Responses to CASAC Questions on the Ozone PA from Consultant Dr. David Parrish

Questions from Dr. James Boylan

Chapter 2 – Air Quality

- *Is the discussion on O_3 and Photochemical Oxidants in the Atmosphere (Section 2.1) accurate and complete? If not, what additional information needs to be included?*

The last sentence of the first paragraph of Chapter 2 lists 4 important factors that affect concentration of ozone and other photochemical products. Deposition to surfaces should be added as a 5th factor, as it has a strong effect on ambient ozone concentrations.

The sentence on lines 31-33 of page 2-2 is not correct. It would be accurate if revised to read: "This mechanism is similar to the chemistry driving summertime O_3 formation, although the photolysis of VOCs is a more important primary radical source in winter. In summer, the major primary radical source is the photolysis of O_3 to form an excited state O atom, which then can react with water to form OH radicals."

- *Is the discussion on Sources and Emissions of O_3 Precursors (Section 2.2) accurate and complete? If not, what additional information needs to be included?*

As I have stated in previous responses, the uncertainty of the ozone precursor emissions estimates should be clearly discussed and defined to the extent possible. This section gives no indication of the precision and accuracy of the estimates, except the total emissions of the precursor classes are given to 5 significant figures, which is misleading. I think that a paragraph should be included that discusses emission inventory uncertainty. One example of inventory uncertainty is the differences in emissions between those discussed in Section 2.2 and those actually used in the photochemical modeling discussed in Appendix 3C. (This comment largely repeats a comment that I made in my response to a similar question regarding the PM PA; more details are given there.)

- *Is the discussion on Ambient Air Monitoring and Data Handling Conventions (Section 2.3) accurate and complete? If not, what additional information needs to be included?*

I find the discussion in this section to be accurate and complete.

- *Is the discussion on Ozone in Ambient Air (Section 2.4) accurate and complete? If not, what additional information needs to be included?*

The discussion in this section is reasonably accurate and complete, but there are some subtleties that should be discussed to more clearly inform the reader. In Figure 2-5 relatively large symbols are used for each monitor color coded to indicate the 2015-2017 design values. The points with the largest design values are plotted last, so in urban areas with many monitors, one can only see the monitors with the largest design values. As a consequence, the plot gives a somewhat biased picture. If this figure used smaller symbols, the bias would at least be partially corrected. Figure 2.6 has a similar bias with larger symbols plotted last indicating the largest decreases, and smaller decreases and increases plotted first and with smaller symbols.

The conclusions drawn from Figures 2-7 and 2-8 do not adequately reflect the tremendous success of the U.S. effort to reduce ambient ozone concentrations. Figure 2-7 does accurately show that there has been a 32% decrease in U.S. annual 4th highest MDA8 levels since 1980, but that 32% does not consider the U.S. background ozone concentration that emission controls cannot directly affect. Parrish et al. (2017) and Parrish and Ennis (2019) show that when the percent decrease is based on the enhancement of those levels above what would be present from U.S. background ozone alone, then the percent decrease since 1980 is >80% (i.e., a decrease of more than a factor of 5). As the discussion notes, "the trend in the annual 4th highest MDA8 concentrations has been relatively flat since 2013, and the design values have been relatively constant since 2015." The primary reason for this behavior is that there is not much room left for improvement: < 20% of the 1980 enhancement above background. In my view this issue should be emphasized in the discussion of Figures 2.7 and 2.8 as well as in a similar plot in Figure 2-14.

The discussion of Figure 2-9 emphasizes that the five eastern U.S. regions have all shown decreases of at least 10 ppb in median annual 4th highest MDA8 values since the early 2000's, while the four western U.S. regions have all shown decreases of less than 10 ppb. It should be emphasized that this is primarily due to the eastern regions having, on average, more anthropogenic ozone in the early 2000s, which could be reduced., than in the western U.S. The reason this is not so obvious from figure 2-9 is that the U.S. background ozone is higher in the west. If that figure showed the enhancement of the 4th highest MDA8 values above the 4th highest MDA8 values that would be present from U.S. background ozone alone, then this point would be more obvious.

In Figures 2-10 and 2-11, the meaning of the boxes, lines and points should be explicitly stated as done in Figure 2-12.

The paragraph on lines 11-17 of page 2-19 reads: "Panel B shows the seasonal pattern for an urban site in Baton Rouge, LA. Throughout the southeastern U.S., the highest O_3 concentrations are often observed in April and May due to the onset of warm temperatures combined with abundant emissions of biogenic VOCs at the start of the growing season. This is often followed by lower concentrations during the summer months, which is associated with high humidity levels that tend to suppress O_3 formation. Some areas, particularly in the states bordering the Gulf of Mexico, may experience a second peak in O_3 concentrations in September and October." My understanding of the double peak behavior of ozone along the Gulf coast is that a particular meteorological pattern (i.e., the development of the Bermuda High) brings cleaner Gulf of Mexico air into the region during the mid-summer months, and more polluted continental air into the region before and after those months. I am not aware of any mechanism by which high humidity levels tends to suppress O_3 formation.

- *Is the discussion on Background O_3 (Section 2.5) accurate and complete? If not, what additional information needs to be included?*

(Note: some of the material here is similar to my responses to questions regarding background ozone in the O_3 ISA.)

In my view the perspective of this entire discussion should be changed. Over the U.S., the large majority of ambient ozone concentrations comes from background sources. Ozone produced from U.S. anthropogenic precursor emissions account for relatively minor, but important, enhancements of ozone concentrations above the concentrations that would be present from USB ozone alone. These enhancements are relatively large in urban areas, which account for ozone exceedances occurring primarily in urban areas. Understanding U.S. ambient ozone concentrations from this perspective would provide a useful basis for air quality policy development.

Footnote 17 is incorrect. Ozone concentrations that do not include contributions from U.S. anthropogenic emissions can indeed be determined exclusively from O_3 measurements (see Parrish et al., 2017; Parrish and Ennis, 2019), although it is true that they cannot be directly measured.

Figure 2-15b is misleading. The second example (Ex 2) is meant to acknowledge that background ozone can be a large contributor to ozone concentrations at some sites, even when the MDA8 ozone concentration exceeds the NAAQS. However, the figure understates the possible contribution of U.S. background ozone. For example, Figure 3 of Jaffe et al. (2018), which is reproduced as Figure 2 below, suggests that U.S. background ozone alone can give ozone design values that exceed 60 ppb over most of the southwestern U.S. An observationally based approach for estimating ozone design values from USB ozone alone (Figure 3 below) gives a similar indication. This is a critical issue that must be faced when attempting to reduce design values to a NAAQS of 70 ppb or lower. Example 2 of Figure 2-15b should be revised to more clearly show the difficulty of this situation.

Section 2.5.1.6 on Post-Industrial Methane has some shortcomings. It is true that in "The U.S. and the rest of the world anthropogenic methane emissions have not been tracked quantitatively in detail until relatively recently." However, it does not follow that "As a result, the pre-industrial methane concentration is relatively unconstrained." Pre-industrial methane concentrations are firmly established from measurements of methane trapped in air bubbles in ice cores.

Section 2.5.1.6 on Post-Industrial Methane should also emphasize that the role methane plays in the determining global tropospheric ozone concentrations has been quantified only by chemistry-climate model simulations. That dependence is expected to be critically dependent upon the model-derived global NOx concentration distribution, and the model simulations of that NOx distribution are quite sensitive to parameterizations of many physical processes within the models. The parameterizations have been tested by observation-model comparisons only to a limited extent, so their success in realistically simulating the physical processes remains uncertain. Finally, the NOx concentration distribution is poorly characterized from the limited measurements available, and the measured concentrations are often at or below the detection limit of the instruments making the measurements. Thus, in my opinion, increasing methane may indeed increase global ozone concentrations, but due to model uncertainties that relationship is uncertain. Conceivably increasing methane may decrease, rather than increase, global ozone concentrations. The uncertainty regarding methane's role should be made clear.

Section 2.5.2.2 – Methodology: Strengths, Limitations and Uncertainties - discusses uncertainties in model estimates of USB. The final concluding sentence is "As a single estimate, this study relies upon the literature based (estimate of USB uncertainty of) ±10 ppb for seasonal means (Jaffe et al., 2018)." However, Jaffe et al. (2018) go on to add the phrase "…and higher for individual days." Since the design value is based on 4 individual days, the USB contribution to the design value fall in the "higher than ±10 ppb category. It would be informative to present model-measurement comparisons for the ODVs recorded at relatively isolated rural CASTNET sites in the southwestern U.S. The influence of U.S. anthropogenic ozone contributions at the sites shown in Figure 1 are minimal, so a comparison of the ODVs calculated in the ZUSA simulation with those observed may be straight forward.

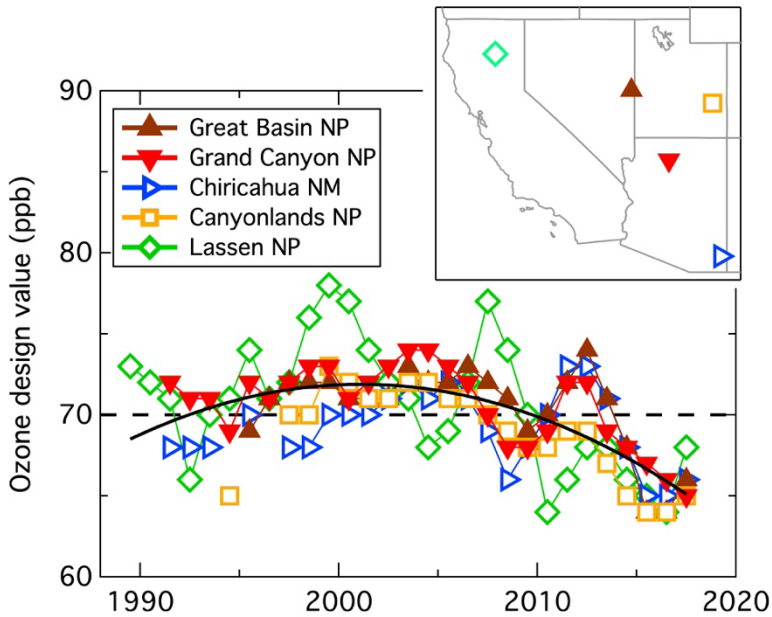


Figure 1. Ozone design values recorded at five relatively isolated CASTNET sites in the southwestern U.S. (Data from EPA's AQS data archive (https://www.epa.gov/aqs).

Figures 2.16 and 2.17 are informative plots. Evidently the minimum and maximum that are given are not minimum or maximum simulated on any day in each season, but are instead the minimum and maximum mean MDA8 O_3 concentration simulated for any grid cell in the domain. This should be clarified.

Figure 2-22 seems to indicate that MDA8 ozone from natural sources can exceed 70 ppb on many days in the western U.S. and even on some days in the eastern U.S. Does this not imply that natural sources alone can give an ozone design value larger than the current NAAQS of 70 ppb, at least in the western U.S.? The right center panel of Figure 2-27 shows that this is indeed the case, with the maximum 4th highest US background O_3 simulated day of 80 ppb. Does this not imply that it is impossible to reach the current NAAQS of 70 ppb through domestic precursor emission controls only? Further, that figure shows that ozone design values can be above ~60 ppb from US background ozone alone over much of the western U.S. This map is roughly similar to the maps that I included in my response to questions regarding the O_3 ISA, and are reproduced here as Figures 2 and 3. These three figures from two model calculations and one observational based analysis show how difficult it is to reach even a 70 ppb NAAQS in large regions of the country. This issue deserves full discussion in this chapter. The final conclusion of this section is a good start for this recommended full discussion: "…a combination of Natural and Canada/Mexico contributions can lead to total USB between 60-80 ppb on specific days, ….".

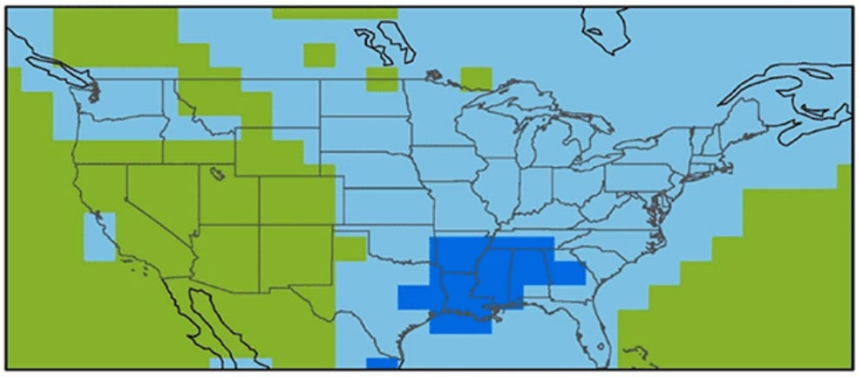


Figure 2. Annual 4th highest MDA8 O_3 in ppb from North American background (i.e., with North American anthropogenic precursor emissions set to zero) averaged over 2010–2014 from a GFDL-AM3 model simulation (Jaffe et al., 2018).

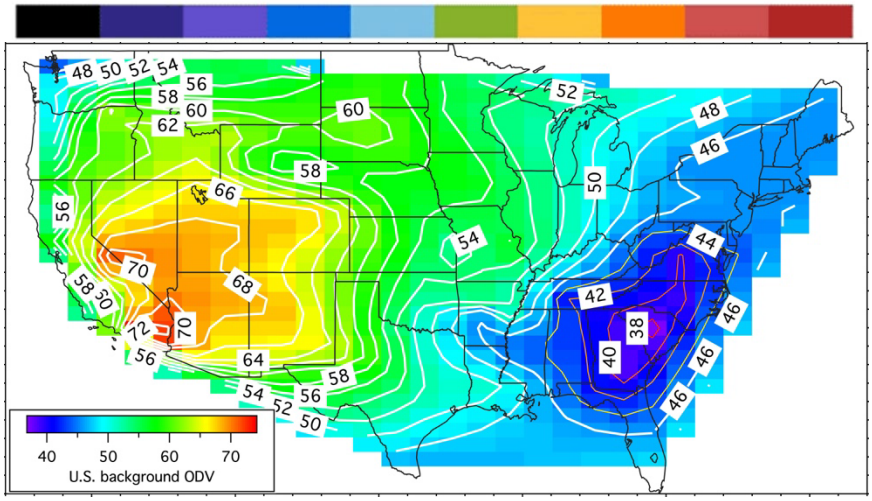


Figure 3. Ozone design values expected from U.S. background (i.e., with U.S. anthropogenic precursor emissions set to zero) in ~ 2015 derived from observations (D.D. Parrish, unpublished figure).

Chapter 3 – Review of the Primary Standard

- *Is the discussion on Exposure and Risk Conceptual Model and Assessment Approach (Section 3.4.1) accurate and complete? If not, what additional information needs to be included?*

I have no relevant expertise in evaluating exposure and risk, so I cannot respond to this question.

- *Is the discussion on Population Exposure and Risk Estimates for Air Quality Just Meeting the Current Standard (Section 3.4.2) accurate and complete? If not, what additional information needs to be included?*

I have no relevant expertise in evaluating exposure and risk, so I cannot respond to this question.

- *Is the discussion on Population Exposure and Risk Estimates for Additional Air Quality Scenarios (Section 3.4.3) accurate and complete? If not, what additional information needs to be included?*

I have no relevant expertise in evaluating exposure and risk, so I cannot respond to this question.

- *Is the discussion on Key Uncertainties (Section 3.4.4) accurate and complete? If not, what additional information needs to be included?*

I have no relevant expertise in evaluating exposure and risk, so I cannot respond to this question.

- *Is the discussion on Public Health Implications (Section 3.4.5) accurate and complete? If not, what additional information needs to be included?*

I have no relevant expertise in evaluating public health implications, so I cannot respond to this question.

Appendix 3C – Air Quality Data Used in Population Exposure and Risk Analyses

- *Is the discussion on Urban Study Areas (Section 3C.2) accurate and complete? If not, what additional information needs to be included?*

Very limited summary data for each urban area are given in Table 3C-1. I have not independently checked those data, but they appear to be accurate and complete.

- *Is the discussion on Ambient Air Ozone Monitoring Data (Section 3C.3) accurate and complete? If not, what additional information needs to be included?*

This section simply describes the data which were downloaded from the EPA's Air Quality System (AQS) database; the discussion appears to be accurate and complete.

- *Is the discussion on Comprehensive Air Quality Model with Extensions (CAMx) (Section 3C.4.1) accurate and complete? If not, what additional information needs to be included?*

I do not have experience with performing photochemical model simulations. To me the discussion of CAMx appears accurate, as expected, since this section is simply a discussion of how a widely-used photochemical model was setup for the application described in this Appendix.

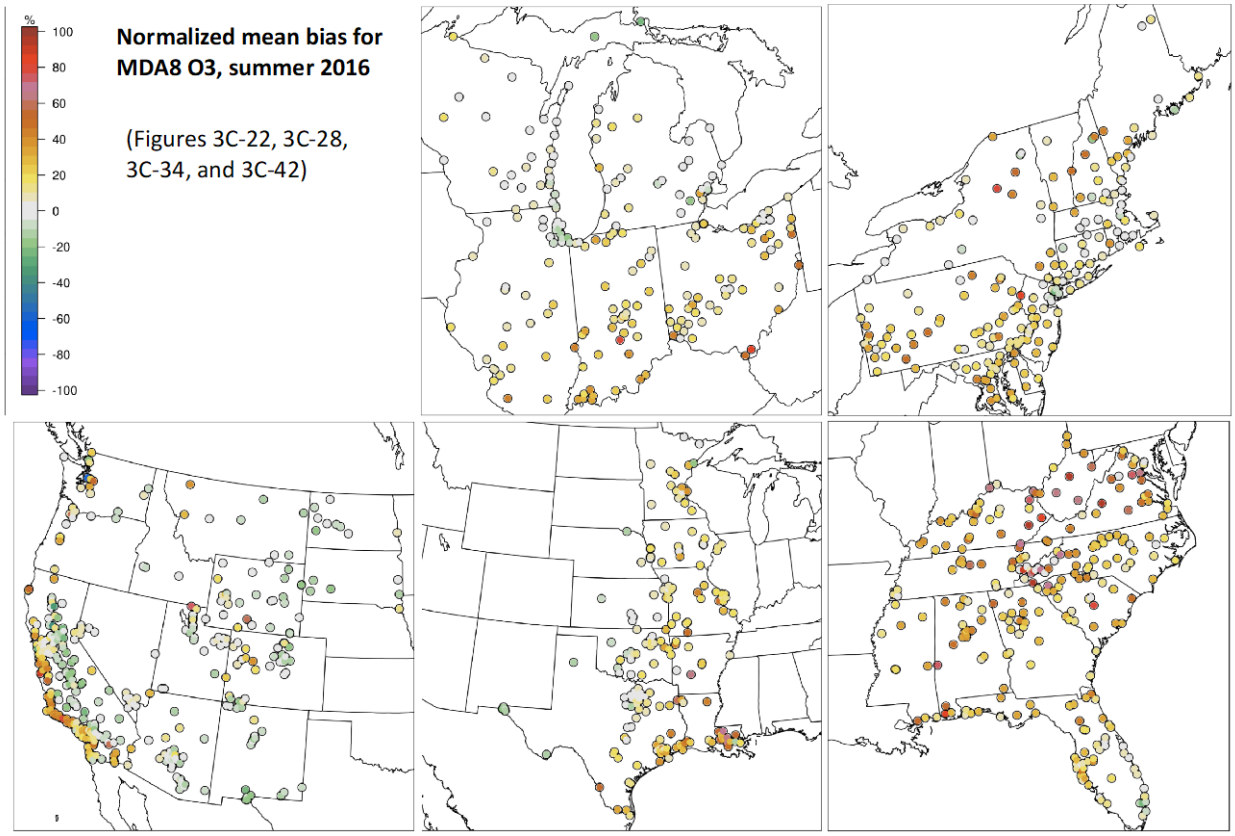
One issue that is always relevant for model calculations is the accuracy of the emission inventory. A paragraph discussing how the emissions assumed for this model compare with other measures of U.S. emissions would provide useful information. For example, a quick comparison between the total emissions in Table 3C-4 with the total emissions given in the pie charts in Figure 2-1 shows some similarities and some surprising differences. For CO, both the anthropogenic and natural components are in close agreement. For VOCs, the anthropogenic components agree well, but in the CAMx inventory the biogenic VOCs are larger by about 11%. Surprisingly, the anthropogenic NOx emissions are about 20% smaller in the CAMx inventory. These differences are certainly within the uncertainty of the inventories, but even these small differences may have an effect on the modeling results. The difference in anthropogenic NOx emissions may be particularly important in this particular modeling study, because NOx emissions are the parameter adjusted in the Air Quality Adjustments in Section 3C.5. A parameter that modelers often use to explain features of atmospheric photochemistry is the VOC to NOx ratio. In the CAMx inventory (Table 3C-4) this ratio (on a wt:wt basis) is about 5.1 compared to 3.9 in the NEI Inventory (Figure 2-1), based on the total emissions. It would be useful to discuss the impact of this difference in VOC to NOx ratio, along with any other significant uncertainties in the emissions that might impact the results.

As second issue that affects the results of the modeling is the accuracy of the boundary conditions calculated by the hemispheric version of the Community Multi-scale Air Quality model (H-CMAQ) v5.2.1. These boundary conditions account for the majority of the ozone throughout the modeling domain; thus, the accuracy of all of the results of this modeling exercise depends on the accuracy of the boundary conditions. A comparison of the modeled ozone concentrations at CASTNET sites,

particularly in the western U.S. (as shown in Figure 1 above), would give an insightful indication of their accuracy. A zero-out model run with all U.S. anthropogenic emissions set to zero should be conducted to calculate U.S. background ozone, and the results compared with other determinations of U.S. background ozone (also see maps in Figures 2 and 3 above).

- *Is the discussion on Evaluation of Modeled Ozone Concentrations (Section 3C.4.2) accurate and complete? If not, what additional information needs to be included?*

This section contains 33 pages with 13 Tables and 36 Figures, many with multiple panels. More numbers and graphs are not needed for completeness, but a better synthesis of the results would be useful. Figures could be combined to allow an easier approach to that synthesis. For example, the following figure combines 5 figures from the report so that a reader can easily compare and contrast results across the country. The discussion of these results could then be more concise and insightful.



Much more of this nature could be done to increase the value of this section. Another example is figures of the style 3C-17; instead of time series of hourly data, it would be useful to plot all observed and modeled hourly data in one 24-hour span, with means and standard deviations of each indicated, much as in Figure 3C-67 and following figures. Such plots would much better inform the reader regarding possible causes of model-observation differences.

I am not an expert in modeling, so I cannot critique the modeling procedures described in this section. I have not identified any inaccuracies or incompleteness in the description of the modeling. However, to my mind this section is incomplete in two regards. First, an overview of the reasons for choosing the emissions adjustments (NOx emission reductions alone) used in this section should be given. Figure 3C-

48 is a flow diagram demonstrating the HDDM model-based O_3 adjustment approach. One part of Step 3 is to select emissions reductions to which sensitivities will be applied. How are these reductions selected? Throughout this section, only NOx emissions are reduced, but in the real world, anthropogenic VOC emissions are reduced simultaneously with NOx reductions. The introduction to this section should give the reader some idea of what guided the choices made during this modeling exercise. Second, a discussion of the likely uncertainties of the final results should be given.

- *Is the discussion on Air Quality Adjustment to Meet Current and Alternative Air Quality Scenarios (Section 3C.5) accurate and complete? If not, what additional information needs to be included?*

I can identify one zero-order test of the accuracy of the final outcome summarized in Table 3C-19; if I understand correctly, this table gives the percent reductions of anthropogenic NOx emissions required to lower the 2017 ozone design values to just meet three air quality scenarios. For Phoenix to reach a design value of 65 ppb, NOx emissions would have to be reduced by 68% (all other emissions remaining constant). However, the ODV that would be recorded in the absence of all U.S. anthropogenic precursor emissions would likely be above 65 ppb in 2017 (see maps in Figures 2 and 3 above). In that case it would not be possible to lower the ODV to 65 ppb in Phoenix. In my opinion the modeling approach described in this section is probably state-of-the-art work, but the uncertainty of the results is large. This modeling uncertainty should be thoroughly discussed in this Section.

Apparently, there are some unrealistic results included in the summary plots and tables; I suggest that they be removed. For urban areas that already had design values below 75 ppb in 2017, modeling was done for NOx emission **increases** necessary to **raise** the design values up to 75 ppb (Table 3C-19). This may be a modeling exercise that is useful for completeness, but is simply confusing to at least this reader. Figures like the left panel of Figure 3C-84 should not be included. Similarly, for the respective panes in Figures 3C-91 through 3-114.

- *Is the discussion on Interpolation of Adjusted Air Quality using Voronoi Neighbor Averaging (Section 3C.6) accurate and complete? If not, what additional information needs to be included?*

The discussion in Section 3C.6 appears accurate to me. What is missing is a discussion of the uncertainty of this approach. I suggest that several trials be run for some of the 8 urban areas to approximately quantify the uncertainty. Each trial would select a census tract that actually has a monitor to provide a time-series of "known" concentrations. Then the interpolation of that census track concentration using Voronoi neighbor averaging would be calculated, but without including data from the census track monitor; this would provide "interpolated" concentrations. A comparison of the "known" versus "interpolated" concentrations for the subject census tract would be illuminating regarding the accuracy of this procedure.

- *Is the discussion on Results for Urban Study Areas (Section 3C.7) accurate and complete? If not, what additional information needs to be included?*

This section has an effective and complete presentation of the results. In each of the eight panels in Figures 3C-107 through 3C-114, I suggest that the average, population-weighted annual 4th highest MDA8 O_3 or May-September mean MDA8 O_3 be indicated in annotations.

In my opinion, the summary sentence for this section is inadequate. It currently reads "In summary, these figures show that using the CAMx/HDDM adjustment methodology, peak O_3 concentrations are

reduced in urban areas with large domain wide reductions in U.S. anthropogenic NOx emissions." I think that a statement should be added to the effect that the total population weighted average ambient MDA8 ozone concentrations decrease with emission reductions designed to reduce the annual 4th highest MDA8 O3 concentration. The success of the U.S. program in reducing ambient ozone concentrations requires emphasis, regardless of whether the NAAQS has been, or even can be, reached in some urban areas.

Questions from Dr. Sabine Lange

Air Quality

1) *Multiple ozone chemistry analyses (e.g. Downey et al., 2015; Simon et al., 2012) have demonstrated that in an area where peak daily ozone concentrations have decreased over time, over the same period of time the lowest daily ozone concentrations have also decreased (due to the NOx disbenefit aspect of ozone chemistry). An example is provided in Figure 1. What are your thoughts about the change of annual average ozone concentrations (which tend to be the focus of epidemiology studies) with decreases in annual peak ozone concentrations?*

The general situation exemplified in Figure 1 is more or less typical of the temporal evolution of urban ozone concentration distributions, where maximum daily 8-hour average (MDA8) ozone concentrations have decreased, but the minimum MDA8 values have increased. This causes the distribution of MDA8 ozone concentrations to narrow, as shown in the figure. The cause of the increase in the minimum MDA8 ozone concentrations is a reduction in fresh NO emissions in the urban area. The effect of these emissions on days of low photochemical activity is for NO to react with ozone, forming NO_2. Thus, between the early 2001-2003 period and the later 2013-2015 period, on days of low photochemical activity the MDA8 ozone concentrations have increased but the NO_2 concentrations have decreased. Since the mean and median MDA8 have not changed significantly over this time interval, it may well be that the annual average ozone concentrations have not changed much. The possibility that annual average ozone concentrations have not changed, but that NO_2 concentrations have decreased, would be important to consider in the interpretation of epidemiology studies that focus on annual average ozone concentrations.

Epidemiology

2) *Is an epidemiology study with higher statistical power (sample size) innately more protected against problems of confounding, error, and bias, than an epidemiology study with lower statistical power (sample size)?*

I have no relevant epidemiological expertise, so I cannot respond to this question.

3) *In section 3.3.3 (Exposure Concentrations Associated with Effects) and section 3.3.4 (Uncertainties in the Health Effects Evidence), the EPA notes that the epidemiology studies are generally assessing the associations between ambient ozone and specific health outcomes and are not investigating the details of the exposure circumstances eliciting these effects (e.g. pg. 3-40 and pg. 3-43). Do you think that this statement is correct? If so, is this statement generally true of air pollution epidemiology studies, or is it peculiarly specific to ozone? If it is not specific to ozone, then should this caveat always be considered when evaluating exposure concentrations associated with these types of epidemiology studies?*

I have no relevant epidemiological expertise, so I cannot respond to this question.

<u>Exposure-Response Modeling</u>

4) *In section 3.4.4 (Key Uncertainties) of this PA, the EPA notes that "In recognition of the lack of data for some at risk groups and the potential for such groups, such as children with asthma, to experience lung function decrements at lower exposures than healthy adults, both models generate nonzero predictions for 7-hour concentrations below the 6.6-hour concentrations investigated in the controlled human exposure studies." Is assuming a lack of threshold in an exposure-response relationship a standard method for considering potential at-risk populations that may not have been characterized in an exposure-response assessment?*

I have no relevant health effects expertise, so I cannot respond to this question.

5) *The EPA also notes in this section that there is a lack of information about the factors that make people more susceptible to ozone-related effects, and that the risk assessment could therefore be underestimating the risk. However, the exposure-response model used to estimate the risk of lung function decrements uses those people in the health population with a greater response to ozone than the mean response (i.e. that fraction of the people in controlled human exposure studies who had FEV1 responses >10%, 15%, or 20%). Does this method already include consideration for more susceptible people in the population?*

I have no relevant health effects expertise, so I cannot respond to this question.

<u>Questions from Dr. Corey Masuca</u>

1) 2.1. Ozone and Photochemical Oxidants in the Atmosphere

How sound science is this mechanism of ozone transfer between the stratosphere and the troposphere?

The scientific evidence that ozone transfer from the stratosphere to the troposphere occurs in stratospheric intrusions associated with tropopause folds is very strong. The science that underlies our understanding of the injection of stratospheric intrusions into the troposphere, their transport within the troposphere, and their dispersion into the background troposphere is also strong, because it is based on our understanding of meteorology, which has a long history of extensive research. The work by Langford et al. (2018) is a good example of the state-of-the-art of our ability to use observations and transport modeling to characterize the impact of a specific stratospheric intrusion event.

A second mechanism for stratosphere to the troposphere exchange occurs over northern mid-latitude continents, where strong convection associated with thunderstorms penetrates to the stratosphere, and brings stratospheric air into the troposphere. I believe that less research has been devoted to this mechanism, but on a global scale it is thought to have a smaller impact than tropopause folding events. Ultimately, it would be valuable to be able to accurately quantify the contribution that ozone from the stratosphere makes to observed surface ozone at any particular time and place; the science is not yet advanced enough for this to be possible. Models can provide partial answers (e.g., Langford et al., 2017) but the accuracy of those answers is not well quantified.

2) 2.3.1 Ambient Air Monitoring Requirements and Monitoring Networks

While a number of types of sites are mentioned in this section such as PAMS, NCore, CASTNET, National Park Service (NPS), and Special Purpose Monitors (SPMs), what about Near Road Monitoring Sites, especially for NOy?

As of September, 2019, there were apparently 82 Near Road Monitoring Sites in many states throughout the U.S. (https://www3.epa.gov/ttnamti1/nearroad.html) that operated for at least some period of time. The goal of this network is to quantify NO_2 concentrations in the near field of vehicle emissions. As far as I know, there is no emphasis on measurement of NOy at these sites. Adding a brief discussion of this network to Section 2.3.1 would be useful.

3) 2.3.2 Data Handling Conventions and Comparisons for Determining Whether Standards Are Met

There is a reference to the hourly concentrations being utilized to compute 8-hour averages. Is this short-term 8-hour rolling average consistent with short-term actual and scientific studies?

The maximum of the 8-hour rolling averages (MDA8) recorded on a given day is useful for scientific studies. On sunny days that usually experience the largest ozone concentrations, this average generally characterizes the ozone concentration during the period of the day when 1) the largest ozone concentrations have accumulated, and 2) when the convective boundary layer is well developed.

4) 2.4.3 Diurnal Patterns

While this section refers diurnal patterns of relative ozone concentrations between day and night, are these diurnal patterns solely (although mostly are) attributable to temperature? What about stagnant weather conditions? What about the effects on topography/geography in determining diurnal patterns?

The diurnal pattern of ozone at surface sites is driven by several processes. The influence of each factor at a particular site varies depending upon the characteristics of each site, so each site has its own characteristic diurnal pattern.

At most sites in relatively flat terrain, the most important factor is usually the evolution of the convective boundary layer. At night during relatively calm wind periods, the boundary layer is shallow (nominally 10s of meters to ~100m). Ozone is lost to surfaces, and this surface deposition can reduce surface ozone to low concentrations within this shallow layer, which includes the ozone monitor. In areas with significant surface NOx emissions, reaction of ozone with freshly emitted NO also contributes to the depletion of near-surface ozone. After sunrise, solar radiation heats the surface, initiating convection that in the morning hours increases the depth of the boundary layer by entraining air from aloft. This air was above the nocturnal boundary layer, so its ozone concentration has not changed appreciably overnight; surface ozone concentrations increase due to this entrainment.

A second important factor is photochemical production of ozone from precursors contained in the boundary layer. The contributions to the ozone increase from entrainment of air aloft and photochemical production within the boundary layer are not easily distinguished from measurements, since both processes are occurring simultaneously.

A third factor is advection (horizontal transport) of air to the site. If there is an urban area upwind, then rural ozone may increase later in the afternoon, when urban pollution ozone is finally advected to the site.

These three factors are each affected by temperature during the day (with higher temperature generally favoring both faster boundary layer growth and faster photochemical ozone production) and meteorology including the degree of stagnation (which affects boundary layer growth and advection).

Finally, topography/geography does play a major role. For example, on a mountaintop the nocturnal boundary layer generally does not form and there is usually only small precursor concentrations, so the diurnal pattern is much flatter than at a site in flatter terrain.

Thus, it is difficult to give a simple explanation of diurnal ozone patterns. The discussion of Figure 2-10 in this section gives a reasonably accurate overview.

5) Background Ozone

There, in general appears to be a lot of discussion about background ozone concentrations from transport and natural sources. However, are most salient ozone concentrations more localized and from anthropogenic sources?

The short answer is no. As I noted in my comments on Section 1.8 of the ISA on U.S. background ozone concentrations, at present U.S. background ozone contributes the majority of urban ozone concentrations, even on most days when ozone exceeds the NAAQS. The figures in Section 2.5 of the PA agree with this statement. In my response to a question on background ozone that was posed during the review of the ISA, I included two contour maps showing estimates of USB across the country, one from a model calculation and one from an observational based analysis. They are reproduced above as Figures 2 and 3. Broadly speaking the two maps agree that the ozone design value that would be measured in the absence of U.S. anthropogenic emissions of ozone precursors would vary from ~40 ppb to ~70 ppb, with the larger values in the southwest and the lower values in the southeast. During exceedance episodes, the more localized ozone concentrations from anthropogenic sources can usually be conceptually viewed as a relatively smaller contribution that raises the U.S. background ozone concentration above the NAAQS.

This section references the utilization of photochemical grid models due to the lack of ability to characterize the origins of ozone and the ability to estimate the magnitude of background ozone. However, how predictable are these photochemical models, especially given the highly photolytic and relative instability of ozone in the atmosphere?

The results from photochemical grid model simulations have poorly quantified uncertainties. However, these uncertainties are relatively large compared to the margin between the NAAQS and the observed ozone design values in most nonattainment areas of the country. For example, Jaffe et al. (2018) estimates that the uncertainty in U.S. background ozone concentrations calculated by models is around ±10 ppb for seasonal mean values and higher for individual days. Attainment vs. nonattainment decisions are often based on ozone concentration differences that are smaller that this uncertainty. The U.S. EPA recognizes that the absolute ozone concentrations simulated by models have significant uncertainties, so the use of Relative Response Factors (RRF) are recommended during the development of state implementation plans (for example, see https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=306790). The RRF

approach assumes that models can accurately calculate the response of ambient ozone concentrations to precursor emission changes, even while the model cannot accurately calculate the absolute ozone concentrations. In looking through the ozone ISA and PA, I find no discussion of the RRF approach, which I believe is a major shortcoming of these documents.

This section mentions that international emissions sources via transport mostly originate from anthropogenic sources. However, is there a possibility that there can be international transports from non-anthropogenic/biogenic sources?

Also, this section noticeably leaves out non-international, interstate transport of ozone.

International transport from non-anthropogenic/biogenic sources is extremely important. Ozone from stratospheric intrusions and ozone precursors from wild fires are two very important examples. I think that the discussion of the U.S. background correctly focuses on the international transport because non-international, interstate transport of ozone is adequately treated in the regional photochemical modeling.

6) 2.5.1.6 Pre-Industrial Methane

There is a whole section devoted to long-lasting atmospheric methane. However, what is the importance of methane with respect to the formation of and consideration of ozone? Is a discussion on methane warranted?

Methane as a participant in atmospheric photochemistry and may well make a significant contribution to U.S. background ozone concentrations. Section 2.5.1.6, which constitutes about 1 page of the 64-page chapter, is I think warranted.

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