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

Questions from Dr. James Boylan

Appendix 1 – Atmospheric Source, Chemistry, Meteorology, Trends, and Background

• *Is the discussion on metrics and definitions (Section 1.2) accurate and complete? If not, what additional information needs to be included?*

Section 1.2 is complete and accurate with a couple of exceptions.

Section 1.2.2.1 states that "… USB is a model construct that cannot be measured using ambient monitoring data." This statement is correct, in that USB cannot be **directly** measured; however it can be estimated from ambient monitoring data as shown by Parrish et al. (2017) and Parrish and Ennis (2019). This will be discussed in more detail below in response to the question regarding Section 1.8.

Section 1.2.2.5 discusses baseline ozone, which is defined as "the measured ozone concentration at rural or remote sites that have not been influenced by recent, local emissions (Jaffe et al., 2018)." This definition would be more accurate if "local emissions" were replaced with "local continental effects". Ambient ozone concentrations are affected not only by emissions, but also by surface deposition, particularly to vegetation. Measured concentrations at rural or remote sites can be greatly reduced from true baseline concentrations by surface deposition even in the absence of emissions. This is an important issue.

• *Is the discussion on sources of U.S. ozone and its precursors (Section 1.3) accurate and complete? If not, what additional information needs to be included?*

Generally this entire Section 1.3 has an important shortcoming. On pg. lxxvii of the Preface the purpose of the ozone ISA is stated: "This ISA communicates critical science judgments of the health and welfare criteria for ozone, and serves as the scientific foundation for the review of the current primary (health-based) and secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for ozone." In reading through Section 1.3 a great deal of scientific information is summarized, but there is little or no discussion of the relevance of this science to the NAAQS or the ozone design values upon which the NAAQS is based. For example, wildfires (here included in the broader category of landscape fires) and stratosphere-troposphere exchange are discussed. These are two natural sources of ozone that are specifically addressed in EPA's exceptional events rule. A crucial issue is the extent to which these sources can affect the ozone design value and perhaps cause an exceedance of the NAAQS that would be eligible for addressing under that exceptional events rule. How often do either of these natural sources cause exceedances? It is difficult to evaluate the significance of a particular scientific issue without the context of how that issue might affect the NAAQS that is being reviewed.

Another significant shortcoming in Section 1.3 is that the uncertainty of the ozone precursor emissions estimates should be clearly discussed and defined to the extent possible. The words "approximately" and "estimate" are often used, but such terms are not defined. I think that a few paragraphs should be devoted to a discussion of emission inventory uncertainty; this discussion might be based on material in Miller et al. (2006) or a similar, more recent emission inventory assessment. (This comment repeats a comment that I made in my response to a similar question regarding the PM PA; more details are given there.)

Section 1.3 discusses the role that global methane plays in the global tropospheric ozone budget, which is based on chemistry-climate model simulations. Simulations by different models generally agree, but the models generally use similar parameterizations of critical physical processes. In my opinion, increasing methane may increase global ozone concentrations, but due to model uncertainties that relationship is uncertain. Conceivably increasing methane may decrease, rather than increase, global ozone concentrations. (See expanded discussion in my response to a similar question from Dr. Corey Masuca.)

Section 1.3.1.3.1 mentions that "soil NO emissions rates can be high enough to affect local and regional ozone concentrations under certain circumstances", but largely dismisses the importance by noting that "Biogenic emissions of NO_X are estimated to contribute only a small part to national NO_X emissions, …." However, there is evidence (Oikawa et al., 2015; Almaraz et al., 2018) that NOx emissions from agricultural soils plays a major role in degraded air quality in the Imperial Valley, located in an ozone no-attainment area in California. This issue deserves more discussion since it may play a significant role in an important no-attainment areas in the country.

Section 1.3.1.3.3 Landscape Fires deserves improvement. It provides a synopsis of literature results, but there is no synthesis of the current state of knowledge. A summarizing statement in the context of recorded ozone design values would be valuable. It is stated that "*Wildfires contribute a few parts per billion (ppb) to seasonal mean ozone values in the U.S., but episodic contributions may be as high as 30 ppb*." My understanding is that wildfires vary in location and intensity from year to year, but have been generally increasing over the last decade or two. However, in one example northern rural state where high impacts of wildfires are expected (Montana), the ozone design values at all monitors in the state have averaged 55.4 ppb with a standard deviation of 2.2 ppb and no apparent trend over the 1979–2017 period, i.e. over nearly 4 decades (Parrish and Ennis, 2019). Similarly small variability in ozone design values without an apparent trend are found in the Dakotas. If wildfires have relatively large, episodic effects, why are these effects not seen in the ozone design values in these rural northern U.S. states where wildfire impacts are expected to be most obvious?

Section 1.3.2 discusses the influence of stratosphere-troposphere exchange processes. In reading this section one gets the impression that ozone from the stratosphere is an episodic phenomenon that has only occasional impacts on surface ozone. However, ozone from the stratosphere enters the upper troposphere where the lifetime of ozone is weeks. Hence, even if a deep stratospheric intrusion does not reach the surface, it does mix into the background troposphere, and that contributes to U.S. Background Ozone (USB), even if the stratospheric source of that ozone is not obvious. Hence the influence of stratospheric ozone is ubiquitous (often 10's of ppb), but highly variable in time. This section should make that clear.

• *Is the discussion on ozone photochemistry (Section 1.4) accurate and complete? If not, what additional information needs to be included?*

Page 1-25, line 32 refers to "NO_X as an oxidant". That is incorrect; hydroxide and peroxy radicals are generally the oxidants in ozone photochemistry. The role of NO_X is better characterized as a catalyst.

The final paragraph of this section is entitled: "*Oil and gas sector impacts on ambient ozone levels extend beyond wintertime ozone episodes.*" This section cites two studies suggesting that "on specific summer days oil- and gas-related precursor emissions could contribute locally up to 30 ppb ozone." However, efforts to find evidence for increases in ozone design values that can be attributed to oil and

gas development have failed. For example, ozone design values in North Dakota have remained nearly constant across the state (59.3 ppb with a standard deviation of 2.7 ppb) with no significant trend over the 1982–2017 period (Parrish and Ennis, 2019). During this period the Bakken oil and gas field was developed and began producing, with no discernable effects on ozone design values, either at monitoring sites located within the oil and gas development region, or in the surrounding areas. Similar results were found for Texas oil and gas fields.

• *Is the discussion on inter-annual variability and longer term trends in meteorological effects on anthropogenic and U.S. background ozone (Section 1.5) accurate and complete? If not, what additional information needs to be included?*

The discussion in Section 1.5 is generally accurate. What is missing is a clear, quantitative summary of the impact that inter-annual variability has on ozone design values, which are the most relevant statistic from a NAAQS perspective. Section 1.5.1 discusses meteorological effects on ozone concentrations at ground level by citing three studies that investigate mean max 8-hour ozone concentrations in various parts of the country. Section 1.5.2 discusses inter-annual and multidecadal climate variability in a qualitative manner, with only brief mentions of quantitative impacts on maximum daily 8-hour ozone.

Parrish et al. (2017) Parrish and Ennis (2019) show that the a very large fraction of the variance in ozone design values recorded in the largest U.S. urban areas over the past two to four decades is dominated by changes in precursor emissions, and that interannual variability plays only a small role. For example in six of California's southern air basin (including Los Angeles's South Coast Air Basin) simple exponential fits based on decreasing U.S. anthropogenic emissions of ozone precursors account for 98.4% of the variability of ozone design values in that region (Parrish et al., 2017). In the three rural northern states discussed earlier (Montana and the Dakotas) ozone design values over 3 to 4 decades have remained constant within standard deviations of 2 to 4 ppb (Parrish and Ennis, 2019). In the northeastern U.S. similar simple exponential fits accurately capture the temporal variation of ozone design values over 18 years (2000-2017) with root-mean-square deviations of only 2 to 5 ppb. Clearly inter-annual variability and longer term trends in meteorological effects do not contribute large variability to ozone design values. This should be made clear in the discussion.

• *Is the discussion on measurements and modeling (Section 1.6) accurate and complete? If not, what additional information needs to be included?*

With regard to measurements, ground-based ozone lidar instruments are providing a new dimension to our understanding of tropospheric ozone, as these instruments can map out the vertical structure of ozone, and quantify the mixing of plumes aloft to the ground, where the ozone they carry impact the population and surface measurements (e.g., Langford et al., 2017). A review of these instruments and their capability should be added to this section.

With regard to modeling, an overall synthesis of the current state of model performance is lacking. For the development of state implementation plans (SIPs), EPA requires regional chemical transport modeling to demonstrate that proposed emission reductions will lower the ozone design values within the state to the extent that the NAAQS will be achieved. A clear quantification of the accuracy that can be expected from these models must be included. Currently, a summary of model improvements and some model intercomparison studies are discussed. This discussion includes statements such as:

> "The normalized mean error for hourly ozone ranged between 21 and 47 ppb, while the normalized mean error for the 1-hour max ozone concentration ranged between 19 and 22 ppb (25th−75th percentile of reported studies)."

When attainment vs. nonattainment decisions are based on differences of only 1 or a few ppb, these apparently large errors in modeling would seem to indicate that the current generation of regional chemical transport models are inadequate for the task of developing realistic SIP plans. In my view, a much more comprehensive discussion of modeling is required, and that discussion should give a clear, concise summary of the accuracy of model results, shortcomings of the models, and how these shortcomings are likely to affect SIP modeling.

• *Is the discussion on ambient air concentrations and trends (Section 1.7) accurate and complete? If not, what additional information needs to be included?*

The discussion is accurate, but a tremendous resource remains unexplored. With over 1000 monitors collecting ozone data for at least the warm-season months throughout the country over many years, this data set has tremendous potential for informing us about the sources and sinks of ambient ozone in the U.S., and how these vary between regions of the country, land use, ecological environment, and many other variables. Research into this data set is important if the country is to develop ozone control policies that are protective of public health and ecological health, and at the same time economically efficient and feasible to implement. Some recent analyses based on this data set is discussed in response to the next question regarding U.S. background ozone concentrations.

• *Is the discussion on U.S. background ozone concentrations (Section 1.8) accurate and complete? If not, what additional information needs to be included?*

In my opinion the discussion of U.S. background ozone concentrations (Section 1.8) is neither accurate nor complete. The entire discussion should be written from a different perspective. Two or three decades ago urban ozone concentrations were high enough that on days with the highest ozone, background ozone made a relatively minor contribution. However, emission controls have reduced ozone in the U.S. to the extent that now background ozone contributes the majority of urban ozone concentrations, even on most days when ozone exceeds the NAAQS.

The following 2 figures show estimates of the ozone design value (ODV) that would be present in the absence of U.S. or North American anthropogenic emissions.

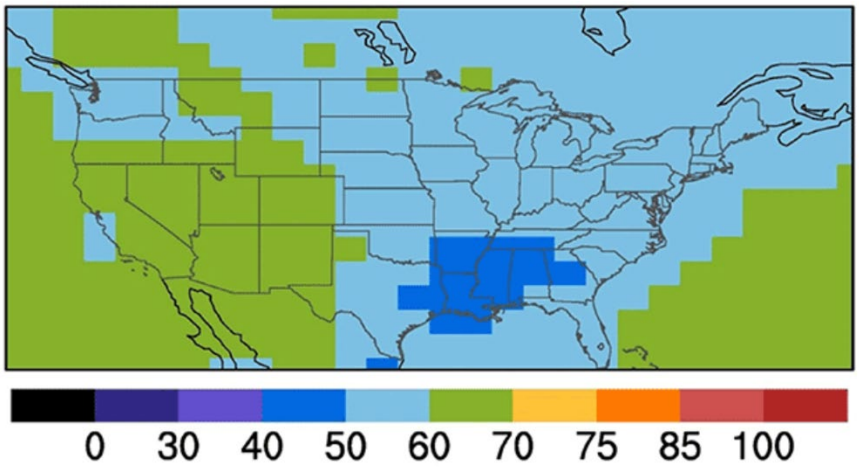

Figure 1. Annual 4th highest MDA8 O_3 in ppb from North American background (i.e., with North American anthropogenic precursor emissions set to zero) averaged over 2010–2014 from a GFDL-AM3 model simulation (Jaffe et al., 2018).

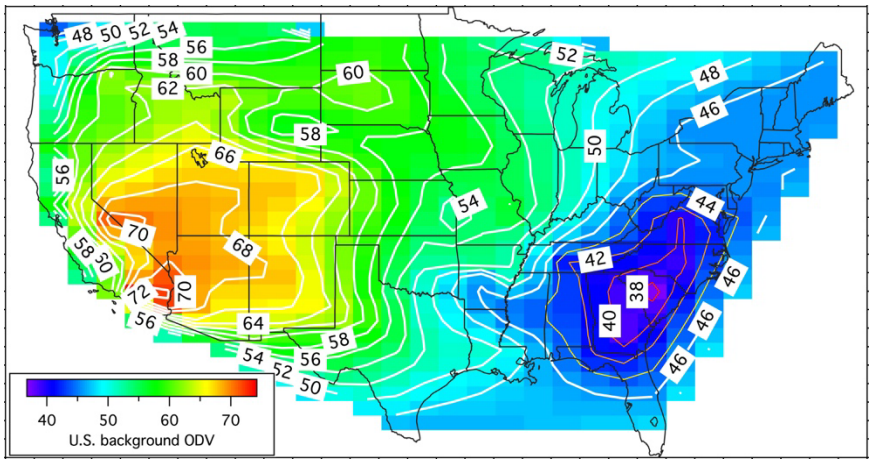

Figure 2. Ozone design values expected from U.S. background (i.e., with U.S. anthropogenic precursor emissions set to zero) in ~ 2015 derived from observations (D.D. Parrish, unpublished figure).

Figure 1 is from a model calculation using the "zero-out sensitivity approach" as described in Section 1.8.1.1. This figure is a summary plot included in a recent assessment of background ozone over the U.S. (Jaffe et al., 2018). Figure 2 is developed from an observational-based approach (Parrish et al., 2017; Parrish and Ennis, 2019) applied to the entire country. Both of these maps have unquantified uncertainties, but the agreement between them regarding the general features and their magnitude is encouraging. A critical message from these two maps is that in the southwestern U.S., background ozone makes such a large contribution (ODV up to ~70 ppb) that it will be extremely difficult (perhaps impossible) to reach the 70 ppb NAAQS, unless the background contribution decreases. This background contribution is largely unaffected by U.S. precursor emission controls. The much lower background ozone concentrations in the eastern U.S. makes it easier to achieve the NAAQS in that part of the country.

The high estimated ODVs shown in Figs. 1 and 2 for the southwestern U.S. can be evaluated by examining ODVs recorded at CASTNET (Clean Air Status and Trends Network) sites. These sites are intended for measuring rural, regionally representative O_3 concentrations and assessing changes in background O_3 contributions. The map in Fig. 3 shows the locations of five CASNET sites in the southwestern U.S. selected to 1) be as isolated as possible from urban areas, 2) have relatively complete ozone measurement records, and 3) lie at similar elevations. The ODVs recorded at these five sites (Fig.

3) are similar among all sites (overall average 70.0 ppb with a standard deviation of 3.0 ppb) and follow a very similar long-term change (increasing before the mid-2000's, reaching a maximum, and decreasing after that maximum). Importantly, this long-term change is very different from that of the U.S. anthropogenic ozone contribution, which has continually decreased over this same period. The similarity in the ODVs and their long-term changes at these sites, which are separated by several 100s of miles, indicate that the ozone concentrations measured at these sites are approximately direct measures of the U.S. background ozone concentration. Hence, these measured ODVs support the estimates given in Figs. 2 and 3. It is significant that from ~1995 to ~ 2010 the ODVs recorded at these relatively isolated rural sites would all have frequently exceeded the 70 ppb NAAQS, solely from U.S. background ozone.

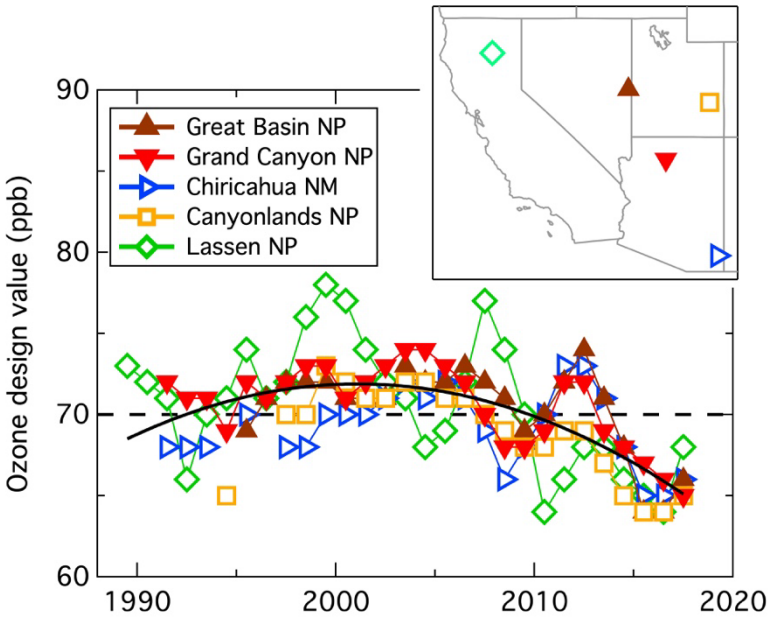

Figure 3. Ozone design values recorded at five relatively isolated CASTNET sites in the southwestern U.S. (Data from EPA's AQS data archive (https://www.epa.gov/aqs).

Figures 1 and 2 show that U.S. background ozone concentrations differ markedly between Los Angeles in southern California and New York City in the northeastern U.S. The observational-based approach of Figure 2 estimates that in the absence of U.S. anthropogenic ozone contributions, the ODV in Los Angeles and New York City would be 62 and 46 ppb, respectively (Parrish et al., 2017; Parrish and Ennis, 2019). Figure 4 shows the difference this has made in each city's efforts to attain the NAQS. In each of these metropolitan areas, the ODVs have decreased at similar rates after ~2000, with the ODVs in New York City projected to decrease to 70 ppb in the early 2020's. However, it is much more difficult for Los Angeles to attain the NAAQS because the U.S. background ozone contribution is much larger, only 8 ppb below the NAAQS. Consequently, it is projected that the maximum ODVs in the Los Angeles urban area will not attain the NAAQS until ~2050 (assuming that the U.S. background contribution remains constant and the current trend of reduction of the US anthropogenic contribution can be maintained through continually strengthened emission controls).

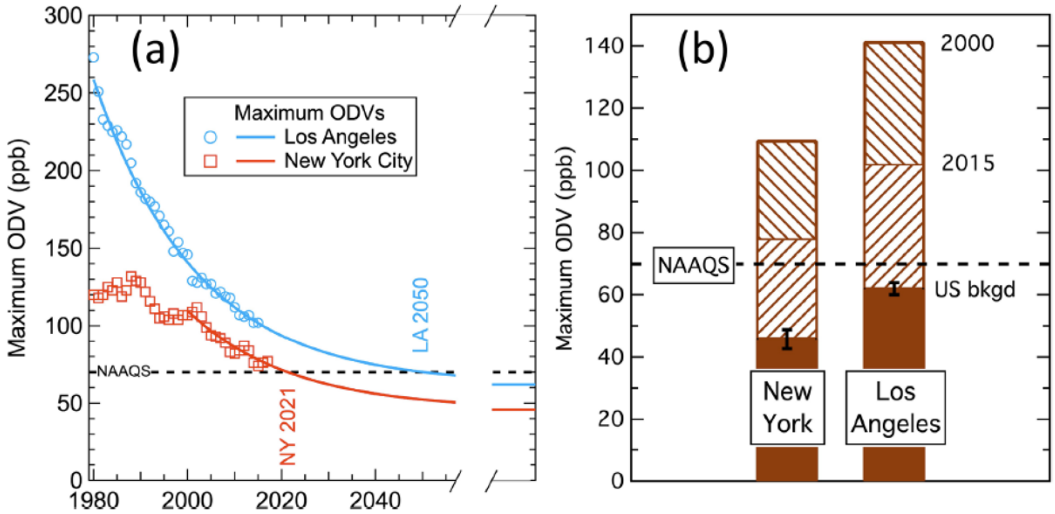

Figure 4. Comparison of maximum ozone design values (ODV) observed in the Los Angeles and New York City urban areas. (a) Temporal trend and parametric fit; annotations indicate year that extrapolations decrease to 70 ppb. (b) Bar graph indicating maximum ODVs in 2000 and 2015 (hatched bars) and the estimated US background (bkgd) ODV (solid bars) (Parrish and Ennis, 2019).

In addition to failing to clearly include the perspective described in the preceding paragraphs, Section 1.8 has other shortcomings. Section 1.8.1 begins with the statement "As described in Section 1.2.2.1, USB ozone cannot be reliably estimated using ambient monitoring data because monitors can be influenced by U.S. emissions, including both relatively nearby emissions and interstate and hemispheric transport of ozone produced from U.S. emissions." As Parrish et al. (2017) and Parrish and Ennis (2019) show, and as illustrated in the 4 figures above, USB ozone can indeed be reliably estimated using ambient monitoring data. Monitors can be (and usually are) influenced by U.S. emissions, but it is possible to account for these influences. The estimates from this measurement-based approach and from the modeling-based approaches have significant uncertainties; our best avenue to obtaining reliable estimates of U.S. background ozone with minimum uncertainty is to use both approaches, and to attempt to understand differences in the estimates when differences arise. Section 1.8 simply ignores the measurement-based approach based on insufficiently supported reasoning (Section 1.8.1.4).

Section 1.8.1.5 discusses uncertainties in and disagreement among model results. A useful summary statement is provided: "… USB ozone estimates contain uncertainties of about 10 ppb for seasonal average concentrations, with higher uncertainty for MDA8 average concentrations." Modeling MDA8 concentrations on the specific 4 days per year with the largest background ozone are required for determination of the concentrations illustrated in Figure1; thus the uncertainties of such determinations from models must be larger than 10 ppb. Since attainment vs. non-attainment decisions are often based on only 1 or a few ppb, the usefulness of these model estimates is greatly limited by this uncertainty. Section 1.8.1.5 should emphasize that this state-of-the-science of the models is a serious impediment to our understanding of U.S. ozone concentrations.

Section 1.8.2.1 discusses new USB and North American Background estimates, but all of these estimates are for seasonal means. It is critical to evaluate the ODV that can result from USB, because that informs us of the "headroom" available for anthropogenic ozone production on those high background days. This concept is illustrated in Figure 4 above.

Section 1.8.2.3 discusses the contribution of USB to ambient air ozone as a function of ozone concentration. The discussion misses an essential point: as the ODV in an area is reduced and approaches the NAAQS, the relative importance of the USB will increase, because the USB contribution will remain (approximately) constant while the anthropogenic contribution decreases. For modeling relevant for reducing the ODV to concentrations equal to or below the NAAQS, one should focus not only on today's high ozone days, but also on the days in the future that determine the ODV when it is still slightly above the NAAQS. It is likely that those days will have a much higher relative contribution from USB, much as the situation in the high-elevation locations in the western U.S described in this section; at those locations USB is consistently predicted to increase with total ozone concentration.

Appendix 2 – Exposure to Ambient Ozone

• *Is the discussion on exposure concepts (Section 2.2) accurate and complete? If not, what additional information needs to be included?*

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

• *Is the discussion on exposure assessment methods (Section 2.3) accurate and complete? If not, what additional information needs to be included?*

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

• *Is the discussion on personal exposure (Section 2.4) accurate and complete? If not, what additional information needs to be included?*

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

• *Is the discussion on copollutant correlations and potential for confounding (Section 2.5) accurate and complete? If not, what additional information needs to be included?*

As an atmospheric chemist, I am not surprised by the low correlations reported in Figures 2.1 and 2.2, since each pollutant is measured over a time interval different from the ozone measurement; the results in these figures do not provide much useful information. At a minimum, these correlations should be conducted between measurements of pollutants over the same time period; were this done, I would expect substantially larger correlations in some cases.

Overall, this section does not adequately support the stated conclusion that "… confounding of the relationship between ambient ozone exposure and a health effect by exposure to CO, SO_2, NO_2, PM_{10}, or $PM_{2.5}$ is less of a concern for studies of the health effects of ambient ozone exposure compared with studies of the health effects related to exposure of other criteria air pollutants."

• *Is the discussion on interpreting exposure measurement error for use in epidemiology studies (Section 2.6) accurate and complete? If not, what additional information needs to be included?*

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

Appendix 9 – The Role of Tropospheric Ozone in Climate Effects

• *Is the discussion on ozone impacts on radiative forcing (Section 9.2) accurate and complete? If not, what additional information needs to be included?*

The discussion in Section is complete and reasonably accurate. The evidence for a causal relationship between tropospheric ozone and radiative forcing is very robust. This section relies on IPCC's AR5 report, and quotes its best estimate of tropospheric ozone radiative forcing 0.40 ± 0.20 W/m^2 (from 1750 to 2011). However, in my opinion this quantity may be underestimated by more than indicated by the quoted uncertainty. This estimate is based solely on global chemistry-climate model simulations of the evolution of the global ozone distribution from pre-industrial times to the present. As noted in Appendix 9, long-term changes in free tropospheric ozone and upper tropospheric ozone (where RF is particularly sensitive to changes in ozone) are not captured well by models. The models also do not accurately capture the seasonal cycle of ozone, at least in the marine boundary layer (e.g., Derwent et al., 2018), as well as other observed features of the global ozone distribution. The possible underestimate of the tropospheric ozone radiative forcing should be acknowledged in Appendix 9.

• *Is the discussion on ozone impacts on temperature, precipitation, and climate related variables (Section 9.3) accurate and complete? If not, what additional information needs to be included?*

Section 9.3 reviews the limited research that has been conducted into a variety of extremely complex questions. I know of no additional information that needs to be included. I believe that the overall conclusion - there is "likely to be causal relationship between tropospheric ozone and temperature, precipitation, and related climate variables." – is accurate and supported by the discussion in the section.

<u>Questions from Dr. Tony Cox</u>

Overarching Questions:

I am not an expert in these questions, so I have no response.

Specific questions:

1. *Question: My question is: Can valid determinations of manipulative or interventional causation – that is, how and whether changing exposure would change health risks – be made based on observed associations of the types analyzed in the ISA?*

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

2. *Questions: The following questions are intended to help assess the conceptual clarity and meaning of the causal determination categories, and of key conclusions expressed using them, such as those in Table ES-1 (p. E-5) of the Draft ISA.*

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

3. *Questions: Based on these spot checks, I have the following questions:*

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

4. *Is the biological evidence presented in the ISA to support causal determinations correctly stated, correctly interpreted, relevant for predicting effects of changes in the ozone NAAQS, and up-to-date?*

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

5. *Does the biological evidence presented in the ISA provide well-validated scientific information suitable for predicting the effects on public health of changing NAAQS standard for ozone?*

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

6. *Is each of the causal determinations summarized in Table ES-1 (especially those labeled "causal relationship" or "likely to be causal relationship") the only possible causal determination conclusion that is justified by, or consistent, with current scientific evidence? Could different causal determinations be equally well justified (or better justified) by the information presented, or by the totality of current scientific evidence?*

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

7. *Are there changes in the design, analysis, selection, or interpretation of individual studies or in the ISA's processes for interpreting and summarizing them that would improve the validity, credibility, and transparency of the ISA's scientific reasoning and conclusions?*

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

<u>Questions from Dr. Mark Frampton</u>

1. Change in causality determination for short-term cardiovascular effects since the 2013 ISA.

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

2. Metabolic effects, new determination of "likely" for both short- and long-term exposure.

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to this question.

3. Change in causality determination for total mortality since the 2013 ISA.

I have no relevant expertise, and I am not familiar with the science on ozone and health effects so I cannot respond to these questions

Questions from Dr. Sabine Lange

1. *It has been established that associations found in an epidemiology study can be due to: causation, bias, chance, and/or confounding. If the concept of statistical significance is not useful in epidemiology studies, then how do the study authors/EPA rule out that chance has caused the observed association?*

I can respond to this question as a scientist with extensive experience in interpretation of results based on statistical significance, but not as an epidemiological expert. The concept of statistical significance is useful in interpreting the results of most scientific studies, but it is not of yes-or-no utility. Recent literature (e.g., Amrhein et al., 2019; Hurlbert et al., 2019) emphasizes the importance of not using statistical significance in a dichotomous manner, e.g. to decide whether the results of an analysis rules in or out any particular cause of an observed association. It is recommended to simply present *p*-values without label or category. With regard to the present question, the results of any particular epidemiology study can provide an estimate of the probability that chance has caused the observed association, but that probability can never be reduced to zero. The same statement can be generally applied to the results of all studies that attempt to understand the cause of an observed correlation or association.

2. *Am I correct in understanding that the intention of ozone case-crossover studies is to compare the ozone concentrations on a day when a health effect occurred for a person, to the ozone concentrations on a day when that health effect did not occur for that person?*

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

3. *If so, then it would be important that some other factor (not related to ozone) did not prevent the health event from occurring on a control day. These studies often use days before and after the health event as control days, but for mortality studies (such as Di et al., 2017), how can a day after death be used as a control day? It doesn't matter what the ozone concentrations are after a person's death, that person would not be able to respond to that concentration. How should we interpret case-crossover studies that use control days after the event (particularly mortality) occurred?*

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

4. *What is the importance of dose-concordance in establishing the biological likelihood of ozone-mediated effects occurring at relevant exposure concentrations in humans? Particularly in the context of known dose information about ozone: total inhaled dose includes concentration, exposure time, and exercise duration; Hatch et al., (2013) have shown that humans and rats that are exposed to ozone at rest achieve similar alveolar ozone doses, and that humans exercising at 5-times a resting ventilation rate achieved an ~ 5-times higher alveolar ozone dose; and that ozone concentrations are 2-10 times lower indoors where people spend most of their time.*

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

5. *Is there evidence that the animal models used to assess ozone effects (largely rats, mice, and non-human primates) are more, less, or similarly sensitive to ozone-mediated adverse effects compared to humans, at approximately equal inhaled doses?*

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

6. *In the absence of a causality diagram to direct the choice of variables to control in an epidemiological study, how can we judge whether a study has appropriately controlled for confounders, and has not inappropriately controlled for colliders (which can open up pathways between variables that otherwise would not be connected) or mediators (and thereby controlled away the effect)?*

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

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

Appendix 1 Atmospheric Source, Chemistry, Meteorology, Trends, and Background Ozone

1.3.1 Precursor Sources

Are there not other chemicals besides CO and CH4 that also are contained in the precursor mix of ozone formation with its rapidly forming and degradation in the atmosphere?

This introductory paragraph also lists volatile organic compounds (VOCs), along with CO and methane. From the perspective of urban ozone pollution, the VOCs are more important than CO and methane as the "fuel" for ozone formation.

Does the singling out of these two constituents of the ozone "cocktail" significant as push toward climate change/global warming instead of just evaluation ozone formation?

My interpretation of this paragraph is that it serves as the foundation for discussion of both ozone formation in urban and rural areas and climate change/global warming.

1.3.1.2.1 Global Methane

Again, is a teasing out/focusing on CH4 important in discussing the virtual "cocktail" of chemicals that may be associated with ozone formation/degradation?

Methane is one of the few species in the "cocktail" of chemicals (carbon monoxide is another) that has a lifetime long enough for it to be transported on intercontinental distances, and thus can directly affect the photochemical production of ozone within the US. However, methane plays only a minor role of in urban photochemistry.

From a US ozone pollution perspective, transport of background ozone into the US makes a major contribution to observed ozone concentrations in urban and rural areas, even during episodes when the NAAQS is exceeded. As discussed in Section 1.3.1.2.1, model studies indicate that these background ozone concentrations increase when methane increases.

However, the dependence of global tropospheric ozone concentrations on methane 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 these model simulations 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. Testing the simulations of the global NOx concentration distribution is critically needed for improving chemistry-climate model simulations of the global distribution of tropospheric ozone concentrations, and the role that methane plays in determining that distribution.

In summary, the role that global methane plays in the global tropospheric ozone budget is derived from chemistry-climate model simulations. Simulations by different models generally agree, but the models generally use similar parameterizations of critical physical processes. Thus, in my opinion, increasing methane may increase global ozone concentrations, but due to model uncertainties that relationship is uncertain. Conceivably increasing methane may decrease, rather than increase, global ozone concentrations.

1.3.1.2.2 International Emissions of Ozone Precursors

This section focuses on international transport of ozone precursors.

What about local/state/regional transport of ozone precursors?

From the perspective of US ozone NAAQS exceedances, local/state/regional transport of ozone precursors is more important than international transport of ozone precursors. Regional photochemical modeling designed to simulate local and regional ozone pollution events simulate all local/state/regional processes, including precursor emissions and transport. To the extent that these simulations are physically realistic, the local/state/regional transport of ozone precursors are properly considered.

As mentioned above, transport of background ozone into the US makes a major contribution to urban and rural ozone concentrations. Accurate simulation of international emissions of ozone precursors and their transport is critical for successful chemistry-climate model simulations of global ozone concentrations.

1.3.1.3.2 Biogenic Volatile Organic Compounds (VOCs)

It has been stated that biogenic VOCs and contributions are greater than anthropogenic sources (i.e., motor vehicles).

Is there greater confidence in using models and remote sensing (both with relative degrees of uncertainty) to estimate biogenic ozone source contributions that vehicle emissions estimates (manufacturing vehicle emission standards and testing), in making this assessment?

Estimating VOC emissions, whether biogenic or anthropogenic, is a highly uncertain undertaking due to:

- Multitude of sources (anthropogenic: on-road and off-road vehicles, oil and gas production, solvent use, wild and prescribed fires; biogenic: very many species of vegetation.)
- Multitude of species emitted (literally 100s of different anthropogenic species, and many known and unknown biogenic species).
- High temporal variability on wide scales (diurnal patterns of activity and temperature, seasonal patterns of both biogenic and anthropogenic emissions, longer-term changes, such as evolution of vehicle fleet, industrial processes, and land-use patterns).

- Emissions dependence on details of source use (emissions depend on make and model of vehicle, operation of vehicle, species of plant, etc. etc.)
- Many other sources of uncertainty.

A great deal of effort has been expended to incorporate these details into emission inventory estimates, but large uncertainties remain. Further, any inventory is quickly out of date due to changes in source magnitude and character. Thus, it is difficult to judge whether the biogenic or the anthropogenic emissions are estimated with greater confidence. The remote sensing of formaldehyde by satellite does provide added information regarding biogenic emissions. A similar tool is not available for anthropogenic emissions, but considerably more effort has been invested in quantifying anthropogenic VOC emissions through source characterization studies. However, the satellite estimates have their own uncertainties, and oxidation of anthropogenic VOCs also produce formaldehyde, so the interpretation of the satellite data is often ambiguous in large urban areas. On a national or large regional scale, uncertainties in total annual anthropogenic and biogenic emissions may be as small as a factor of two or even less, but on smaller spatial or temporal scales, or more detailed speciation, the uncertainty is likely significantly larger, and will vary widely depending on the particular emissions in question.

1.4 Ozone Photochemistry

With the advent of monitoring for speciated compounds including PAMS and Near-Road Monitoring (NOy), should there be further discussions about the individual chemicals gleaned from the specialized monitoring.

I see no need for further discussion of any additional individual chemicals. PAMS provides a wealth of information regarding specific VOC species in major US urban areas, but this is detailed information that would not add substantially to Section 1.4, as the aim of this section is to give an overview of recent developments in our understanding of the atmospheric photochemistry that produces ground-level ozone. I do not believe that the PAMS data would be relevant to either the high wintertime ozone observed in western oil and gas production regions, or the role of halogen chemistry in the ozone budget. The Near-Road Monitoring program is designed to collect data at the locations that are most highly impacted by vehicle emissions. These data are needed for transportation system planning, environmental impact assessments, and exposure assessments in health studies. The species monitored are the same as in other urban monitoring programs, so no additional information regarding individual chemicals is obtained.

1.5 Inter-Annual Variability and Longer Term Trends in Meteorological Effects on Anthropogenic and US Background (USB) Ozone

While temperature, wind patterns, cloud cover, and precipitation are highlighted as very important variables in ozone formation, does topography play a role (such as in Birmingham where summertime pollutants are trapped in a "mountainous bowl?"

Topography does play a major role in ozone formation. When air is trapped over an urban area due to surrounding mountains, ozone produced over hours accumulates in that trapped air. The most notable example is the South Coast Air Basin in California, which contains the Los Angeles urban area. It is surrounded on three sides by mountain ranges, with the Pacific Ocean to the west. The interaction of the land-sea breeze circulation with the mountains leads to air circulating over the basin while accumulating ozone, which contributes to Los Angeles recording the highest summertime ozone concentrations in the US. It is very difficult to accurately model the wind fields within the Los Angeles basin, due to the

relatively light meteorological forcing and the interactions of the wind with the topographical features. This difficulty contributes to the uncertainty in the photochemical modeling for that region. I am not familiar with Birmingham's topography or air quality, so I cannot comment specifically on that area.

Are there any independent effects on formation formation due to relative humidity?

Relative humidity determines the amount of water taken up by ambient particulate matter, which in turn affects their interaction with the gas phase species involved in ozone photochemistry. Absolute humidity is also important, as water is a reactant in some of the important photochemical reactions that are involved in the formation and destruction of ozone in the atmosphere. Photochemical models incorporate these effects into their photochemical mechanisms.

Appendix 2 Exposure to Ambient Ozone

2.3 Exposure Assessment Methods

While monitoring, including fixed, ambient monitors and personal and microenvironmental monitors are highlighted, what about remote sensing? Biological sampling in blood or tissue?

Remote sensing of ozone is possible with expensive research grade equipment. Even if the difficulties (i.e., laser radiation that is not eye safe) of deploying those instruments in a populated area, their range is limited to a few km. I cannot foresee any role for remote sensing of ozone in exposure assessment studies.

I have no relevant expertise regarding biological sampling in blood or tissue.

2.3.2.1 Spatial Interpolation

While attempting to quantity concentrations at locations and areas between concentration points is included under 2.3.2 Modeling, many of these exact same methods (i.e., data averaging, IDW, and kriging) are also utilized for Monitoring data shortcomings.

2.4.1 Time-Activity Data

Is it possible that ozone exposure through time-activity data may be reduced due to temperature alone, as more people tend to avoid time spent outdoors in the summers during extremely warm/hot/humid, stagnant days which are oftentimes conditions for greater ozone formation?

I have no relevant expertise regarding outdoor activity as a function of outdoor temperature.

Miscellaneous Question(s)

Due to exposure to ozone being disproportionate for disparate (i.e., lower income, children), should this be emphasis in a this section, in lieu of regression analysis confounding/covariate in epidemiological studies for low(er) SES?

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

Questions from Dr. Steven Packham

Question 1: When a causal relationship is conclusive to a high degree of scientific certainty as it is in this case, should this take precedence over causal inference when drafting a NAAQS ISA?

I have no relevant expertise, so I cannot respond to this question as an expert; however, to a non-expert the answer is obviously, Yes.

Question 2: Given evidence available from controlled human exposures substantiating causal relationships with a number of physiological responses, including beneficially confounding interactions of ozone on PM clearance, should Sub-section ES4.1 Health Effects in the Draft's Executive Summary, and the entire Integrated Synthesis section of the Draft be rewritten?

I have no relevant health effects expertise, so I cannot respond to this question. However, as an atmospheric chemist, I would dispute details of the second Background Statement of Fact. A human taking about 20 breaths of about 1 liter volume per minute for 6.6 hours with 75 ppb ozone would inhale about 1.3 mg of ozone, not 1,362 mg. However, that 1.3 mg of ozone corresponds to about 160 million trillion ozone molecules, not a mere 2,439 trillion.

Question 3: Looking ahead, do you think toxicology, clinical human studies, and biomedical research disciplines should be given more explicit and balanced consideration in the development of the present, and future, O3 ISAs with the objective to validate causal relationships and determine hourly inhalation dosage rates for adverse inflammatory responses in pulmonary tissues?

Again, my limited familiarity with pulmonary physiology and inhalation toxicology means that I cannot respond to this question.

References

Almaraz, M., et al. (2018). Agriculture is a major source of NO_X pollution in California, *Science Advances,* 4(1) eaao3477, DOI: 10.1126/sciadv.aao3477.

Amrhein, V., S. Greenland and B. McShane (2019). Retire statistical significance, *Nature, 567*, 305-307, https://www.nature.com/magazine-assets/d41586-019-00857-9/d41586-019-00857-9.pdf.

Derwent, R. G., D. D. Parrish, I. E. Galbally, D. S. Stevenson, R. M. Doherty, V. Naik and P. J. Young (2018). Uncertainties in models of tropospheric ozone based on Monte Carlo analysis: Tropospheric ozone burdens, atmospheric lifetimes and surface distributions, *Atmos. Environ., 180,* 93–102, doi.org/10.1016/j.atmosenv.2018.02.047.

Hurlbert, S. H., Levine, R. A., and Utts, J. (2019). Coup de grâce for a tough old bull: "Statistically significant" expires. *The American Statistician, 73*(sup1), 352-357.

Jaffe D. A., et al. (2018) Scientific assessment of background ozone over the U.S.: Implications for air quality management. *Elem. Sci. Anth.,* 6 56 doi.org/10.1525/elementa.309.

Langford, A. O., et al. (2017), Entrainment of stratospheric air and Asian pollution by the convective boundary layer in the southwestern U.S., *J. Geophys. Res. Atmos., 122*, 1312–1337, doi:10.1002/2016JD025987.

Miller, C. A., G. Hidy, J. Hales, C.E. Kolb, A.S. Werner, B. Haneke, D. Parrish, H.C. Frey, L. Rojas-Bracho, M. Deslauriers, B. Pennell, J.D. Mobley (2006) Air Emission Inventories in North America: A Critical Assessment, *J. Air & Waste Manage. Assoc., 56*, 1115–1129.

Oikawa, P. Y., et al. (2015). Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region, *Nature Communications*, 6:8753 | DOI: 10.1038/ncomms9753.

Parrish, D. D., Young, L. M., Newman, M. H., Aikin, K. C., and Ryerson, T. B. (2017) Ozone Design Values in Southern California's Air Basins: Temporal Evolution and U.S. Background Contribution, *J. Geophys. Res.-Atmos., 122*, 11166–11182, https://doi.org/10.1002/2016JD026329.

Parrish, D. D. and C. A. Ennis (2019). Estimating background contributions and US anthropogenic enhancements to maximum ozone concentrations in the northern US, *Atmos. Chem. Phys., 19*, 12587–12605, https://doi.org/10.5194/acp-19-12587-2019.