Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-1174-AC1, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimating background contributions and U.S. anthropogenic enhancements to maximum ozone concentrations in the northern U.S." *by* David D. Parrish

Parrish

david.d.parrish@noaa.gov

Received and published: 11 December 2018

The author is grateful for the referee's thoughtful comments regarding this paper. However, I believe that these comments are incorrect in some respects, as detailed below, and more importantly miss the significant value of the analysis presented. U.S. policy makers must set national ambient air quality standards (NAAQS) for criteria air pollutants including ozone. A major uncertainty they face is the contribution to measured ambient concentrations made by transported background ozone. It is possible that a standard could be set at a concentration below that background contribution, at least in some regions of the country, and thus be impossible to meet through control of U.S.

precursor emissions. If it is also possible, indeed likely, that the background contribution varies over the country, so any standard would be more difficult to meet in some regions of the country than others. Currently policy makers must rely on estimates of the background ozone contribution calculated by models of atmospheric transport and chemistry. However, these estimates vary widely among different models, and are recognized to be so uncertain that their utility to policy makers is limited. The value of the reviewed paper is that it presents an observationally based estimate of the background contribution that policy makers can compare and contrast with model estimates. As noted by the referee, this observationally based approach is not perfect, but I believe that the results are more accurate than the model results. Each of the referee's comments is reproduced below (*in italics*) followed by my response (in plain text). For reference, I have numbered the paragraphs from the referee's comment; if a paragraph included multiple comments, those are addressed separately with numbers and letters (e.g., paragraph 3 is divided into 3a and 3b).

1) This paper fits long-term trends of ozone design values (ODVs) in the northeastern and rural western US to exponential decay forms with a pre-derived decay scale (21 years) from prior work for Los Angeles, and infers US background ODVs from the asymptote. It concludes that the ODV in the northeastern US is 45.8 ppb, points out that it represents a large fraction (65%) of the current NAAQS over which the US has no regulatory authority, and that it is much larger than models implying that models have large errors.

This summary is mostly accurate, if perhaps overly concise. However, the last phrase is not accurate; the response to comment 5 below discusses the issues that imply large model errors.

2) I have a number of problems with this paper, and not sure that they can be fixed, so ACP may need to do arbitration or seek another reviewer. As I see it, there is no reason that the 21-year ODV decay time scale from LA would apply to other regions. The rural western US is mostly flat, and the northeastern US has a very different trend *history initiated with the early 2000s NOx SIP Call. In fact, it seems from Figure 6 that the trend in the Northeast since 2000 could be fit to a linear decrease just as well as to an exponential decrease, and the linear decrease would imply a zero backgound ODV – which does not make sense of course but makes the point that there is no robustness to the estimate of background ODV presented here from the aymptote to the exponential decay curve. As the paper points out, a 10% change in the decay time scale would lead to a 5 ppb change in background ODV – but there is much more than 10% leeway to the fit in Figure 6.*

The referee correctly identifies one of the more difficult aspects of the analysis presented in this paper. In the northeastern U.S., the long-term decreases of ozone design values have not continued in a consistent manner long enough for all three parameters of Equation 1 to be precisely extracted from the available data sets. Thus, applying the exponential decay time from the entire southern California region (not just LA) is a convenient approximation. However, there are reasons to believe that this is appropriate, as discussed in Section 4.2 of the paper. The significance of the referee's comment on topography is not clear to me, since the time constant reflects the decrease in the anthropogenic precursor emissions, which (as far as is known) is independent of topography. The northeastern U.S. does have a mixed trend history before 2000, but ODVs over much of this region have decreased similarly to those in California. Figure 12a illustrates the great value of comparing the two most populous U.S. urban areas in this manner.

The referee suggests that a linear fit to the data would be appropriate. Indeed, the estimation of background ODVs can be based on linear fits, as discussed by Parrish et al. (2017) with reference to their Figure 4. For the northeastern U.S. a similar analysis is possible as illustrated in Figure 1 below. Importantly, a linear decrease by itself does not imply a zero backgound ODV, or any other specific value; rather it implies that the ODVs can decrease indefinitely, even to increasingly negative ODVs – which indeed does not make sense. However, two linear fits to different time series of

ODVs in a region with a uniform background ODVs, do imply a particular background ODV value, which is given by the intersection of the extrapolations of the two linear fits. This follows because the background ODV does not depend upon the magnitude of the anthropogenic enhancement of ODVs, so both time series should meet at that intersection when U.S. emissions of anthropogenic ozone precrusors are reduced to zero. For two extreme data sets from the northeastern U.S. (maximum ODVs observed in the New York City urban area, and all of the ODVs observed in the much more rural state of Vermont) the background ODV from the intersection of the linear fits (48.5 ppb) is in reasonable accord with the asymptotes approached by the two exponential curves for New York City and Vermont (45.8 and 45.6 ppb, respectively). The important point of this illustration is not that the linear fits are realistic (they are not), but rather that the estimation of the background ODV is not strongly dependent on the validity of the exponential fits, because they can be estimated nearly as well from linear fits. Thus, the estimates of background ODVs are quite robust.

3a) There is also no physical rationale for a single time scale in the exponential decay of ODV, and in the absence of such a rationale any interpretation or extrapolation can be very foolish. The decrease of ODV in the Northeast is thought to be driven mainly by US NOx emissions, which have decreased linearly since 2000 according to EPA although Jiang et al. (PNAS 2018) suggest that they have been flat since 2009 – in any case, I don't see how either scenario would drive an exponential decay of ozone. Even if the response of ozone to NOx emissions was exponential, we would need a sum of exponentials to describe the ozone decrease because different anthropogenic NOx sources have decreased at different rates, and NOx emissions from fertilizer use and small industries have not decreased at all according to EPA. The effect of anthropogenic emissions on ozone is thus much more complicated than can be explained with a single exponential, and even if one can achieve such a fit to the data there is no rationale for extrapolation without understanding.

There is a strong rationale for a single time scale in the exponential decay of ODVs, but that rationale is more mathematical than physical. In the entire southern California region considered by Parrish et al. (2017), a single time scale in the exponential decay of ODVs captured 98.4% of the total variability in the maximum ODVs in 7 air basins, as indicated by the r2=0.984 for the correlation between the values predicted from the single time scale in the exponential decay of Equation 1 (see Figure 5 of Parrish et al., 2017). Such strong correlations are only rarely encountered in geophysical research. In 4 of the 7 air basins, this exponential decay covered the entire 36-year 1980-2015 time series of ODVs. In the present manuscript, a single time scale in the exponential decay of Equation 1 captures 89% of the total variability in the maximum ODVs in the 8 northeastern U.S. states, but only over the 18-year 2000-2017 period. The shorter time period accounts for the smaller r2 found in the present work. This strong agreement between the fits to Equation 1 and the observations in these two diverse U.S. regions is the primary rationale for using a single time scale in the exponential decay, and this strong agreement clearly demonstrates that the effect of anthropogenic emissions on ozone is not more complicated than can be explained with a single exponential. It would be of interest to understand the origin of this strong agreement, but until robust model calculation can reproduce the observed long-term trends in ODVs such an understanding is not available. The response to comment 2) shows that the extrapolation and interpretation of the exponential decay is not foolish.

3b) Considering that NOx emissions from fertilizer use and small industries have not decreased, and that some VOC emissions have not decreased (reference in the paper to McDonald), one must conclude that the background ODV derived in this paper is biased high, possibly by a large amount.

The referee is correct that the background ODVs derived in this paper can be biased high. This is because the fits to Equation 1 separate the ODV time trend into two contributions, one time independent, y_0, and a second that is time dependent. Any contribution to ODVs from emissions that have not decreased would contribute to y_0, and thus bias its estimate high compared to the true U.S. background ODV. However,

generally speaking there are no indications that this bias is significant, and we have some checks on the magnitude of the potential bias. For example, the same y_0 value is found throughout the northeastern U.S. in regions that are highly industrialized with no significant agriculture (i.e., the major metropolitan areas), rural areas with significant agriculture (e.g., the Hudson River Valley), and forested regions with little agriculture. If NOx emissions from fertilizer use or small industries were important, this importance is expected to be reflected in spatial variability of the derived y_0 values. A similar argument was made by Parrish et al. (2017), where the same y_0 value was found for 6 of the 7 California air basins, where the degree of industrialization and land use varied from the Los Angeles urban area, to the rich agricultural areas of the San Joaquin Valley, and to the sparsely populated Mojave desert. Some significant examples of derived y_0 values that are biased high have been identified and discussed. In the present paper, the y_0 values derived for the most densely populated areas (see discussion of Figure 8) are higher than expected from comparison with nearby areas; this is discussed as possibly caused by emissions of the volatile chemical products discussed by McDonald et al. (2018). Parrish et al. (2017) discuss the source of the high bias of the derived y_0 value for the Salton Sea air basin (NOx emissions from the highly fertilized agriculture of California's Imperial Valley). Beyond these limited examples, there is no indication of a general high bias in the results.

4) Indeed, a punch line of the paper is that the background ODVs inferred from the exponential fit are 65-90% of the NAAQS. That seems like a big fraction, but the background ODV estimates are biased high (see above). In addition this is misleading, considering that the ODV is depleted under polluted conditions. In the northeastern US in particular, the ozone background is highest in subsiding northerly flow, whereas the ODV exceedances are under stagnant conditions with southerly flow where background ozone is much lower.

It is difficult to respond to this comment, as several issues are combined. First, there is no evidence that the background ODV estimates are generally biased high by a significant amount, although there are some specific instances of biases that are discussed, and their influence avoided (see response to comment 3b). It is not clear what the referee means by the statement "that the ODV is depleted under polluted conditions"; the ODV is defined as the 3-year average of the annual fourth-highest MDA8 ozone concentration, and these highest MDA8 ozone concentrations do occur under polluted conditions. If they are the highest concentrations, how can they be depleted? The analysis presented in the paper makes no assumption about, and does not depend upon, any particular flow regime, whether subsiding northerly flow or stagnant conditions with southerly flow. I can find no relevance in this comment.

5) As the paper points out, model estimates of background ozone are much lower than what is presented in this paper. The paper attributes this to error in the models. It is fair to say that there is a ± 10 ppb uncertainty in model estimates, as quoted in the paper. But that uncertainty is not a bias, whereas the background estimate in this paper is unarguably biased high. The paper does point out to some extent the uncertainties in its estimate of background ODVs, but that disappears in the abstract where the message is about the high contribution of the background to the NAAQS and how the models need to be corrected.

Model estimates of background ozone are both higher and lower than the result presented in this paper. The 45.8 $\pm$ 1.7 ppb estimate of the background ODV derived in our analysis for the northeastern US is smaller than the model results illustrated in a recent assessment of background ozone over the U.S. (Jaffe et al., 2018); the color scale of their figure 3 indicates a U.S. background ODV in the northeastern U.S. in the range of 50-60 ppb. Our paper does cite other model calculations that give results that are 4 to 12 ppb lower than the 45.8 ppb estimate.

The uncertainty in model estimates of ODVs is actually significantly larger than ± 10 ppb. The paper does have the sentence: "Jaffe et al. (2018) estimate an uncertainty in modeled seasonal mean U.S. background ozone of about ± 10 ppb, with greater uncertainty for individual days (such as those that define the ODV), and Guo et al.

(2018) find biases as high as 19 ppb in modeled seasonal mean MDA8 ozone." Much of the model uncertainties are indeed due to biases. The referee's reference to a high bias in our analysis is discussed in the response to comment 3b) above.

It is clear from the large systematic, average differences among the results from different models that models have large errors, and that to be more useful to policy makers, the models do need to be improved.

The abstract does focus on the high contribution of the background to the NAAQS and the need for further model improvement, since those are among the primary conclusions of the paper. During revision, a brief statement will be added to the abstract regarding the uncertainty of the analysis.

6) Aside from these basic issues of scientific content, I found the paper to be much longer than it needs to be. Figures 1 and 2 show the Pacific Northwest and the Midwest but these then drop from the radar screen, why even bother? Descriptive discussions of population, topography, etc. don't seem necessary. There's a lot of chattiness and repetition.

The description of the Pacific Northwest and the Midwest are necessary for two reasons: first, to show that the ozone design values measured throughout the entire tier of northern U.S. states follow a common pattern (i.e., the magnitude of ODV enhancements correlate with population density, and have decreased in at least a qualitatively similar manner), and second, to justify the focus on two of the four regions, namely on the two regions presenting the greatest extremes. This paper is intended for a journal with an international readership, so I believe that descriptive discussions of population and topography are needed for readers that are not familiar with these U.S. details. During revision, the paper will be reviewed to remove chattiness and repetition.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1174, 2018.

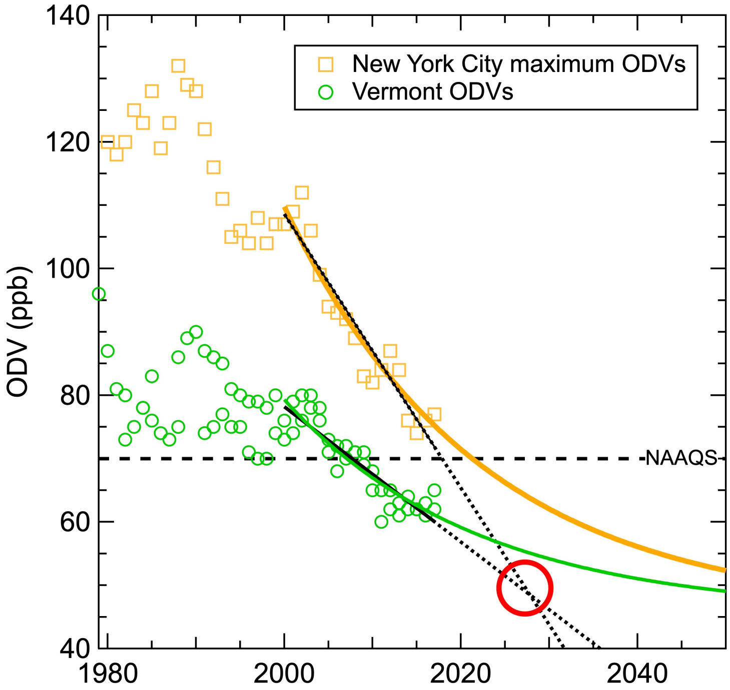

Fig. 1. Comparison of linear and exponential fits to the maximum observed ODVs in the New York City urban area and all of the ODVs observed in Vermont. The dotted lines are extrapolations of the linear fits.