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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of the temperature dependent response of ozone to NO_x reductions in the Sacramento, CA urban plume" *by* B. W. LaFranchi et al.

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Response to referee 1:

The referee raises some important questions and comments that we will address individually.

The question of whether a corresponding change in NO_x emissions with temperature would influence our analysis is a valid one. In fact there is some evidence (Day et al., 2008), based on total NO_y observations at UC-BFRS, to suggest that there is increased NO_x emissions at higher temperatures. An alternative explanation would be that NO_y deposition rates decrease with temperature. It is worthwhile, therefore to consider the

implications of temperature dependent NO_x emissions.

An implicit assumption in performing our analysis is that NO_x emissions across a plume segment are linearly correlated with the observed NO_x at the upwind monitoring station of the segment. That is, for a given observed NO_x concentration, the average emissions along the plume segment are constant regardless of temperature or any other effect. We can test this assumption by re-analyzing our $\Delta[O_x]_{chem}/\Delta t$ calculations as a function of day-of-week, where we expect to have significantly lower NO_x emissions on weekends relative to weekdays. We see no difference in $\Delta[O_x]_{chem}/\Delta t$ for any given NO_x concentration between weekdays and weekends, suggesting that the observed NO_x at the segment starting point is a suitable indicator of NO_x along the rest of the plume segment. We have added text to the manuscript to clarify this assumption.

In Figures 3a-c, we use error bars to express how well we can determine the mean $\Delta[O_x]_{chem}/\Delta t$ with temperature and NO_x rather than the total variability. Therefore, we have chosen to use the "standard error of the mean," or $\sigma/(N)^{1/2}$, rather than the standard deviation. We have changed the wording in the caption of Figure 3 to clarify.

As both referee's have observed, we neglected to include Equation 6 and an associated discussion in the manuscript. This was somehow omitted from the final drafts of our submitted manuscript. The dashed lines in Figs. 3d-f represent the direct calculations of $P(O_x)$ using the following commonly used equation: $P(O_x) = J_{NO2}[NO_2] - k_{NO+O3}[NO][O_3]$ (Eq. 6). We consider this an important aspect of our analysis as it shows the similar relationship between a direct calculation of $P(O_x)$ in the model and the calculation of $\Delta[O_x]_{chem}/\Delta t$ using model outputs along the plume. We have inserted text in Sec. 5 explaining this calculation and its relevance.

The referee's questions regarding our projected time frames for eliminating 1-h ozone exceedances suggests that we need to clarify our description of these calculations. The confidence levels for eliminating exceedances refer to the probability of there being zero exceedances within a given year. So the projected 50% confidence time-frame

ACPD
11, C3827–C3834, 2011

(which we calculate simply by extrapolating the linear fits in Fig. 5 to 0% exceedance probability) suggests that by 2012, there will be a 50% chance that there will not be a single exceedance day along the Sacramento urban plume. Given that the region has not had a single year since the original U.S. Clean Air Act was passed and monitoring began in which the California 1-h standard has not been violated, a 50% probability of no violations is relevant to our discussion. The 95% confidence time frame is calculated by extrapolating a linear fit of the upper bounds on the exceedance probabilities in Fig. 5 (as we describe on page 6276 of our manuscript, uncertainty in the annual exceedance probability is defined by counting statistics on the number of days in each temperature bin: $0.5(N)^{1/2}/N$). Our projected time-frame at this confidence level suggests that by 2018, there will be only a 5% chance that there is a single exceedance day during the year. We have added text to the manuscript to incorporate this clarification and justification for use of the 50% confidence time frame. We have also added an explanation of the uncertainty calculation in the caption for Fig. 5.

Response to referee 2:

Referee 2 raises the general concern that we have neglected the influence of other temperature-dependent effects in addition to increased biogenic VOCs on ozone evolution in the plume. In our discussion, we do not mean to suggest that increased biogenic VOCs are the only way in which temperature affects ozone in the plume, only that they are likely a major driver. As the referee suggests, there is likely a complex array of photochemical effects influencing not only O_x production, but also O_x loss, as a function of temperature. Meteorological and ecological effects such as extreme temperatures and drought may also play a role. A quantitative analysis of the different temperature-dependent processes driving photochemistry and ozone levels in California's Central Valley was the subject of a previous manuscript (Steiner et al., 2006), which we discuss briefly on page 6269 of our manuscript. The authors of that study found that increases in water vapor and radical propagating reaction rates are important drivers of ozone production with temperature, but that the largest influence comes

ACPD
11, C3827–C3834, 2011

from increased BVOCs.

A quantitative analysis of these effects in the Sacramento urban plume is beyond the scope of this study, but could be readily performed using our time-dependent photochemical plume model, which takes into account increases in primary HO_x production with temperature (e.g. via increased water vapor or increased O_3 concentrations), changes in reaction kinetics, changes in NO_y chemistry, and any important feedback processes. That we arrive at similar qualitative conclusions when using both a simple steady-state photochemical model and a detailed time-dependent model suggests that the BVOC-temperature effect serves as a good, though admittedly simplistic, qualitative predictor for O_3 levels in the plume. The point of our analysis is not to prove or quantify the influence of BVOCs vs all of the other temperature-dependent process on P(O_x), but rather to show that by decoupling the temperature-dependent effects on O_x production from the effects of NO_x , we are able to better quantify the relationship between NO_x and O_x production in the plume. We have made some modifications to the manuscript to more clearly emphasize this point.

The referee raises some important specific points that are relevant to better understanding the impact of temperature on O_3 evolution in an urban plume rich in BVOCs, which we will briefly discuss below. In general, however, we view the specific temperature-dependent processes influencing O_x production as a separate, though also important, discussion from that given in our manuscript.

The fraction of NO_x emitted as NO_2 (f(NO_2))in the vehicle fleet is, in theory, an important factor in understanding O_x production in urban plumes. Emission of an NO_2 molecule is functionally equivalent to direct emission of an O_3 molecule since, NO_2 will rapidly photolyze during the day to produce O_3 . On the other hand, emission of an NO molecule will only lead to O_3 production if it is converted to NO_2 through reaction with a peroxy radical (RO_2 or HO_2). Direct emission of NO_2 would be interpreted in our analysis as O_x production, contributing to the calculated Δ [O_x]$_{chem}$ /Δt. Our interpretation of the results could, therefore, be impacted if there is a change in f(NO_2) that is

ACPD

11, C3827–C3834, 2011

correlated with temperature or with NO_x . Any change in f(NO_2) with turn-over of the vehicle fleet implies that it would correlate with NO_x concentrations over the long term, but not across day-of-week time scales. The fact that Δ [O_x]$_{chem}$ /Δt appears to be equally influenced by changes in NO_x across both day-of-week and inter-annual time scales (as discussed in Appendix C) suggests that there has not been an observable change in f(NO_2) over the study period. While we cannot rule out a change in f(NO_2) with temperature, we do not find any evidence to suggest that this in a significant factor.

We derive our estimate for O_x losses based on previously published observations of O_3 and NO_2 fluxes over Blodgett Forest (Kurpius and Goldstein, 2003; Farmer and Cohen, 2008) and observations of VOCs at Granite Bay and at Blodgett Forest (Dillon et al., 2002; Cleary et al., 2005). These observations are primarily what feed the time-dependent plume model from which we calculate O_x lifetimes of 20-30 hrs across all temperature and NO_x scenarios. Our prediction of O_3 concentrations at UC-BFRS compare well to observations (Perez et al., 2009), suggesting that these loss rates are of the correct order of magnitude. We have included these references above in a more detailed description of this calculation in the manuscript.

The influence of extreme temperatures and drought on vegetative uptake of O_3 , NO_2 , and PAN is very uncertain. There have been studies attempting to better understand the relationship between temperature and/or seasonal changes on dry deposition at Blodgett Forest from observed fluxes of these species (Farmer and Cohen, 2008; Wolfe et al., 2009). In each case it was found to be challenging to resolve the effects of photochemistry vs dry deposition to the surface. To our knowledge, there has been no characterization of fluxes of these species with drought severity. This, coupled with the high uncertainty related to drought influence on atmospheric water vapor and the associated photochemical effects gives us no basis for speculating on how drought might influence O_x production and loss in an urban plume.

In our analysis, an increase in dry deposition of O_x with temperature would be perceived as an increase in Δ[O_x]$_{chem}$ /Δt; however, it is unlikely that this effect would be

ACPD
11, C3827–C3834, 2011

large enough to impact the qualitative conclusions of our analysis. For example, across the range of observed deposition fluxes observed across two years by Kurpius et al. (2002), the O_3 lifetime with respect to deposition varies from 22 hours to 150 hours. While these lifetimes do vary quite immensely, the lifetimes are never short enough to significantly influence variability in $\Delta[O_x]_{chem}/\Delta t$. Similarly, changes in deposition rates for NO_2 and PAN are not likely to significantly affect NO_x lifetimes which are on the order of a few hours in a BVOC rich urban atmosphere.

Lastly, the referee questions how the relationship between PAN and temperature affects the link between temperature and $P(O_x)$. The chemistry of PAN in the Sacramento urban plume is discussed in detail by Cleary et al. (2007), Day et al. (2008), Wolfe et al. (2009), and LaFranchi et al. (2009). The latter 3 studies provide an analysis of PAN sources and sinks as a function of temperature. In our analysis, the role of PAN is incorporated into the time-dependent model, including the trade-off between enhanced production from increased BVOCs vs decreased stability at high temperatures – at least to the extent that we understand the chemistry. We feel that it is beyond the scope of this study to specifically quantify the influence of temperature on PAN and its impact on $P(O_x)$.

Response to other comments:

Equation 6 and the description of the dashed lines in Fig. 3d-f have been added to the manuscript.

We have included the slope of the relationship between exceedance probability and NO_y in the discussion.

We have added references to the manuscript justifying the relationship between temperature and VOC reactivity.

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ACPD

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