Replies are in italics

5 Anonymous Referee #1

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This manuscript applies a relatively new technique, the path-integral method, to characterize contributions to ozone over the United States. It applies two widely used models, CAMx nested within GEOS-Chem, to conduct its analysis. The main focus is on characterizing background and base ozone conditions, which have received background interest as the U.S. has moved to tighter ozone standards.

10 $\,$ heightened interest as the U.S. has moved to tighter ozone standards.

The manuscript is clearly written and its methods are sound. Model performance and results are in line with previous studies.

- 15 What is relatively novel here is the use of the path-integral method. As such, additional explanation and illustration should be provided in the final paper. Specifically, in Figure 2, it would be helpful to illustrate what happens in the "PIM" box. Also, a bit more explanation would be helpful regarding Equation 1. In particular, it is unclear to me what is happening along the 4 steps is each source being reduced 1/4 at a time?
- 20 We have revised Figure 2 and its caption to clarify the source apportionment process. We also made some changes to Section 2.3 to improve the description of the method there. In Eq. (1), the sum is over the number of sources, now indicated as M, not the number of points at which the sensitivities are calculated. In our application, M = 4 and the 4 integrals are each estimated by a Gauss-Legendre integration formula using sensitivities calculated at three levels of emissions and BCs. This is described in the last paragraph of Section 2.3.
- ²⁵ The levels of emissions and BCs are not equally spaced but are determined by the zeroes of the 3rd order Legendre polynomial. The points and weights needed for Gauss-Legendre integration have been tabulated and are readily available. We have added a reference to the Gauss-Legendre integration formula that contains the points and weights. Further details of the PIM, including the transformation of the integration variable, are available in the earlier reference Dunker (2015).
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Moreover, it is unclear to me that PIM has a "unique capability to allocate the difference in O3 between two simulations..." (p. 2, lines 27-28). Don't zero-out and tracer methods also do so? Given the nonlinearities of ozone response to emissions, there is no uniquely correct answer to apportionment. Better clarity on how to interpret PIM relative to other methods would be useful.

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We clarified the statement on p.2, lines 27-28 to indicate that the unique capability of the PIM is that the sum of the source contributions is equal to the difference in O_3 between the base and background simulations (within numerical error). As mentioned in the preceding paragraph of the manuscript, the sum of the source contributions from zero-out or tracer methods is not required to and usually does not equal the difference in O_3

40 between the base and background simulations. I.e., the total anthropogenic contribution from the zero-out or tracer methods may over- or under-represent the actual contribution as determined by difference between simulations with and without the anthropogenic emissions. We also added a sentence at the end of the first paragraph of Section 2.3 stating that the sum of the PIM source contributions is mathematically required to equal the concentration difference between the two simulations.

We agree that there is no unique source apportionment. However, because the focus of regulations is on the anthropogenic emissions, we feel that the PIM has an important advantage over other methods in requiring that the sum of the source contributions equals the anthropogenic O_3 increment.

Soil NOx, lightning NOx, biogenic VOC, and wildfire emissions are all very important to background O3. It should be clarified how soil NOx was estimated, and whether each of these sources was modeled consistently between GEOS-Chem and CAMx.

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We have added detail on sources of these emissions for the GEOS-Chem and CAMx simulations in sections 2.1 and 2.2, respectively. The data sources are different, in part due to differing requirements of the global and regional models, and we do not consider that consistency is required because CAMx is one-way nested within GEOS-Chem.

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Finally, the authors could consider discussing the implications of their findings for the setting of ambient standards for O3, which is an urgent topic in the US now. That so many sites have base T10 concentrations above 60 ppb suggests certain limits under consideration may be unattainable in some regions. US NAAQS are formulated based on 4th highest O3 at the most polluted monitor in a region. Given that this study looks at T10

20 rather than 4th highest, at a single monitor rather than worst, with models that tend to underpredict peak O3, and with the impossibility of removing all anthropogenic emissions globally all suggests attainment of NAAQS below 70 ppb may be unrealistic.

We agree that there are implications of our findings for setting an O₃ standard below 70 ppb. However, given
 the focus of the journal, we do not think that it is appropriate to comment specifically on regulatory issues. We
 hope that US regulators or other interested parties will review our results and consider them alongside other
 scientific information in analyzing whether the current or lower standards are achievable.

30 Anonymous Referee #2

Received and published: 27 June 2017

The manuscript by Dunker et al. estimates source contributions to the anthropogenic increment of O3 in the US. A one-way nested modeling framework combining GEOS-Chem and CAMx is used, allowing the authors to address global anthropogenic vs. background contributions. A relatively novel source attribution method, the

- 35 path-integral approach, is used to alleviate some drawbacks of more traditional (brute-force, tracer) methods). The authors evaluate model performance as well as source attributions. The findings are useful, timely, and generally well explained and examined. Model performance is typical for these types of tools, and the authors explore reasons for discrepancies as well as alternative global modeling values. While some more work could be done to propagate this level of uncertainty into the final source attribution estimates, the overall technical
- 40 approach is adequate. The introduction is a bit rough and needs some more work, the abstract is too vague, more rigorous and careful discussion and analysis is required to highlight the benefits of PIM, and there are a few other clarifying questions throughout on minor details. I believe in total these amount to minor revisions, and expect this article will be ready for publication in ACP without need for further review.

Main comments:

1.18-26: This is a good qualitative summary, but I would appreciate a more quantitative abstract. Meanwhile, with these very general descriptions, many of the statements are very obvious to readers familiar with the issue

- of background O3. For example, stating that contributions to background O3 from lateral BC's is largest for sites located near the boundaries seems quite obvious, although here one might wonder if this statement truly applies to all sites or just those near boundaries with mostly inflow conditions. Other qualitative descriptions (largest, closest, larger, reduced, increases, increased,...) would significantly benefit from quantitative support. The abstract is not presently overly long and could easily be revised to contain such information.
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We lengthened the abstract and added quantitative details. We also revised the statement on the contribution of lateral BCs to the T10Base ozone at sites on the boundaries.

general: The introduction is rather limited. The writing style is curt and almost shorthand at times (see a few
 specific comments below); references and explanations are used somewhat casually. Overall, it reads like a first draft and would benefit from a much more polished presentation befitting the extensive experience of the authors.

We have revised and somewhat expanded the Introduction and made changes in response to the specific comments below.

general: The authors perform some adequate model evaluation, and discuss reasons for different model biases. However, this sense of the magnitude of the model performance does not make its way, quantitatively, into presentation of the source attribution results. Would the authors be able to e.g. include some estimates of ranges in Table 3, or elsewhere?

25 ranges in Table 3, or elsewhere?

We do not know how to estimate the impact of errors or bias in model performance on the source contributions in Table 3 without greatly expanding the scope of the work. Probably the best approach would be to re-run the calculations with a different global and/or regional model, but this would require as much or more work than the results reported in the manuscript, depending on the alternative model(s) employed.

6.2. This is an interesting and useful finding. GEOS-Chem is a widely used model. Have previous studies made similar characterizations?

35 We are not aware of other studies reporting a similar characterization. We obtained our finding by using two different thresholds in the analysis but other studies have apparently used just a single threshold.

6.30 - 7.4: I believe other studies have also indicated that lacking halogen chemistry (Br and Cl) can lead to high GEOS-Chem concentrations, as well as how isoprene nitrate species are recycled, or underestimation of O3 dry deposition. Later I see that halogen chemistry is mentioned in the conclusions.

We added a sentence noting that lack of halogen chemistry may contribute to the O_3 overpredictions. p. 7, line 3

Fig 7 and associated text: Indeed, background concentrations are higher than normal in an absolute sense when focusing just on days with the base case concentrations are high. But are they also higher in a relative sense? I would like to see another column to Fig 7 that shows the background values divided by the base for each row. Relative concentrations are currently only mentioned in this section for Denver, on line 10 of page 10. I can

5 evaluate them myself for select sites using Table 3, but would appreciate more discussion be added.

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We added the requested plots as a new Figure 8 in the revised manuscript. We also added Table S8 to the Supplement, which gives the ratios of background to base concentrations for the 12 sites in Table 3, calculated using the spring, summer, T10Base and T10 Bkgd averages. We added a paragraph at the end of Section 3.4 discussing the new Figure 8 and Table S8 and also summarized the results in the abstract.

general: The title and framing makes me anticipate a bit more rigorous discussion of source attribution methods than what was included in this paper. The 6 specific points below address specific questions about methodology; in general though I wonder if the authors would really like to demonstrate the advantage of PIM

15 if they would present their findings side-by-side with those from brute-force or tracer methods, both in terms of the estimates of background concentrations and attributions and also the computational intensity (CPU and memory) of obtaining these estimates.

We have expanded the Introduction to include more discussion of the PIM vs. the brute-force and tracer 20 methods and responded to the specific points below.

2.23-26: While the description of the downsides of tracer methods is technically correct, I'm not sure the extent to which these are real limitations. For example, by how much do modern tracer methods not sum to the total increment? And while all nonlinear indirect reactions may not be included, to what extent are the most important ones included, which capture e.g. >90% of the O3 formation mechanism? A more practical downside,

25 important ones included, which capture e.g. >90% of the O3 formation mechanism? A more practical downside, not mentioned here but which should be, is the computational burden of these tracer methods does not scale well when many sources (regions, times) are required, as the approach becomes memory intensive.

Our view is that the PIM and tracer methods have different strengths and limitations, and that both are useful improvements upon the brute force method. We have expanded the discussion here, and in response to the next review comment, accordingly. Here, we added the following statement to illustrate how nonlinear chemistry may complicate interpretation of tracer method results: "If the chemistry changes significantly from the base to background cases, e.g., O₃ production per nitrogen oxides (NO_x) molecule becomes more efficient as NO_x emissions are reduced, then an estimate of the anthropogenic increment using just the base-case chemistry can

- 35 have important errors." The degree of this non-linearity varies, e.g., with emissions intensity and grid-resolution, which we believe precludes general statements about the accuracy for tracer methods. Our experience with memory requirements for tracer methods has been that CAMx can compute hundreds of source contributions in a single simulation and so we see memory footprint as an advantage of tracer methods rather than a limitation. We added the statement: "Tracer methods can be more efficient than both brute-force and the PIM as long as
- 40 relatively few tracers (i.e., fewer tracers than chemical mechanisms have species) are used to perform source apportionment."

3.1: I feel like this statement is a bit unfair to PIM. The approach is more computationally intensive than a single brute-force sensitivity calculation. But PIM is efficient for obtaining the type of results that it is designed to calculate, compared to estimating the same contributions using other approaches. It also may be more CPU intensive whereas tracer methods would be more memory intensive. So, some more nuanced text here would be appreciated.

5 be appreciated.

Our view is that the PIM and tracer methods have different strengths and limitations, and that both are useful improvements upon the brute force method. We have added several sentences after p. 3, line 1 to expand the comparison between the PIM and the brute-force and tracer methods. In our previous study, Dunker et al.

- 10 (2015), we found that the PIM required 2.7 times the computational effort of the brute-force method to apportion O₃ and other species to five major source categories. Thus, the increased runtime for the PIM is a disadvantage. The PIM does produce concentrations (and sensitivities) at intermediate emission levels between the base and background cases, which is useful information on how pollutants change as emissions are reduced. This is now noted in the paragraph.
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4.7: Particulates impact O3 via heterogeneous chemistry and photolysis. Many studies in the literature report these influences, which may be several ppb under particular conditions. Please explain further, quantitatively, and with references, why such effects are negligible in this case. My hunch is the authors will be forced to admit this decision was based, at least in part, on computational convenience, although I'm not explicitly sure why (does CAMx 6.3 not support DDM calculations for particulates? etc.).

CAMx 6.3 does include DDM for PM. However, we agree with the referee that the influence of secondary PM formation on O_3 will be only a few ppb or less, and that including PM in the simulations would significantly increase the computational effort. We confirm the reviewer's hunch by making this statement: "Formation of particulates was not included to reduce computational burden and because the focus was on O_3 "

5.4-6: There is no evidence provided to support the claim that this approach is "unbiased". It seems that in fact this assumption introduces a subjective bias in the analysis, which is the restriction that all precursor emissions change uniformly, which is clearly not representative of real-life conditions wherein emissions control measures

- 30 target individual species (e.g., diesel NOx regulations). I think the rational here is one of simplicity and generality; if the study were more directed at the effects of particular control measures, different paths could be selected. One could also consider how emissions have changed, historically, and use those to define the path. But it doesn't appear that an analysis of emissions trends formed the basis of this statement, at least none is presented or cited.
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We revised this sentence to remove "unbiased." We also revised p. 5, lines 5-6 and added additional sentences about historical, long-term, national reductions of VOCs and NOx in the US. Although emission controls target specific sources and species (e.g., diesel NOx), we are focusing on large geographic regions (US, Canada and Mexico, and the remainder of the world) as sources. What is most important in this case is how the total VOC

40 and NOx emissions in each of these large regions will change in the future. Our assumption seems reasonable based on long-term US history. An assumption based on detailed projections of worldwide emissions was beyond the scope of this work, and may not be possible for many countries outside the US. 5.11: Does this really account for the impact of all anthropogenic emissions on US O3? For example, if US anthropogenic NOx depleted some biogenic VOC concentrations, which then transported out of the US domain temporarily and then recirculated back into the domain at lower concentrations than would have occurred w/o these anthropogenic NOx emissions, would this be captured? I don't think so. At least this isn't mentioned on

5 lines 5.14-15. I'm not arguing this is a substantial impact, quantitatively, just that the description of the method is neglecting some assumptions.

If US emitted species and the secondary pollutants generated from them move into Canada or Mexico, stay within the CAMx domain, and then return to the US, their impact is captured in our source contributions and assigned to the US. If the emitted species and secondary pollutants move outside the CAMx domain but then return to the CAMx domain via the BCs, the impact will also be captured, to the extent that GEOS-Chem has similar emissions, circulation patterns and chemistry as CAMx within the CAMx domain. What would happen in our calculations is that the effect of the recirculation would be ascribed to the lateral boundaries, not the US emissions. If the PIM were used with a single global model, the impact of the US anthropogenic emissions would

- 15 be ascribed to the US, regardless of where the US emitted species and secondary pollutants are transported. Current tracer methods used in regional models estimate the contribution of the total BCs but do not separate out the contribution of anthropogenic pollutants arriving via the boundaries. The brute-force method could estimate the contribution of anthropogenic pollutants entering from the boundaries by difference between two simulations with different BCs. Again, the BCs would be derived from global model simulations with and without
- 20 anthropogenic emissions. We are not aware, however, that the brute-force method has been applied to obtain such estimates of the contribution of anthropogenic pollutants arriving via the BCs. We have added a paragraph in Section 2.3 discussing recirculation of pollutants.

Section 3.4: The T10 metric is interesting, but it isn't clear to my why it was chosen. Are their findings sensitive to the use of 10 days rather than 3 or 30? Is there a policy relevance, like the 4th highest MDA8?

The H4MDA8 has the limitation of being a single day that may not represent high ozone days in general. In averaging over 10 days, our goal was to include a reasonable variety of days with high total (T10Base) or high background (T10Bkgd) ozone over the 7 months of the simulation. Neither metric is directly related to the 4th

- 30 highest MDA8 ozone, and we have not explored whether the results differ depending on the number of days that are included in the averages. There is some relevance of the T10Base average to policy in that calculation of relative reduction factors for a nonattainment region by the U.S. EPA's procedure typically uses the top 10 days of MDA8 ozone. We feel that it is important to compare the T10Base and T10Bkgd results because they correspond to quite different transport, chemistry, etc. conditions. However, we also show source
- 35 apportionments averaged over the spring and summer seasons (Figs. S10 S13) and source apportionments for 23 sites over the full 7 months (Figs. 10, S13, S14). Although more analysis of results is always possible, the T10Base and T10Bkgd results along with the spring and summer averages and the time series at sites should give the reader a reasonably complete picture of the results. We have added a sentence in Section 3.4 explaining that T10Base is not directly related to a regulatory standard.

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Minor comments / corrections:

Title: Is CAMx really "nested" within GEOS-Chem in the usual sense of a nested grid model, or is it just using boundary conditions from GEOS-Chem (i.e., a one-way nesting)?

The term "nesting" includes both one-way and two-way nesting. To make clear that we are using one-way nesting, we added "one-way nested" to the second sentence of the abstract, p. 1, line 11.

5 1.24: Not sure that a verb "increased" is appropriate here â A T consider "higher". *Changed "increased" to "greater." p. 1, line 24*

2.1: "O3 background in the absence of anthropogenic emissions" is a vague phrase that needs to be more carefully written. A formal definition of what is meant by "background O3" in this particular manuscript should

10 be clearly defined before this term is used. Further, assuming this has been defined, the rest of this statement seems redundant, for what other O3 besides the background would be present in the absence of anthropogenic emissions?

Revised to "An important consideration is how difficult it will be to meet this standard by reducing US emissions
alone because anthropogenic emissions outside the US can contribute to US O₃. This can occur by the transport of foreign anthropogenic emitted species into the US but more importantly by the transport of O₃ and other secondary pollutants formed outside the US from the foreign emissions." Also, at the end of the next paragraph, stated that the focus of this work is on natural background O₃.

20 2.3: Emissions are not transported, they are emitted. Species that are emitted are transported. Please tighten of the language in this regard here, and throughout.
 Changed to "emitted species." p. 2, line 3; p. 5, line 16; p. 11, line 9

2.3-4: Please provide a reference or references.

25 Added three references.

2.8: Unless the acronym "NAB" is introduced here and used later, it doesn't make sense to capitalize Background.

Made "background" lower case. p. 2, line 8.

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2.13: the phrase in parentheses is missing some words in order to be grammatically correct. *Changed to "known as the brute-force or zero-out method." p. 2, line 13*

2.18: The chemistry â Ă T> Chemistry
35 Deleted "The." p.2, line 18.

2.19: parenthesis not needed. Deleted parentheses. p.2, line 19

40 3.30: Use "CMAx" or "The CAMx model". Remove extra comma. *Deleted "The"; removed comma. p. 2, line 30* Eq 1: This would be a more general equation if the "4" were replaced by e.g. M, where M is defined to be the number of sources. Also, it seems implicit that the integral bounds are lambda=0 to lambda=1; it's not clear why "P" is used instead.

- 5 Replaced "4" by "M" and added a definition of M. p. 4, lines 26, 28. Keeping P is important to keep the equation general because the path is not necessarily a straight line in lambda space. Using integral bounds of 0 and 1 may imply a straight line. To make this clearer, changed the last sentence of the paragraph to "P is some path from *A* = 0 to *A* = 1, not necessarily a straight line." Also, the standard mathematical representation of path or line integrals uses a symbol for the path unless the integral has been reduced to a definite integral incorporating the functions defining the specific path of interest.
- 10 the functions defining the specific path of interest.

4.28: An "array" is a computational object, not a mathematical one. Perhaps the authors mean "vector"? *Changed to "vector." p. 4, line 29*

15 5.1: This first sentence is confusing. What is the "direction" being referred to here? Some model time integration? How are "emissions added"?

Changed to "In the integration direction of Eq. (1), emissions increase along the path as the λ_m increase, ..." p. 5, line 1

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Fig 1: A small point of clarification â Ă T how are shipping emissions within the US Exclusive Economic Zone but outside the CAMx domain on the west classified?

These emissions are in the global anthropogenic emissions used by GEOS-Chem but are not included in the CAMx simulation. Thus, they will affect the CAMx simulation via the boundary concentrations.

Fig 2: Is there a difference, conceptually, between blue vs orange vs black lines? If so, please clarify. If not, making them the same color may be an improvement (less distracting).

- 30 In response to this comment and a comment by Referee #1, we revised Figure 2 and its caption to make the procedure for source apportionment clearer. The blue boxes and arrows now represent the flow of information to and from the basic model, CAMx. The orange boxes and arrows represent the flow of information to and from the PIM. Black lines have been removed.
- 35 Fig 5: These types of scatter plots can be improved by adding color ranges to indicate the density of points. We thank the reviewer for this comment and will investigate this option in future work.

Contributions of foreign, domestic and natural emissions to US ozone estimated using the path-integral method in CAMx nested within GEOS-Chem

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Abstract. The Goddard Earth Observing System global chemical transport (GEOS-Chem) model was used at 2° x 2.5° resolution to simulate ozone formation for a base case representing year 2010 and a natural background case without worldwide anthropogenic emissions. These simulations provided boundary concentrations for base and natural background simulations with the Comprehensive Air Quality Model with Extensions (CAMx) on a North American domain (one-way nested) at 12 km x 12 km resolution over March–September 2010. The predicted maximum daily average 8-hour (MDA8) background ozone for the US is largest in the mountainous areas of Colorado, New Mexico, Arizona, and California. The background MDA8 ozone in some of these locations exceeds 60 ppb, when averaged over the 10 days with the largest base-

- 15 case ozone (T10Base average). The background ozone generally becomes both a larger fraction of the base-case ozone in the western US and a smaller fraction in the eastern US when proceeding from spring to summer to the T10Base average. The ozone difference between the base and background cases represents the increment to ozone from all anthropogenic sources. Using T the Path-Integral Method was applied to allocate, the this anthropogenic ozone increment was allocated to US anthropogenic emissions. Canadian/Mexican anthropogenic emissions, and the anthropogenic components of the lateral
- 20 and top boundary concentrations (BCs). For the largerUsing the T10Base average -MDA8 ozone concentrations in the base case, the relative importance of the sources is generally US emissions > anthropogenic lateral BCs > Canadian/Mexican emissions >> anthropogenic top BCs. Specifically, for 10 US urban areas, the source contributions were: US emissions, 12–53 ppb; lateral BCs, 3–9 ppb; Canadian/Mexican emissions, 0.2–3 ppb, top BCs, ≤0.1 ppb. The contributions of the lateral BCs are largest for the higher elevation US sites in the Intermountain West and sites closest to the boundaries along the
- 25 western boundary of the domain. At Denver, for example, the lateral BCs contribute 44% to the T10Base anthropogenic increment. Averaging over the 10 days in the background case with the largest MDA8 ozone (T10Bkgd), the contribution from US emissions is reduced to 3–13 ppb at the 10 urban sites. If the focus instead is on the larger ozone concentrations in the background case, the contribution from US emissions is reduced leading to a reduction in the anthropogenic ozone increment. The contribution of the Canadian/Mexican emissions remains about the same (0.3–2 ppb), and the contribution
- 30 from the lateral BCs increases (5–10 ppb), especially at the lower elevation urban sites. The net effect at the urban sites is that the relative importance of the anthropogenic lateral BCs is significantly increased greater for the days with the largest background concentrations T10Bkgd average than the T10Base average. This is also true for rural sites studied, where the

anthropogenic lateral BC contribution becomes as large as 68% of the anthropogenic increment for the T10Bkgd average. In addition to the source apportionment, we also used surface and ozonesonde measurements to evaluate GEOS-Chem and CAMx performance.

1 Introduction

- 5 In 2008, the US Environmental Protection Agency (EPA) reduced the National Ambient Air Quality Standard (NAAQS) for 8-hour ozone (O₃) to 75 ppb, and in October 2015, further reduced the NAAQS to 70 ppb. An important consideration is how difficult it will be to meet this standard by reducing US emissions alone because anthropogenic emissions outside the US can contribute to US O₃. This can occur by the transport of foreign anthropogenic emitted species into the US but more importantly by the transport of O₃ and other secondary pollutants formed outside the US from the foreign emissions (Zhang
- 10 <u>et al., 2008; Jiang et al., 2016; Lin et al., 2017</u>). One issue is the magnitude of the O_3 -background in the absence of anthropogenic emissions. Another issue is the contribution of anthropogenic emissions outside the US to US O_3 . This can occur by the transport of the foreign anthropogenic emissions but more importantly by the transport of the foreign O_3 and other secondary pollutants.

Background O_3 must be estimated from model simulations, though a related quantity, termed baseline O_3 , can be estimated from data at relatively remote monitoring sites (Parrish et al., 2012). McDonald-Buller et al. (2011) review background and

- baseline O_3 and how the latter can be used to test model results. There are three common definitions of background O_3 : US background, North American <u>Background background</u> and natural background, which correspond to elimination of US, North American or worldwide anthropogenic emissions, respectively (Zhang et al., 2011; Emery et al., 2012; Fiore et al., 2014; Zhang et al., 2014; Dolwick et al., 2015; Nopmongcol et al., 2016). The anthropogenic increment of O_3 is the
- 20 difference between a base-case simulation with all emissions present and the chosen type of background simulation. The focus of this work is on the anthropogenic increment over natural background O_{3} .

One approach to apportioning the anthropogenic increment is to remove sources one at a time and determine the change in O_3 from the base case (known as the brute-force or zero-out method) (Zhang et al., 2014; Dolwick et al., 2015). A limitation is that the sum of all the anthropogenic source contributions generally does not equal the anthropogenic increment due to the

- 25 nonlinear chemistry. Another approach is to add reactive tracers (tagged species) to the base case for the emissions from anthropogenic sources and/or the secondary pollutants formed from the emissions and then use the tracers to estimate the contribution of the sources to the total O₃ concentration (Zhang et al., 2008; Lefohn et al., 2014; Baker et al., 2015; Dolwick et al., 2015; Nopmongcol et al., 2017). The Cehemistry causes interactions between the sources through direct and indirect effects. For example, if O₃ (generated from anthropogenic emissions) is transported into the domain through the boundaries,
- 30 direct effects are destruction of the O₃ by reaction with anthropogenic NO emissions in the domain, $O_3 + NO \rightarrow NO_2 + O_2$, or reaction with HO₂ formed from volatile organic compound (VOC) emissions, $O_3 + HO_2 \rightarrow OH + 2 O_2$. Indirect effects are the photolysis of the NO₂ to recreate O₃ and the reaction of the OH with anthropogenic VOC emissions to form O₃. Reactive

tracers can follow some indirect effects (Baker et al., 2015; Nopmongcol et al., 2017) but ultimately <u>it is difficult to follow</u> not all the nonlinear chemical interactions among emissions from different sources<u>can be included</u>. In addition, there is no requirement that the sum of tracer contributions ascribed to the anthropogenic sources equals the anthropogenic increment (as defined above). Also, the focus in the tracer approach is solely on the chemistry in the base case. <u>If the chemistry</u>

5 changes significantly from the base to background cases, e.g., O_3 production per nitrogen oxides (NO_x) molecule becomes more efficient as NO_x emissions are reduced, then an estimate of the anthropogenic increment using just the base-case chemistry can have important errors.

The Path-Integral Method (PIM) for source apportionment has the unique capability to allocate the difference in O₃ between two simulations (e.g., the anthropogenic increment) to portions of the emissions and boundary concentration (BC) changes

- 10 between the two simulations such that the sum of the source contributions equals the difference in O_3 (Dunker, 2015; Dunker et al., 2015). The PIM determines the source contributions by integrating first-order sensitivity coefficients over the range of emissions from the background case to the base case, and thus the source contributions are not determined just from the chemistry in the base case. Calculating the sensitivity coefficients involves the same Jacobian matrix used in solving the chemical reaction equations. Consequently, the source contributions implicitly include all the direct and indirect effects
- 15 represented by the chemical mechanism. <u>The PIM does not perturb the model's chemistry and can determine the</u> <u>contributions of all emitted species.</u> The sum of the source contributions is constrained to equal the anthropogenic increment, within the accuracy of the numerical integration.

The disadvantage of the PIM is that it requires more computational effort than the brute-force or tracer methods. Compared to brute-force, the PIM required 2.7 times more effort in a previous study_{τ} (Dunker et al., 2015). Tracer methods can be

- 20 more efficient than both brute-force and the PIM as long as by using-relatively few tracers (i.e., fewer tracers than chemical mechanisms have species) are used to perform source apportionment. However, the added effort for PIM provides concentrations (as well as the sensitivities) for multiple emission levels along the control path from the base to background cases, showing how concentrations change as emissions are reduced. Moreover, the PIM can allocate any of the species in the chemical mechanism to the emission sources with only a small incremental effort beyond that needed for O₃. Dunker et
- 25 al. (2015) determined the anthropogenic increments in O₃₂ and other species formaldehyde and NO₂ defined by the difference between a base case for 2030 and the US background and allocated the increments to US source categories using the PIM. For this study, we used the Comprehensive Air Quality Model with Extensions (CAMx; Ramboll-Environ, 2016) in a one-way nest within the Goddard Earth Observing System global chemical transport (GEOS-Chem) model (Bey et al., 2001) to estimate the anthropogenic increment in O₃ equal to the difference between a 2010 base case and the natural background.
- 30 Using the PIM, this increment was then allocated to the US and Canadian/Mexican anthropogenic emissions within the CAMx North American modeling domain and to worldwide anthropogenic emissions outside the domain that impact the CAMx simulation via the BCs. We also conducted an evaluation of the CAMx and GEOS-Chem model performance for the base case using various surface and ozonesonde measurements.

2 Methods

2.1. GEOS-Chem simulations

Two global model simulations were conducted to provide BCs for North American regional model simulations using the latest version of GEOS-Chem available for this work, version 10-01 (http://www.geos-chem.org). The base-case global

- 5 simulation (G-Base) used global anthropogenic emissions from the Emissions Database for Global Atmospheric Research (EDGAR v4.2) (European Commission, 2011) with anthropogenic volatile organic compound (VOC) emissions from the Reanalysis of the Tropospheric chemical composition (RETRO) emission inventory. Additional global databases provided anthropogenic emissions from aircraft, ship, fertilizer, and biofuel sources. Regional anthropogenic emission inventories superseded the global emissions for specific regions of the world, e.g., the US, Canada, Mexico, Europe, and Southeast Asia.
- 10 The natural emissions included biogenic emissions from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006), biomass burning from the Global Fire Emissions Database (GFED-3) (Giglio et al., 2010), nitrogen oxides (NO_x) from lightning (Murray et al., 2012) and soil (Hudman et al., 2012), volcanic emissions, and wind-blown dust. The second (background) global simulation (G-Bkgd) used natural emissions only without any anthropogenic emissions. However, the methane concentration for G-Bkgd was the same as for G-Base, ~1750 ppb (2007)
- 15 data), and thus represents the current, not pre-industrial level.

Both GEOS-Chem simulations were driven by off-line meteorological fields generated by the GEOS-5 general circulation model with 2° latitude x 2.5° longitude horizontal grid resolution and 72 vertical layers (GEOS-5, 2013). Simulations ran from the beginning of 2009 to the end of 2010 to match the North American regional modeling period (2010). (Year 2009 was the model spin-up period.) Table S1 describes the model configuration further, and Tables S2, S3, and S4 give more detail on the global anthropogenic, regional anthropogenic, and natural emission inventories, respectively.

2.2 CAMx simulations

The CAMx version 6.30 (Ramboll-Environ, 2016), was used to simulate O_3 over a North American modeling domain, which covers the continental US and parts of Canada and Mexico with a 12km horizontal grid (Fig. 1) and 26 vertical layers. The top boundary is defined by a fixed pressure level, approximately 14–17 km above ground level, which is generally in the

- 25 lower stratosphere (Seidel and Randel, 2006). The simulation period covered the O₃ season in 2010 (March to September) with 10 spin-up days. For the base-case simulation (NA-Base), which included all anthropogenic emissions, BCs were obtained from the G-Base simulation with GEOS-Chem. The background simulation (NA-Bkgd) used only natural emissions in the entire domain and BCs from the G-Bkgd simulation. Gas-phase chemistry was represented by the Carbon Bond 2005 (CB05) chemical mechanism (Yarwood et al., 2005). Formation of particulates was not included to reduce
- 30 <u>computational burden and because the focus was on O₃</u>.

Anthropogenic and fire emissions were obtained from the 2010 database developed for the Air Quality Model Evaluation International Initiative (AQMEII) Phases 2 and 3 (Pouliot et al., 2015). For the US, these emissions were developed by

projecting the National Emissions Inventory (NEI) for 2008 (US EPA, 2013) to 2010. We added lightning NO_x emissions using the CAMx lightning emission preprocessor (Koo et al., 2010; Morris et al., 2012). Biogenic emissions, including soil NO_{xx} were estimated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006) with updated land cover data and emission factors (Yu et al., 2015). Canadian and Mexican wildfire emissions are not

- 5 included in the AQMEII database because spatial and temporal information for these emissions was unavailable (Pouliot et al., 2015). Consequently, contributions of natural emissions in Canada and Mexico to US O₃ may be somewhat underestimated in our simulations. However, the absence of the Canadian/Mexican wildfire emissions should have minimal impact on our allocation of the anthropogenic O₃ increment to the anthropogenic Canadian/Mexican emissions. A summary of the emissions is in Table 1, divided into the contributions from the US and the remainder of the CAMx domain.
- 10 Meteorological conditions and other auxiliary model inputs are also from the AQMEII modeling database. The meteorological fields are from a simulation for 2010 with the Weather Research and Forecasting (WRF) model (Skamarock et al., 2008) conducted by the US EPA as part of AQMEII.

2.3. Source apportionment by the Path-Integral Method

The PIM determines the source contributions by integrating first-order sensitivity coefficients over a range of emissions from the background case to the base case (Dunker, 2015). The equation relating the anthropogenic increment to the source contributions is

$$c_i^{base}(\mathbf{x},t; \mathbf{\Lambda}=1) - c_i^{bkgd}(\mathbf{x},t; \mathbf{\Lambda}=0) = \sum_{m=1}^{M4} \int_P \frac{\partial c_i(\mathbf{x},t;\mathbf{\Lambda})}{\partial \lambda_m} d\lambda_m$$
(1)

Here, c_i^{base} is the concentration of species *i* in the base simulation at location *x* and time t, c_i^{bkgd} is the concentration in the background simulation, <u>M is the number of sources</u>, and $\partial c_i(x, t; \Lambda))/\partial \lambda_m$ is the sensitivity of c_i to the parameter λ_m . The array-vector Λ contains the parameters λ_m , $m = 1, ..., 4\underline{M}$. Each λ_m scales the difference in emissions or BCs between the base and background cases such that when all $\lambda_m = 0$ (i.e., $\Lambda = 0$), we have the background case and when all $\lambda_m = 1$ ($\Lambda = 1$), the base case. P is some path from $\Lambda = 0$ to $\Lambda = 1$, not necessarily a straight line. The source contributions are the integrals on the right side of Eq. (1), and, as indicated, the sum of the source contributions is mathematically required to equal the difference between the base and background concentrations.

- In the forward-integration direction of Eq. (1), emissions are addedincrease along the path as the λ_m increase, and the integrals accumulate the contributions to O₃ from the sources due to the added emissions. Viewed in reverse, the path is a scenario for reducing emissions from the base case to achieve the background case. We chose a path on which all emissions are reduced by the same factor (a synchronous or diagonal path, represented by $\lambda_m = \lambda$, m = 1, ..., 4M). This is an unbiased approach that assumes that future controls on anthropogenic emissions will produce similar fractional reductions in different
- 30 regions and for different species. A different path could be chosen for the integration based on detailed projections of future emission controls in the US, Canada, Mexico, and countries outside the modelling domain. At least in the US, regulators have generally chosen to reduce all precursors of O₃ by similar fractions, e.g., from 1990 to 2015 emissions of NO_x, VOCs,

and CO were reduced by 54%, 41%, and 65%, respectively (US EPA, 2017). Thus, our assumption on controls, though simple, is reasonably consistent with long-term US history. Significant additional work would be necessary to create a more detailed control path for all the countries., but we know of no other assumption for emission controls that has a better justification.

- 5 For this work, we divided the anthropogenic increment to US O_3 into the <u>four</u> source contributions (M = 4): 1) US anthropogenic emissions in the CAMx domain; 2) Canadian/Mexican anthropogenic emissions in the domain; 3) the anthropogenic component of the lateral BCs; 4) the anthropogenic component of the top BCs. The latter two sources represent pollutants from anthropogenic emissions outside the domain that arrive through the boundaries. Together, the four sources account for the impact of all anthropogenic emissions, worldwide, on the US O_3 . Regarding the first two sources,
- 10 we separated shipping emissions within the CAMx domain into emissions inside and outside the US Exclusive Economic Zone (NOAA, 2016a), generally a 200-nautical mile limit of the coast (Fig. 1). Emissions inside the limit were assigned to the US; outside the limit, to the Canadian/Mexican category. <u>The latter two sources represent pollutants from outside the domain that arrive through the boundaries</u>. <u>Also, for the last two sources, the pollutants arriving through the boundaries consist of both primary anthropogenic emissions emitted species and secondary pollutants, e.g., O₃, formed from the</u>
- 15 emissionsemitted species. The PIM, as implemented for this study, includes the impact of all the boundary species, and <u>T</u>the anthropogenic component of the BCs is determined by the difference in BCs between the base and background cases. Anthropogenic species emitted within the CAMx domain and secondary pollutants resulting from them may move outside the domain and then recirculate back into the domain. The PIM includes this effect via the anthropogenic component of the BCs, to the extent that GEOS-Chem has similar emissions, circulation patterns and chemistry as CAMx within the CAMx
- 20 domain. In our calculations, the impact of such recirculation of anthropogenic pollutants will be ascribed to the BCs, rather than to anthropogenic emissions from the US or Canada/Mexico. If the PIM were used with a single global model, the impact of the US anthropogenic emissions would be ascribed to the US, regardless of where the US emitted species and secondary pollutants are transported. Current tracer methods used in regional models (e.g., Ozone Source Apportionment Technology; Yarwood et al., 1996; Ramboll-Environ, 2016) estimate the contribution of the total BCs but do not separate
- 25 <u>out the contribution of anthropogenic pollutants arriving via the boundaries. The brute-force method could estimate the contribution of anthropogenic pollutants entering from the boundaries by difference between two simulations with different BCs, i.e., derived from global model simulations with and without anthropogenic emissions.</u>

Equation (1) is an exact mathematical relationship, but in an application, the integration must be done numerically. We used a Gauss-Legendre formula with 3 points (Fullerton, 2003) and transformed the integration variable from λ to $r = \lambda^{0.5}$ to

30 improve accuracy. The sensitivities were calculated at the 3 points (different levels of emissions and BCs) by the Decoupled Direct Method (DDM) (Dunker, 1984; Dunker et al., 2002). Additional details of the PIM are in Dunker (2015) and Dunker et al. (2015). Figure 2 illustrates schematically the relationship of the PIM to the GEOS-Chem and CAMx simulations.

3 Results

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3.1. Model performance for GEOS-Chem

We evaluated modeled O_3 from the G-Base simulation at selected surface sites outside the US: one site in Ireland, four sites in Japan, and five sites in Canada (WMO, 2016). The site in Ireland (Mace Head) is influenced by outflow transport across

- 5 the Atlantic Ocean from North America. The Japanese sites experience O₃ export from continental Asia to the Pacific Ocean, and the five rural sites in Canada are near the northern boundary of the CAMx modeling domain. For averages over March–September using a 40 ppb threshold, GEOS-Chem underestimated O₃ at all the selected sites except for Kejimkujik in Nova Scotia, which is influenced by US outflow (Table 2). With no threshold, GEOS-Chem over-predicted O₃ at all sites except Mace Head. Thus, GEOS-Chem has less dynamic range than observations and tends to underestimate the larger
- 10 surface O₃ concentrations outside the CAMx domain but overestimate the lower concentrations. With the 40 ppb threshold, the normalized mean error is 13%–28%. The error and the correlation are both generally greater with no threshold. Vertical O₃ profiles were compared to ozonesonde measurements (NOAA, 2016b) at Trinidad Head, CA, Hilo, HI, Boulder, CO, Huntsville, AL, Narragansett, RI, Summit, Greenland, and the South Pole (Table S5). Figure 3 shows the comparisons
- 15 Figures S1 and S2 give comparisons for the other sites. In addition to the measurement data and results for the G-Base simulation, results are also included for the G-Bkgd simulation to indicate the impact of worldwide anthropogenic emissions on O₃ above the surface.

At Trinidad Head, there is relatively good agreement between the G-Base O_3 and the ozonesonde measurements at altitudes up to the mid-troposphere (~7 km) that are most influential to ground-level O_3 in the Intermountain West and Eastern US

for Trinidad Head and Hilo in April and August, 2010, two sites likely to be influenced by transport of O₃ from Asia.

- 20 (Nopmongcol et al., 2017). However, the G-Base O₃ is greater than the measurements in the marine boundary layer (<1 km) in August and less than the measurements at upper altitudes in April. At Hilo, the G-Base O₃ is very close to the measurements in April and to the surface measurements in August but overestimates the measurements above the surface in August. At sites interior to the US (Boulder, Huntsville Narragansett), the modeled O₃ agrees well with the measurements in April below 7 km but is consistently greater than the measurements by ≥20 ppb in August. The G-Base O₃ at Summit agrees
- 25 reasonably well with the measurements below 7 km in August but underpredicts the measurements in April. Agreement at the South Pole is very good at all altitudes.

Near the top boundary of the CAMx domain, GEOS-Chem consistently overpredicts O₃ for mid-latitude sites (Boulder, Hilo, Huntsville, Narragansett, Trinidad Head) (Fig. S3). From 15–25 km, the predictions for the G-Base case are up to 1200 ppb greater than measurements. To the extent that this stratospheric air is mixed downward, it would contribute to any overpredictions by GEOS-Chem and CAMx in the troposphere.

We also compared GEOS-Chem predictions to observations at CASTNet sites, which are rural locations (US EPA, 2016a). Following Fiore et al. (2014), Fig. 4 presents a comparison of monthly average MDA8 O₃ from the G-Base and G-Bkgd simulations to the observations at high-altitude (>1.5 km) Intermountain West sites (except CA) and at low-altitude (<1.5 km) sites. (Sites are shown in Fig. S4.) In March and April, the G-Base O_3 agrees well with observations at low-altitude sites and somewhat underestimates observations at the high-altitude sites but, in summer, significantly overestimates the observations at all altitudes. Also, the observations show a small decreasing trend from spring to summer whereas the G-Base results show a clear increasing trend. The G-Bkgd results parallel those of G-Base, approaching the observed mean

- 5 MDA8 O₃ for the high-altitude sites in August, suggesting that the summer O₃ overestimation of the G-Base simulation is largely caused by overestimating the non-anthropogenic contribution. Other studies indicate that overestimated lightning NO_x emissions in the southern US (below 35° N) may explain the positive GEOS-Chem bias in summer at the Intermountain West sites (Zhang et al., 2014; Travis et al., 2016). The positive bias in summer at the low-altitude sites may be due to overestimated lightning NO_x emissions and/or excessive vertical mixing (Travis et al., 2016). GEOS-Chem may also
- 10 overestimate the contribution of US anthropogenic emissions to summer O₃, e.g. because of coarse horizontal grid resolution or because NO_x emissions are overestimated in EPA's 2011 National Emissions Inventory (Travis et al., 2016), but the August ozone soundings at continental US sites (Fig S1) suggest otherwise because the O₃ overprediction is larger in the mid-troposphere than near ground level. Lack of halogen chemistry may also contribute to the O₃ overpredictions (Schmidt et al., 2016; Sherwen et al., 2016). Seasonal averages and the 4th highest MDA8 O₃ concentrations in the North American
- The GEOS-Chem evaluation at surface and ozonesonde sites outside the US shows both over- and underprediction compared to measurements (Table 2, Figs. 3, S2), which introduces uncertainty in the BCs for CAMx. The GEOS-Chem positive bias in summer at sites within the US (Figs. 4, S1) should not directly influence our modeling with CAMx for the North American domain.

domain for the G-Base and G-Bkgd cases are shown in Fig. S5.

- 20 It is difficult to compare our performance with the GEOS-Chem model to that in recent studies due to differences in the version and configuration of the model, the emissions used, the year simulated, and the observational data compared to the model results. Given these limitations, our performance is similar to what some others have obtained (Zhang et al., 2008; Emery et al., 2012; Nopmongcol, 2016). However, Zhang et al (2014), who reduced lightning NO_x emissions, Travis et al. (2016), who reduced lightning and anthropogenic NO_x emissions, and Yan et al. (2016), who used three two-way nested
- 25 models within GEOS-Chem, obtained better performance than we did. Fiore et al. (2014) also found better performance for GEOS-Chem in their analysis corresponding to Fig. 4. An alternative global model is the Geophysical Fluid Dynamics Laboratory's Atmospheric Model 3 (AM3) (Donner et al., 2011). GEOS-Chem and AM3 have important differences in biogenic isoprene emissions and chemistry, lightning NO_x and wildfire emissions, and stratosphere–to–troposphere transport (Fiore et al., 2014). Fiore et al. (2014) found that AM3 gives
- 30 greater background O₃ at high-altitude western surface sites in spring than GEOS-Chem. This may be due to more stratosphere–to–troposphere transport in AM3 (Lin et al., 2012) and/or more efficient mixing of free tropospheric air into the planetary boundary layer. Emery et al. (2013) found that CAMx simulations using BCs from GEOS-Chem had better performance for maximum daily average 8-hour (MDA8) O₃ at EPA's Clean Air Status and Trends Network (CASTNet) sites (US EPA, 2016a) in April–May than simulations using BCs from AM3; BCs from GEOS-Chem and AM3 gave similar

CAMx performance for June–September. Considering this work, we chose GEOS-Chem for the present study. However, AM3 may simulate the day-to-day variation in the stratospheric contribution to spring O_3 in the western US better than GEOS-Chem (Lin et al., 2012; Fiore et al., 2014).

3.2. Model performance for CAMx

- 5 Figure 4 also contains results for the CAMx NA-Base and NA-Bkgd simulations at CASTNet sites. The NA-Base results are closer to the mean of the observations at both the high-and low altitude sites than are the G-Base results, and the NA-Base results are always within one standard deviation of the mean. However, the NA-Base results show essentially no trend from spring to summer whereas the measurements show a downward trend. The NA-Bkgd results parallel the NA-Base results ~20 ppb lower at the low-altitude sites and ~15 ppb lower at the high-altitude sites.
- In addition to comparing CAMx predictions to observations at CASTNet sites, we evaluated performance for the sites reporting to EPA's Air Quality System (AQS), which are urban and suburban locations (US EPA, 2016b). Figure 5 presents a comparison of predicted MDA8 O₃ concentrations from the NA-Base case with observations at AQS and CASTNet sites, using a zero threshold for the observations. The normalized mean bias (NMB) is 4.5%–5.1% and the normalized mean error (NME) is 17.1%–18.1%, which suggest good performance. However, there is overprediction at the lower concentrations and
- 15 underprediction at the higher concentrations similar to, but more pronounced than, that in other work (Emery et al., 2012; Nopmongcol et al., 2016, 2017).

To investigate further, we compared our BCs from GEOS-Chem to those provided by the European Centre for Medium-Range Weather Forecasts (ECMWF) for the Air Quality Model Evaluation International Initiative (AQMEII) Phase 3 (Nopmongcol et al., 2017). Figure S6 compares simulations for summer with the two sets of BCs; deposition was included

- 20 but chemistry and emissions were inactive. At the AQS and CASTNet sites, the GEOS-Chem BCs generally gave greater MDA8 O₃ than the ECMWF BCs. This suggests that the GEOS-Chem BCs contribute to the overprediction in Fig. 5 at the lower concentrations. Plots of the simulated MDA8 O₃ from the NA-Bkgd case vs. the observations (not shown) display overprediction for observations < 20 ppb, so overprediction at low concentrations apparently exists in the background case also. The reasons for the underprediction at observed concentrations > 70 ppb in Fig. 5 are not clear. Some of the
- 25 underprediction could be due to the absence of the Canadian/Mexican wildfire emissions. Deriving CAMx BCs from the ECMWF model rather than GEOS-Chem would have improved performance of our NA Base case but was not viable because there was no matching simulation with zero anthropogenic emissions for our NA Bkgd case.
 We have include DMFD and DMFD for the DMFD and DMFD and DMFD.

We also determined the NMB and NME for the NA-Base simulation, focusing on the larger concentrations by using a 40ppb threshold for the MDA8 O₃ observations (Table S6). The NMB and NME ranged from -4.9 % to 4.3 % and 12.1% to

30 14.2 %, respectively, at the AQS and CASTNet sites in spring and summer, which are similar magnitude NMB and smaller NME than with the zero threshold. This performance is comparable to that obtained by Nopmongcol et al. (2017) for AQMEII Phase 3 (Table S6) using a similar CAMx configuration and inputs (except for BCs, dry deposition scheme, lightning NO_x and biogenic emissions), indicating that factors shared by these two simulations (e.g., anthropogenic emissions, chemistry scheme, meteorology) are most influential on the larger O_3 concentrations.

3.3. Boundary concentrations from GEOS-Chem

The monthly average O₃ concentrations on the lateral boundaries of the CAMx domain are shown in Fig. 6 for the surface

- 5 layer and layer 23, which is centered near 10 km altitude. Mostly, layer 23 represents the upper troposphere except near the northern boundary in late spring, where the tropopause is lower (Seidel and Randel, 2006) and layer 23 represents the lower stratosphere. In the surface layer for the west, east, and south boundaries, the O₃ concentration is 30-45 ppb for the base case, and there is a minimum in June or July. On the north boundary, the concentration is generally lower by up to 9 ppb than on the other boundaries. For layer 23, there is a decreasing trend from spring to summer on the north, west, and east
- boundaries and no clear trend on the south boundary; the O_3 concentration is greatest on the north, similar on the west and east and least on the south boundary. In April, layer 23 of the west boundary shows a springtime maximum in upper tropospheric O_3 , which has been associated with events of high ground level O_3 in the Intermountain West (Zhang et al., 2014) when air descends from high altitude to ground level with little dilution. In the base case, the concentration for layer 23 is 20–134 ppb greater than for the surface layer, reflecting destruction at the surface. These trends in the base-case BCs
- 15 are consistent with our understanding of tropospheric O₃ in the Northern Hemisphere. The boundary concentrations for the NA-Bkgd case closely parallel those for the NA-Base case on all lateral boundaries in layer 23 and on the west in the surface layer. The anthropogenic increment to the lateral boundary concentrations is 7–22 ppb in the surface layer and 8–20 ppb in layer 23. This increment is a large fraction (generally 30–60%) of the base-case boundary concentrations for the surface layer but a moderate fraction (10–21%) for layer 23. The April and August average
- O₃ concentrations on the top boundary of the CAMx domain, at 14–17 km, are shown in Fig. S7 for the base case along with the anthropogenic increment. The increment for the top boundary is of similar magnitude to that on the lateral boundaries for layer 23 and the surface layer. However, the anthropogenic increment on the top boundary is only a small fraction (typically 1–5%) of the top boundary concentration for the base case. Thus, GEOS-Chem predicts a positive but only small influence of anthropogenic emissions on O₃ in the lower stratosphere, and the O₃ difference on the top boundary between the
- 25 NA-Base and NA-Bkgd simulations should give only a small contribution to the source apportionment (confirmed below).

3.4. Base-case and background ozone

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The spring (March–May) and summer (June–August) seasonal averages of MDA8 O_3 from the NA-base and NA-Bkgd simulations are given in Fig. 7. Also shown is the average of the 10 largest MDA8 O_3 concentrations in the base case (T10Base) over March–September and the average over the same days in the background simulation. (The T10Base dates can differ by grid cell.) <u>Our goal with the T10Base metric is to include a reasonable variety of days with large MDA8 O_3 , but this metric is not directly related to a regulatory standard. For the base case in spring, the larger O_3 concentrations are in</u>

an arc from British Columbia through the Rocky Mountains into the Sierra Madre mountains of Mexico, across the Gulf of

Mexico and along the US east coast. The background O_3 in spring has a similar spatial pattern with the largest concentrations of 40–50 ppb in Colorado, New Mexico, Arizona, and Mexico. However, in the base case, the O_3 levels in the western and eastern US are similar, but in the background case the levels are distinctly lower in the eastern than western US.

- 5 The summer average for the base case shows MDA8 O₃ greater than 50 ppb across most of the US. The largest concentrations are near or downwind of urban areas and in Colorado with the maximum of 69 ppb near Washington, DC. The spatial pattern of the background concentration in summer is like that in spring except that concentrations are smaller in Mexico and larger in Canada than in spring. The largest background concentrations are in Colorado and California, and the maximum is 47 ppb in the Sierra Nevada mountains.
- 10 The T10Base average for the base case shows an even more pronounced impact of urban areas with larger concentrations also in Colorado, New Mexico, and Mexico. The maximum concentration is 96 ppb, again near Washington, DC. The T10Base average for the background case assigns the largest concentrations to central Canada, the western US, and Mexico. The maximum background of 64 ppb is in the Sierra Madre Occidental mountains of Mexico, but there are also locations in Colorado, New Mexico, Arizona, and California that exceed 60 ppb.
- 15 Table 3 gives the T10Base concentrations for the base and background cases at 10 urban and two CASTNet sites. In choosing sites to represent urban areas, we selected the site with highest design value in each urban area. (Site IDs are in Table S7.) Also in the table are the base and background concentrations averaged over the 10 days with the largest background concentrations (T10Bkgd). For the base case, the T10Base averages exceed 70 ppb at all the sites except Sacramento, Salt Lake, Big Bend, and Perkinstown, and the T10Bkgd averages exceed 60 ppb at half the sites. The
- 20 background concentrations are largest at the higher elevation (> 1 km) sites: Denver, Salt Lake, and Big Bend. The T10Bkgd average for the background case ranges from 35 to 54 ppb at the 12 sites, and the T10Base average background ranges from 24 to 50 ppb. For Denver, the background concentration is 69% and 79% of the base case concentration with the T10Base and T10Bkgd averages, respectively.

The ratio of the background MDA8 O₃ concentration to the base-case concentration is shown in Fig. 8 for the spring,

- 25 summer, and T10Base averages (ratio = background average/base average). For all three averages, the ratio is larger at most locations in the western US than the eastern US, and the difference between the western and eastern US becomes greater from the spring to summer to T10Base averages. The background O₃ generally becomes both a larger fraction of the base-case O₃ in the western US and a smaller fraction in the eastern US as the base-case O₃ increases across the three averages. Table S8 gives the ratio for the same 12 sites as in Table 3 for the spring, summer, T10Base and T10Bkgd averages. For the
- 30 largest O₃ concentrations (T10Base), Denver, Salt Lake and Big Bend have the largest ratios (69%, 66%, and 74%, respectively) and Boston, Pittsburgh, and Washington, DC the smallest ratios (32%, 33%, and 30%, respectively). There are some exceptions to the general trend of larger ratios in the western than eastern US, e.g. the ratios for Sacramento and Perkinstown are 36% and 66%, respectively.

3.5. Source apportionment of the anthropogenic increment

The PIM quantifies source contributions by numerically integrating Eq. (1), and we evaluated the accuracy of the numerical integration by comparing the sum of the contributions to the anthropogenic increment (right-hand side vs. left-hand side of Eq. (1), respectively). Including all surface grid squares in the CAMx domain, the sum of the contributions to MDA8 O_3

- 5 correlated closely (R² = 0.999, least squares slope = 0.99) with the anthropogenic increment in March and June (Fig. S8). At selected AQS and CASTNet sites, the maximum error and average error over the seven-month simulation are <3.5 ppb and < 1.5 ppb, respectively (Fig. S9). Errors are smaller at the CASTNet sites than at the AQS sites, most likely because the concentrations are smaller at the CASTNet sites. This accuracy is very similar to that in our previous application of the PIM for a 3D simulation. (Dunker et al., 2015).</p>
- 10 The anthropogenic increment to MDA8 O₃ in ppb, based on the T10Base average, is shown in Fig. 8-9 along with the source contributions to the increment from the PIM. Analogous plots for the spring- and summer- average MDA8 O₃ are in Figs. S10 and S11, respectively. The relative source contributions in percent are in Figs. 910, S12, and S13. These figures do not show the contribution from the anthropogenic component of the top BCs because this contribution to surface concentrations is always very small, ≤ 0.5 ppb or $\leq 3\%$ of the increment. The small magnitude is consistent with the small fraction of the
- 15 top BCs arising from anthropogenic emissions, as predicted by GEOS-Chem (Fig. S7). The small contribution of anthropogenic top BCs does not preclude a larger contribution from natural stratospheric O_3 . We omit further analysis of the anthropogenic top BCs contribution.

The anthropogenic increment is larger to the east of mid-Texas and along the west coast than in the states in between and generally larger in summer than spring. The maximum increment is 30 ppb in spring along the Louisiana coast, 42 ppb in

- 20 summer near Washington, DC, and 75 ppb for the T10Base average, also near Washington, DC. The US anthropogenic emissions are the largest contributor in ppb and percent to the anthropogenic increments in the eastern US and California. This is apparent in Figs. <u>89</u>, <u>9-10</u> and also in the source contributions for the T10Base average in Table 3. For the cities in Table 3 in the eastern US and California (all but Denver and Salt Lake), the US anthropogenic emissions contribute 39–53 ppb (86–93%) of the T10Base increments.
- 25 The anthropogenic lateral BCs are the second most important contributor in ppb to the anthropogenic increment at most locations in the domain (Fig. <u>89</u>). The contributions are largest for higher elevation US sites in the Intermountain West and sites closest to the boundaries along the western boundary of the CAMx domain, consistent with transport of pollutants from Asia. The lateral BCs contribute 8–9 ppb (39–51%) of the T10Base anthropogenic increments at Denver, Salt Lake, and Big Bend (Table 3). At Perkinstown (northern WI), the lateral BCs contribute 6 ppb (30%) of the increment. The contribution
- 30 of the lateral BCs is largest near the west boundary of the CAMx domain, decreases from the western boundary across the US, and increases from the US east coast toward the east boundary. The increase toward the east boundary is greatest in spring in the northeast and may be due to transport of Canadian emissions emitted species and O₃ from inside to outside the

CAMx domain and re-circulation back through the east boundary via the BCs from GEOS-Chem. On a relative basis, the lateral BCs are important where the US emissions are not very important and vice versa (Figs. <u>910</u>, S12, S13).

The Canadian/Mexican anthropogenic emissions are third in importance, affecting the northern, east-coast, and southwest US and some interior states. In summer, these emissions also contribute ~2 ppb to the anthropogenic increment along the west coast, south to San Francisco (Fig. S11). The spatial pattern is consistent with prevailing summer surface winds, which circulate anti-cyclonically around the Eastern Pacific subtropical high pressure area. At sites in Table 3 close to Canada and

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Mexico, Cleveland and Big Bend, the Canadian/Mexican emissions contribute 3 ppb (7%) and 2 ppb (12%), respectively, to the T10Base anthropogenic increment.

Table 3 also contains the source contributions obtained with the T10Bkgd average. The anthropogenic increment from the

- 10 T10Bkgd average is 6–37 ppb lower at the urban sites and 4–8 ppb lower at the CASTNet sites compared to the increment from the T10Base average. This reduction is due to a reduced contribution from the US emissions. The contribution of the Canadian/Mexican emissions remains about the same at all the sites with the T10Bkgd average, and the contribution of the lateral BCs increases by 2–5 ppb at the lower elevation urban sites. The net effect is that the relative importance of the lateral BCs is significantly increased for the days with the largest background concentrations. For five sites, the contribution
- 15 exceeds 50% of the anthropogenic increment and at Denver and Big Bend, the lateral BCs account for 71% and 67% of the increment, respectively.
 - Figure <u>10-11</u> has time series of the base-case and background concentrations and the source contributions for five of the sites in Table 3. Time-series plots for other AQS and CASTNet sites are in Figs. S14, S15, respectively. The background concentration is 20–40 ppb at Cleveland and Dallas but generally greater, 30–50 ppb, at Denver and Big Bend and a larger
- 20 fraction of the base-case concentration at the latter sites. At Perkinstown, the background is 20–30 ppb in spring but greater in July and August, including a peak of 58 ppb on July 6. The contribution from the lateral BCs is generally larger in spring (5–15 ppb) than in summer (\leq 5 ppb). At Cleveland, Dallas, and Perkinstown, the larger MDA8 O₃ concentrations in the base case are driven by the US emissions (except for July 6 at Perkinstown). The US emissions contribute to the base-case concentrations at Denver and Big Bend during summer, but are less important (< 20 ppb) than at other sites. The
- 25 contribution of Canadian/Mexican emissions is largest for Cleveland and Big Bend, with maximum contributions at these sites of 22 ppb and 13 ppb, respectively.

There are negative contributions from US anthropogenic emissions on some days in Cleveland, Dallas, and Denver. These are situations in which large NO_x emissions in the base case inhibit O_3 formation. The sensitivity of O_3 to the emissions is positive at the starting point of the integral in Eq. (1) (background case) but negative at the ending point (base case), and if

30 the emissions are large enough, the total integral is negative. The negative contributions, which are small in magnitude, merely indicate that large reductions in the US anthropogenic emissions are necessary on these days before O_3 decreases in response.

4 Conclusions

We used the CAMx regional model in a one-way nest within the GEOS-Chem global model to predict North American O_3 concentrations in March–September 2010 for a base case with all emissions present and a natural-background case without worldwide anthropogenic emissions. The difference between these two simulations, the anthropogenic increment, was

- 5 allocated to the anthropogenic sources: US emissions, Canadian/Mexican emissions, and the anthropogenic components of the lateral BCs and the top BCs. The PIM was used for this source allocation, which required sensitivities from three additional simulations with emissions and BCs intermediate between the base and background cases. The major unique features of the study are allocating the anthropogenic O₃ increment, rather than the total concentration, and estimating contributions of the anthropogenic components of the BCs, rather than the total BCs (Lefohn et al., 2014; Dolwick et al.,
- 10 2015; Baker et al., 2015; Nopmongcol et al., 2017).

The predicted natural background MDA8 O₃ is larger in the western US and Mexico than in the eastern US. The spatial pattern is similar in spring and summer with the exceptions that concentrations are smaller in Mexico and larger in Canada in summer. The largest background MDA8 O₃ in the US is in the mountainous areas of Colorado, New Mexico, Arizona, and California. For the larger MDA8 O₃ concentrations in the base case (T10Base average), the background O₃ at Denver is 50

15 ppb, which is 69% of the corresponding base-case concentration (72 ppb). The background O₃ exceeds 60 ppb in some other western US locations.

Using the T10Base average, the US anthropogenic emissions are the largest contributor in ppb and percent to the anthropogenic O_3 increments in the eastern US and California. Second in importance are the contributions of the anthropogenic lateral BCs, which are largest for the higher elevation US sites in the Intermountain West and sites closest to the boundaries. The Canadian/Mexican emissions are third in importance, affecting the northern, east-coast, and southwest

- 20 the boundaries. The Canadian/Mexican emissions are third in importance, affecting the northern, east-coast, and southwest US and some interior states. The contribution of the anthropogenic top BCs is always very small. We also examined results for the larger MDA8 O₃ in the background case (T10Bkgd average). The anthropogenic O₃ increment is smaller with the T10Bkgd average than the T10Base average due to a reduced contribution from US emissions. The contribution of the Canadian/Mexican emissions remains about the same, and the contribution from the lateral BCs
- 25 increases by up to 5 ppb at lower elevation urban sites. The net effect is that the relative importance of the lateral BCs is significantly increased for the days with the largest background concentrations, up to about 70%. GEOS-Chem may have less stratosphere-troposphere exchange than AM3, which may cause the smaller background O₃ concentrations with GEOS-Chem than AM3 found by Fiore et al. (2014) for the western US in spring. Hence, using BCs from AM3 for the CAMx simulations may give greater background and base-case O₃ at western sites in spring, which could
- affect the T10Bkgd results in Table 3. The T10Base results would not be affected because all the days included in the average are in summer except for the Big Bend average, which includes some spring days.
 Global and regional models are continuing to evolve as new data and analyses become available. Estimates of lightning NO_x

emissions have been reduced in recent studies with GEOS-Chem (Zhang et al., 2014; Travis et al., 2016) from those in the

version of GEOS-Chem we used (Zhang et al., 2011). Using satellite data, Pickering et al. (2016) estimated even lower lightning NO_x emissions (per flash) over the Gulf of Mexico than Zhang et al. (2014) and Travis et al. (2016). Such changes would affect the BCs obtained from GEOS-Chem for the south boundary of our CAMx domain but also the lightning NO_x emissions used in CAMx.

- 5 Several recent studies have concluded that the 2011 NEI overestimates US anthropogenic NO_x emissions (Anderson et al., 2014; Goldberg et al., 2016; Souri et al., 2016; Travis et al., 2016). Our CAMx simulations used the 2008 NEI projected to 2010, but the procedures used in developing different versions of the NEI are similar enough that any overestimation of NO_x emissions in the 2011 NEI likely implies overestimation in the 2008 NEI as well. Any overestimation in our inventory would directly cause an overestimate of the source contribution for US anthropogenic emissions. Our GEOS-Chem
- 10 simulation did not include the changes of Travis et al. (2016), so overestimation in the inventory would also indirectly affect the source contributions via the BCs to the extent that there is recirculation of pollutants from inside the North American domain to the outside and then back.

Other recent work has suggested changes to GEOS-Chem for O_3 generation in wildfire plumes (Zhang et al., 2014; Lu et al., 2016), vertical mixing in the lower troposphere (Travis et al., 2016), and the chemistry (Fisher et al., 2016; Schmidt et al.,

15 2016; Sherwen et al., 2016). Of note, adding halogen chemistry decreases the global tropospheric O₃ burden in GEOS-Chem by 14%–19% (Schmidt et al., 2016; Sherwen et al., 2016). As some of these proposed modifications are implemented in global and regional models, predictions of the background O₃, the anthropogenic increment, and the source contributions to the increment are likely to change.

Supplementary information

20 Supplementary information associated with this article is found in the online version at doi:xxx.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1. Average daily emissions in the CAMx modeling domain for March–September 2010.

Source	US en	nissions (tons/da	y)	Canadian/Mexican emissions (tons/day)			
	NO _x	VOC	CO	NO _x	VOC	CO	
Anthropogenic (inland)	41,206	31,194	139,750	7,377	7,596	26,874	
Shipping	1,927	61	163	1,290	40	106	
Fires	559	6,054	37,851				

Lightning	5,983			4,577		
Biogenic	1,634	125,249	18,092	717	47,471	4,810
Total	51,308	162,557	195,855	13,961	55,107	31,790

Table 2. Model performance metrics for hourly O₃ from the GEOS-Chem base case for the March–September, 2010 period with zero or 40 ppb thresholds for the observed concentrations.

Site	Latitude/	Threshold (pph)	NMB ^a	NME ^a	RMSE ^a	R ^a
Mace Head	53.33/-9.90	none	-4.4	13.1	6.0	0.68
Ireland		40.	-15.2	15.7	8.2	0.25
Tsukuba	36.05/140.13	none	20.9	42.1	15.3	0.73
Japan		40.	-13.8	20.0	14.7	0.60
Ryori	39.03/141.82	none	4.5	23.5	12.2	0.38
Japan		40.	-12.3	15.5	10.3	0.26
Minamitorishima	24.28/153.98	none	20.8	37.7	10.0	0.66
Japan		40.	-28.1	28.1	16.5	0.28
Yonagunijima	24.47/123.02	none	7.5	29.5	11.3	0.84
Japan		40.	-15.4	16.7	11.2	0.52
Algoma	47.03/-84.38	none	46.1	57.6	19.5	0.20
Canada		40.	-14.7	17.3	9.0	0.07
Bratt's Lake	50.20/-104.71	none	33.5	44.8	15.4	0.39
Canada		40.	-5.0	20.5	11.8	0.16
Chapais	49.82/-74.98	none	26.4	36.9	13.7	0.48
Canada		40.	-8.5	13.3	7.3	0.46
Experimental Lakes	49.67/-93.72	none	33.2	40.6	15.5	0.27
Canada		40.	-4.4	14.9	8.7	0.13
Kejimkujik	44.43/-65.20	none	37.7	42.8	16.1	0.35

Canada	40.	1.0	13.8	8.4	0.39	

^a NMB =normalized mean bias; NME = normalized mean error; RMSE = root mean square error; R = correlation coefficient

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Table 3. Contributions of anthropogenic sources to the anthropogenic increment of MDA8 O3 at AQS and CASTNet sites.^a

	T10Base (ppb) ^b			T10Bkgd (ppb) ^c							
Site ^d	Base	Bkgd	US	Can/Mex	Anthro	Base	Bkgd	US	Can/Mex	Anthro	
			anthro	anthro	lateral BCs			anthro	anthro	lateral BCs	
Atlanta, GA	83.3	28.4	48.3	0.4	3.6	60.6	41.2	11.3	0.4	6.3	
Boston, MA	75.5	24.4	45.5	1.8	2.8	55.6	35.1	13.2	1.9	5.2	
Cleveland, OH	73.1	26.1	39.8	3.2	3.4	58.1	40.8	9.7	1.9	5.7	
Dallas, TX	82.5	31.3	45.3	0.6	3.5	57.1	42.6	5.2	0.4	7.8	
Denver, CO	72.2	49.9	11.9	0.2	9.4	68.2	54.1	3.4	0.5	9.6	
Pittsburgh, PA	76.2	25.5	46.0	0.8	3.3	62.7	42.9	12.1	0.9	6.8	
Sacramento, CA	69.8	24.9	39.3	0.3	4.6	60.3	37.3	12.9	0.4	9.5	
Salt Lake, UT	66.2	43.7	13.2	0.3	8.4	62.4	46.2	6.6	0.3	8.9	
St. Louis, MO	76.3	26.1	45.8	0.5	3.0	55.6	40.1	6.9	0.7	8.0	
Washington, D.C.	83.8	25.5	53.4	1.2	2.8	59.7	38.6	13.2	0.7	7.0	
Big Bend, TX	62.7	46.5	6.0	2.0	8.3	60.7	48.6	2.7	1.2	8.2	
Perkinstown, WI	57.6	38.2	13.0	0.6	5.8	54.7	43.0	5.2	1.1	5.5	

15 ^a Anthropogenic component of the top BCs contributes ≤ 0.1 ppb.

^b Average of the 10 days with largest MDA8 O₃ in the base case. Days for the background case are the same as the base case.

^c Average of the 10 days with largest MDA8 O₃ in the background case. Days for the base case are the same as the background case.

^d IDs are in Table S7.



Figure 1. The modeling domain for CAMx showing monitoring sites included in the analysis. The orange line is the US Exclusive Economic Zone. Shipping emissions inside the zone were assigned to the US and outside the zone combined with Canadian and 5 Mexican anthropogenic emissions.

Attributing Ozone by the PIM



Attributing Ozone by the PIM



Figure 2. Schematic diagram of source apportionment by the path-integral method (PIM). Two worldwide GEOS-Chem simulations with and without anthropogenic emissions provide boundary concentrations (BCs) for the corresponding CAMx simulations. Two CAMx simulations with and without anthropogenic emissions give the base and background cases for North America. Three CAMx simulations using the decoupled direct method (DDM) provide the O₃ sensitivity to source category m forwith emissions and BCs scaled between the base and background cases by factors $\lambda_m^1, \lambda_m^2, \lambda_m^3$ using the decoupled direct method (DDM), provide the sensitivities needed to Numerical integration using the sensitivities at $\lambda_m^1, \lambda_m^2, \lambda_m^3$ gives the contribution of source m to allocate the anthropogenic increment to O₃ (base minus background cases), to four source categories using Eq. (1). Blue boxes and arrows indicate information flow for CAMx; orange boxes and arrows indicate information flow for the PIM.



Figure 3. Comparison of GEOS-Chem vertical O₃ profiles for the base and background cases in April and August to ozonesonde measurements at a site on the west of the continental US (Trinidad Head) and west of the CAMx domain (Hilo). Monthly averages are shown.



Figure 4. Observed and modeled monthly average MDA8 O_3 at high-and low-altitude CASTNet sites in 2010. G-Base and G-Bkgd are the GEOS-Chem global model base and background cases whereas NA cases are the CAMx North American model. Error bars for observations indicate one standard deviation. Site locations are shown in Fig. S4.



Figure 5. Scatter plots of modeled MDA8 O₃ concentrations from the CAMx base case vs. observations at AQS and CASTNet sites for March–September, 2010. The black and red lines are one-to-one and linear regression lines, respectively. Normalized mean bias (NMB) and normalized mean error (NME) were calculated with no threshold.



Figure 6. Monthly average lateral boundary O₃ concentrations for the CAMx surface layer and the 23rd layer, as provided by the GEOS-Chem simulations.



Figure 7. MDA8 O₃ concentrations from the CAMx base (a–c) and background (d–f) simulations averaged over spring (March–May), summer (June–August), and the 10 days in the base case with the largest concentrations <u>(during March–September, 2010)</u> (<u>T10Base</u>).



(a) Anthropogenic increment

(b) US anthro emissions



Figure 89. The anthropogenic increment (a) for the average of the top 10 MDA8 O₃ concentrations in the base case (T10Base) and the contributions (b–d) to this increment. The contribution from the anthropogenic component of the top BCs is \leq 0.5 ppb.

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(b) Can/Mex anthro emissions







Min= 0.0 at (1,1), Max=100.0 at (4,143)

Figure <u>910</u>. Relative contributions in percent to the anthropogenic increment of the <u>T10Base-top 10</u> MDA8 O₃ concentrations-in the base case. The contribution from the anthropogenic component of the top BCs is $\leq 3\%$.



Figure 1011. Anthropogenic contributions to MDA8 O₃ at selected AQS and CASTNet sites along with base-case and background concentrations and model performance statistics (no threshold).