Short comment by Ezra Wood

This paper presents some very interesting data and analysis from a study in Beijing using state of-the-art measurements of OH, HO2, and RO2. Similar to a few other recent studies, the authors find that RO2 concentrations and instantaneous ozone formation rates are both underestimated by 0-D models under high NOx conditions. The authors define the instantaneous rate of ozone production using Equation 11:

P(O3) = (kHO2+NO[HO2][NO] + kRO2+NO[RO2][NO]) – (kOH+NO2+M[OH][NO2][M]+kRO2+NO2+M[RO2][NO2][M])

Similar definitions of P(O3) were used in Shirley et al. (2006), Sheehy et al. (2010), Dusanter et al. (2009), and Whalley et al. (2018), in contrast to the simpler earlier definitions which only included the first two terms on the right hand side of the equation, e.g., Kleinman et al. (1994), Thornton et al (2002), and Ren et al. (2003). The last two terms are included to account for the fact that O3 is not actually formed if an NO2 molecule formed by the reaction of NO with HO2 or RO2 is then immediately removed by reaction with OH to form HNO3 or with RO2 to form a peroxy nitrate. The problem with this definition is that those two NO2 removal reactions are just two of several Ox loss reactions, where [Ox] = [O] + [O3] + [NO2] + [O(1D)] + 2[NO3] + 3[N2O5]. For example, the reaction of O(1D) with H2O is just as much of an Ox loss mechanism as is the reaction of NO2 with OH. Including only one Ox loss term in the definition of P(O3) is confusing and not quite accurate. It would be much simpler and more accurate to just define the rate of gross Ox production as P(OX) = kHO2+NO[HO2][NO] + kRO2+NO[RO2][NO] and to separately define L(Ox), which would include the rates of the reactions OH + NO2, O(1D) + H2O, O3 + HO2, etc. The net rate of peroxy nitrate (RO2NO2) formation or loss could also be included. It is worth noting that truly defining the instantaneous formation rate of ozone (rather than Ox) necessitates accounting for variations in jNO2, e.g. P(O3) = jNO2[NO2] – k[NO][O3]. The difficulty of evaluating this expression and its limited utility, especially on days with variable jNO2 (due to clouds), underscore the advantage of considering Ox rather than O3.

Please note the similar open comments made for Dusanter et al., (2009): https://acp.copernicus.org/preprints/8/S5350/2008/acpd-8-S5350-2008.pdf References Dusanter, S., Vimal, D., Stevens, P. S., Volkamer, R., and Molina, L. T.: Measurements of OH and HO2 concentrations during the MCMA-2006 field campaign Part 1: Deployment of the Indiana University laser-induced fluorescence instrument, Atmos. Chem. Phys., 9, 1665-1685, 2009.

We thank Dr. Wood for his useful comment and agree that it would be more accurate to compare the modelled and measured P(O3) rather than the incomplete the net P(O3) that is in the manuscript currently. The loss terms in the calculation represent only a small subtraction and do not significantly change the differences reported between net P(O3) calculated from the measured and modelled peroxy radical concentrations. We will replace Figure 11 with the following figure which shows the modelled and measured P(O3) against NO and make the following changes to the text:

Pg20, line 613 onwards: By approximating the rate of ozone production to the rate of NO_2 production from the reaction of NO with HO_2 and RO_2 radicals, urban radical measurements can be

used to estimate chemical ozone formation (Kanaya et al., 2007; Ren et al., 2013; Brune et al., 2016; Tan et al., 2017; Whalley et al., 2018).

$$P(\mathrm{O_x}) = \left(k_{\mathrm{HO_2+NO}}[\mathrm{HO_2}][\mathrm{NO}] + k_{\mathrm{RO_2+NO}}[\mathrm{RO_2}][\mathrm{NO}]\right) \qquad (11)$$

Losses of O_x ($L(O_x)$) include chemical losses such as the reaction of NO_2 with OH, net PAN formation, the fraction of $O(^1D)$ (formed by the photolysis of O_3) that react with H_2O and the reaction of O_3 with OH and HO_2. Physical loss processes, such as O_3 deposition and ventilation out of the model box (see section 2.4) will also contribute to $L(O_x)$. Physical processes such as advection of O_3 into the model box would also need to be considered in the model to make a direct comparison to the observed O_3 concentrations.

Considering the chemical production of O_x (Eq.11), recent studies where OH, HO_2 and RO_2 observations (via RO_xLIF) were made, demonstrated that models may under-predict ozone production at high NO due to an underestimation of the RO_2 radical concentrations at high NO concentrations (Tan et al., 2017; Whalley et al., 2018).

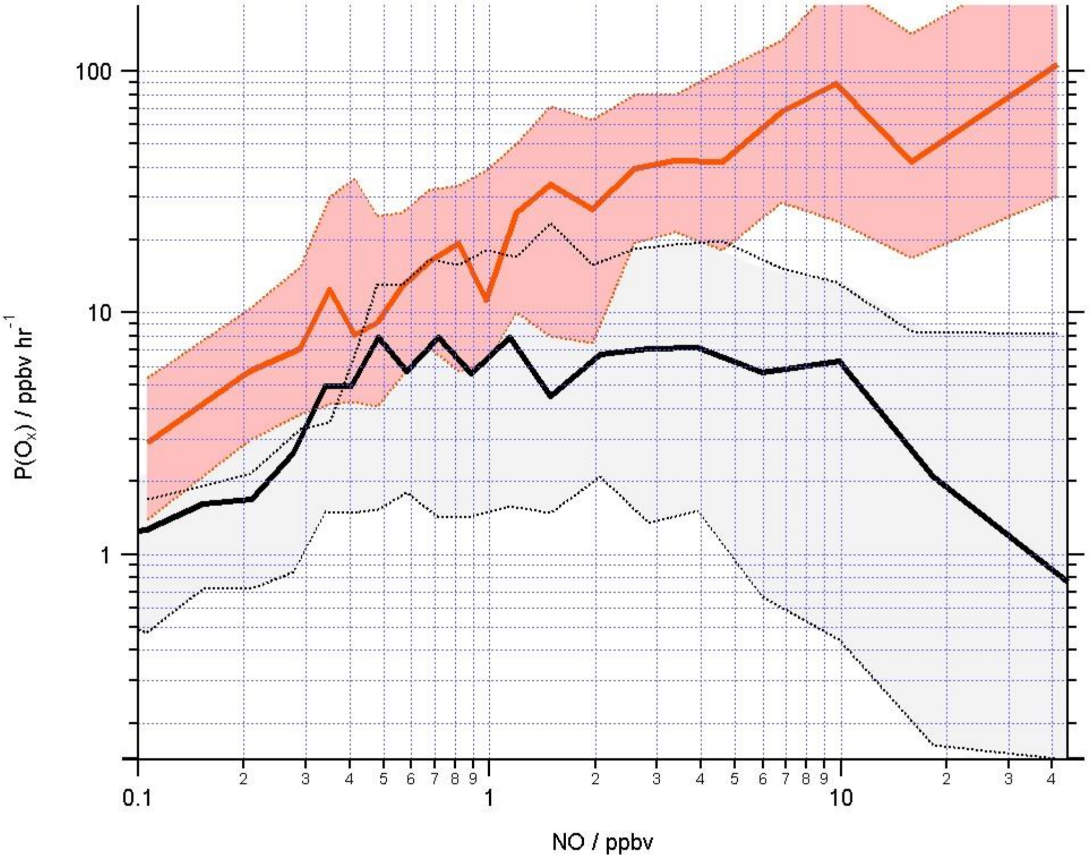

Figure 11: Mean O_x production (ppbv hr−1) calculated from observed (red line) and modelled (black line) RO_x concentrations using Eq. (11) binned over the NO mixing ratio range encountered during the campaign on a logarithmic scale. The shading represents the 25th / 75th percentile confidence limits. The number of data points in each of the NO bins is ~80