone burden (Tg)	OPE (mol/mol)	NH surface (ppb)
Lightning	3.43	80.5	6.85	3.14
Stratosphere	–	75.5	–	3.17
Biogenic	5.04	26.0	1.50	2.57
Oceanic sources	4.28	19.9	1.35	5.33
East Asia	9.97	16.9	0.495	3.01
South East Asia	1.62	15.3	2.76	0.755
Aircraft	0.646	12.2	5.49	1.13
Biomass burning	5.03	12.1	0.704	1.45
South Asia	3.49	10.8	0.907	1.27
North America	4.79	10.4	0.632	2.88
Middle America	1.27	8.81	2.02	1.00
Europe	3.16	4.81	0.444	1.76
Middle East	1.82	4.11	0.659	1.02
RUS/BEL/UKR	1.37	2.15	0.457	0.852
North Africa	0.531	1.72	0.947	0.513
Central Asia	0.287	0.627	0.638	0.238
Rest of World	2.54	15.7	1.80	0.500
Extra production	–	1.47	–	0.132
Total trop. ozone	–	319	–	30.7

Table 3. Attribution of ozone to tagged sources of reactive carbon. Also shown is the contribution of the stratosphere, and the contribution of minor chemical production pathways in the troposphere. Contributions of each tagged source are shown to both the 2010 annual average tropospheric burden and to the annual average Northern Hemisphere surface mixing ratio. Where applicable, the Ozone Production Efficiency (OPE) of reactive carbon emissions from each tagged source is also given.

	Emissions				
Reactive carbon source	VOC (Tg(C)/yr)	CO (Tg(C)/yr)	Ozone burden (Tg)	OPE (mol/mol(C))	NH surface (ppb)
Methane	410	–	113	0.0689	12.4
Biogenic	668	42.2	76.8	0.0270	7.20
Stratosphere	–	–	66.8	–	2.91
Biomass burning	29.8	162	13.4	0.0176	1.25
East Asia	20.0	80.4	10.3	0.0257	1.96
South Asia	16.2	36.5	6.67	0.0316	0.715
North America	12.0	23.8	4.39	0.0307	1.18
Europe	6.12	11.6	2.04	0.0288	0.695
RUS/BEL/UKR	4.04	4.92	1.22	0.0341	0.433
Oceanic sources	11.0	0.587	0.0957	0.00206	0.0162
Rest of World	55.3	82.8	19.5	0.0352	1.43
Extra production	–	–	4.58	–	0.546
Total trop. ozone	–	–	319	–	30.7

Table 4. Change in the contribution of reactive carbon sources to tropospheric and Northern Hemisphere surface ozone in response to a 25% increase in the imposed surface mixing ratio of methane. Absolute changes and percentage changes are both shown.

	Tropospheric Burden		NH Surface mixing ratio	
Ozone source	Change in ozone burden (Tg)	Percentage change	Change in mixing ratio (ppb)	Percentage change
Methane	13.0	13.0	1.47	13.5
Biogenic	-1.88	-2.40	-0.168	-2.28
Stratosphere	-0.683	-1.01	-0.0226	-0.770
Rest of World	-0.379	-1.91	-0.0315	-2.15
Biomass burning	-0.243	-1.78	-0.0316	-2.47
East Asia	-0.238	-2.26	-0.0583	-2.90
South Asia	-0.131	-1.93	-0.0155	-2.13
Extra production	-0.0351	-0.761	-0.00890	-1.60
North America	-0.0975	-2.17	-0.0351	-2.88
Europe	-0.0479	-2.29	-0.0222	-3.09
RUS/BEL/UKR	-0.0286	-2.29	-0.0132	-2.96
Oceanic sources	-0.00287	-2.91	-0	-4.72
Aircraft	-0.00158	-2.59	-0	-3.81
Total trop. ozone	9.22	2.98	1.07	3.59

Table 5. Change in the contribution of $\mathrm{NO_x}$ sources to tropospheric and Northern Hemisphere surface ozone in response to a 25% increase in the imposed surface mixing ratio of methane. Absolute changes and percentage changes are both shown.

	Tropospheric Burden		NH Surface mixing ratio	
Ozone source	Change in ozone burden (Tg)	Percentage change	Change in mixing ratio (ppb)	Percentage change
Lightning	3.37	4.37	0.149	4.97
Stratosphere	-0.0598	-0.0791	0.00980	0.310
Biogenic	0.915	3.65	0.0861	3.47
Oceanic sources	1.04	5.53	0.287	5.70
East Asia	0.532	3.25	0.0884	3.02
Rest of World	0.557	3.68	0.0167	3.45
South East Asia	0.509	3.43	0.0214	2.92
Aircraft	0.558	4.81	0.0557	5.20
Biomass burning	0.277	2.34	0.0361	2.55
South Asia	0.395	3.78	0.0370	3.00
North America	0.340	3.38	0.0928	3.33
Middle America	0.313	3.68	0.0309	3.19
Europe	0.154	3.31	0.0559	3.29
Middle East	0.146	3.67	0.0389	3.96
RUS/BEL/UKR	0.0703	3.38	0.0269	3.26
North Africa	0.0736	4.46	0.0231	4.72
Extra production	0.00229	0.156	-0	-0.00590
Central Asia	0.0235	3.89	0.00936	4.09
Total trop. ozone	9.22	2.98	1.07	3.59