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Atmospheric
Chemistry
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Discussions

Interactive comment on "Ozone production, nitrogen oxides, and radical budgets in Mexico City: observations from Pico de Tres Padres" *by* E. C. Wood et al.

E. C. Wood et al.

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Referee comments are italicized followed by our responses:

The paper describes measurements made on during the MILAGRO campaign. The sampling location was on a mountain top located inside the Mexico City (MC) basin. Using relatively limited observations, the paper mainly focuses on a single day (specifically one hour during this day) and attempts to assess radical budgets, Ox production and loss, and ozone production efficiency.

Much of the discussion presented in section 3 is, in my opinion, a strong overinterpretation of the underlying data set and based on a large number of assumptions and estimates rather than hard observations. Furthermore, the results from one afternoon

- specifically one hour - of measurements should not be portrayed as representative of the Mexico City basin as the paper suggests.

We thank the reviewer for the comments, which we note are similar to those from reviewer 1. Please see the response to reviewer 1's 1st and 2nd comments for the discussion of the goals of the paper and how representative the measurements and analysis are of these goals.

The paper needs to be revised significantly but should be resubmitted as the measurements are unique and interesting. The manuscript would greatly benefit from a significantly shortened section 3, estimating/calculating only those quantities which can be traced back directly to measured data and derived quantities. The discussion would also benefit from using a larger data subset such as average diurnal variations or some combination of several days rather than just one hour.

As described in the response to reviewer 1, we believe comparisons of the predictions of photochemical models to actual measurements, even if only focused on a short period of time, are very useful for testing our understanding of photochemistry. We note that the discussion of the NOy budget is based on 11 days of data and not just one hour. We have shortened section 3 by removing the section on P(HNO3)/P(RONO2) as described below in response to a separate comment.

Specific comments: pp. 15746/7: the inlet loss of HNO3 is stated to be "on the order of 45%," measured by "periodically adding standards." This is very unscientific. Was the loss dependent on parameters like ambient temp., relative humidity, or aerosol loading? What is the stated 50% uncertainty based on? If the loss is about half on average were the measured values corrected, i.e. roughly doubled? Either way if nothing more is known about the nature of the losses the stated uncertainty should be 100%.

We have provided the following text on the NH3 and HNO3 standard additions in the revision that we believe justifies our estimate for the 1 sigma uncertainty of 50% (equivalent to a 2 sigma uncertainty of 100%):

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"In order to assess the inlet transmission for NH3(g) and HNO3, small flows of both gases from permeation tube sources were introduced into the inlet four times. The ambient aerosol loadings (measured with the aerosol mass spectrometer) during these standard additions were in the range 10 to 30 ug/m3. The ambient temperature ranged from 16° to 22° C and the relative humidity ranged from 28% to 45%. For comparison, the range of conditions observed between 06:00 and 20:00 LT at PTP was 10° to 27° C and 12% to 75% relative humidity. Inlet losses of NH3 and HNO3 were on order 28% and 45% respectively; the measurements have been proportionally corrected. Given the size of the inlet losses and the limited range of ambient conditions under which standard additions were performed, we estimate an uncertainty of 50% for the HNO3 measurements (the NH3 measurements are not used quantitatively in this analysis). Only NH3 and HNO3 measurements from PTP are included in the analysis."

p. 15747: the collection efficiency for the AMS is being described as "0.5 for all species." Is this a common assumption for this kind of instrument? Is there a reference for this number?

Yes, a value of 0.5 is commonly used and based on experimental data. This paragraph in section 2 has been revised (w/ two references added):

"Particulate nitrate (vacuum aerodynamic diameters between 60 and 800 nm; 50

Matthew, B. M., Middlebrook, A. M., and Onasch, T. B.: "Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols", Aerosol Science and Technology, 42, 884-898, 2008.

Canagaratna, M. R., et al, "Chemical and microphysical characaterization of ambient aerosols with the Aerodyne Aerosol Mass Spectrometer", Mass Spectrometry Reviews, 26, 185-222, DOI 10.1002/mas.20115 2007.

p. 15748: what about the influence of aerosol optical thickness on the estimate of J-values? This could be very different at To and T1 compared to PTP; especially during

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the expansion of the PBL. There could also be wavelength dependencies creating additional uncertainties in the J-values calculated at PTP. These could greatly exceed the stated 16%. What exactly does "minimal cloud cover" mean?

The influence of aerosol optical thickness is accounted for in the altitude correction calculations made using the TUV model; this has been clarified in the text:

" are the model results and j(measured) is from the T1 measurement. This approach uses TUV to account for the difference in elevation between PTP and T1 (850 m), for which aerosol and absorbing gases affect the optical transmission."

The value of 16% refers to the size of the altitude correction to the J-values and not the total uncertainty, which is stated later as 25%. This has been clarified in the following sentence:

"The combined uncertainties in the photolysis rates (accounting for the altitude, cloud coverage, albedo, and unknown absorbers) is estimated as 25

"minimal cloud clover" means that it was not cloudy; this has been clarified in the revision:

"For the periods in which the photolysis rates were analyzed, there was minimal cloud cover (i.e., it was not cloudy)."

p. 15749: the point made about CO mixing ratios being proportional to the quotient of emission factors and PBL height needs to be demonstrated by a plot.

This statement is actually slightly reduntant and has been removed. The key point is that based on the emission inventory and BL heights, [CO] is calculated to increase by 15% during the "stagnant" hour, very close to the observed increase. The results for earlier times are sensitive to more asumptions, including when CO starts to accumulate in the basin. Since this increase in CO is already described in section 3.1, we thought it best to remove this sentence.

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Also, this would only show that PTP was not influenced by nearby emissions of CO, but not of terpenes (other than isoprene, which is known not to be a major emission from the type of trees common to the hills around MC) or other biogenic VOC from nearby vegetation or other emissions from potential VOC point sources such as small businesses. How did the mix of measured VOC and the VOC/CO ratio vary from day to day?

A description of the benzene/CO ratio has been included in the revised paragraph describing NOy/CO and CH3CN/CO ratios (see response to the comment after next). Also, the final sentence of that paragraph now reads as follows:

"Isoprene (canister) and other biogenic VOCs (e.g., terpenes) typically accounted for less than 10% of the calculated VOC reactivity over the entire PTP dataset, indicating there was only a small influence from biogenic emissions. "

p. 15750: a significant increase of CO mixing ratios at PTP is mentioned to have occurred before the mixing layer height reaches PTP but it is not further explained and subsequently ignored. What caused it? Could this have been a residual layer of CO from the day before? How would the subsequent assumptions and calculations be affected if this CO would be mixed into the PBL?

The increase in [CO] observed at PTP before the mixing layer height at T1 reaches the elevation of PTP was explained in 2 locations in the original manuscript:

line 16, pg 15749: "That pollution reached PTP before the mixing layer height reached the elevation of PTP (as measured at T1) is most likely due to differential heating and upslope winds"

and

line 22, pg 15750: "Concentrations of all species rose sharply starting at 09:00 CST, as upslope winds transported pollutants from below the sampling elevation to PTP"

This is a common and well-known air movement on slopes, whereby air is transported

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upslope. Air from the mixed layer below reaches PTP starting at 09:00 even though the boundary layer height over flatter sections of the city (e.g., T1) had not reached the elevation of PTP yet.

p. 15751: what are the ratios of CO/NOy and BC at PTP and T0? What does it mean they "agree" with one another?

The reader needs to get a feel for the accuracy of the statements made. 600 pptv of CH3CN is significantly elevated over the CH3CN background of 200-250 pptv. The influence of BB cannot be measured by CH3CN mixing ratios alone but the CO/CH3CN ratio. What was this ratio and how does it compare to published ratios measured in BB plumes?

This paragraph has been thoroughly rewritten, and now compares the CO/NOy and CH3CN/CO observations between PTP, T0, and literature studies. A comparison of benzene/CO ratios is included as well. The ratios of black carbon to CO, though relatively invariant between the measurement sites, is no longer mentioned since the discussion of CO, NOy, CH3CN, and benzene appears to be sufficient. The paragraph now reads as follows:

"A comparison of the ratios of several primary pollutants at PTP and T0 (a site greatly impacted by fresh urban emissions) indicates that the air observed at PTP was representative of mainly urban emissions and was not greatly affected by biomass burning, biogenic VOCs, or other non-urban pollutants. The Δ[NOy]/Δ[CO], Δ[benzene]/Δ[CO], and Δ[CH3CN]/Δ[CO] ratios were deduced from linear fits of the correlation graphs of 1-minute data. The Δ[NOy]/Δ[CO] ratio was 0.050 ppbv/ppbv (R = 0.99) on 11 and 12 March, 0.054 ppbv/ppbv (R = 0.95) for the entire PTP dataset, and between 0.04 and 0.07 ppbv/ppbv at T0. The Δ[benzene]/Δ[CO] ratio was 1.8 pptv/ppbv (R = 0.93) on 11 and 12 March 2006, 1.67 pptv/ppbv (R = 0.87) for the entire PTP dataset, and 1.1 to 1.8 at T0. The Δ[CH3CN]/Δ[CO] ratio on 12 March 2006 was between 0.2 to 0.5 pptv/ppbv. Other measurements in urban air have been in the range 0.1 to 0.3

(Kleinman et al., 2008;Knighton et al., 2007), while the ratios observed in air impacted by biomass burning are between 1 and 7 (de Gouw et al., 2006). This suggests that biomass burning probably did not have a significant impact on the air on 12 March until 18:00, when a biomass burning PM plume was observed. Isoprene (canister) and other biogenic VOCs (e.g., terpenes) typically accounted for less than 10% of the calculated VOC reactivity over the entire PTP dataset, indicating there was only a small influence from biogenic emissions."

p. 15752: what if the assumption of horizontal homogeneity is not true? This is just one hour of observations and the observed changes in species mixing ratios could have been at least partially caused by advection. The assumption made here could be strengthened by using several days worth of observations where similar increases were observed. Was this day an isolated event? Do the aircraft observations made in MC during MILAGRO back up the horizontal homogeneity assumption? This is a very critical assumption for the reminder of the discussion and it is not well backed up at all in my opinion.

We would have liked to have been able to use several days worth of data for this analysis, but no other days reached the stringent filtering criteria applied. This has been clarified in the final sentence of the penultimate paragraph of section 3.1:

"This time period was unlike most other days at PTP, when boundary layer dynamics and advection played much greater roles in determining changes in pollutant concentrations."

and the final sentences of the 1st paragraph of section 3.2:

"Other days were excluded from this analysis because of at least one of the following two filtering criteria: 1) the wind speeds were greater than 2 m/s, and 2) [CO] did not show a gradual increase of less than 100 ppbv/hr in the afternoon as observed on 12 March. On most other days, [CO] steadily decreased in the afternoon as the mixing depth grew above PTP."

We note that the assumption of horizontal homogeneity is only for a distance of 5.4 km, and that most of this distance is along the mountain slope and not populated - we have added a comment to this effect in the text (1st paragraph of section 3.2):

"The average wind speed during this time period was 1.5 m/s from the southeast, so the air sampled spanned less than a 6 km horizontal range, most of which is unpopulated land along the mountain slope, with no urban emission sources."

If this assumption is untrue, then the quantification of P(Ox), P(NOz), and a few related quantities are inaccurate. The uncertainty caused by this assumption is difficult to quantify, but has been incorporated into the error estimate: the quoted 25% accounts for uncertainty in BL height and uncertainty in the horizontal homogeneity of the air mass. Observations aboard the C-130 show some 6 km stretches where there is very little variation in CO, and other sections with greater variations. However, there were no flights over PTP on days showing similar boundary layer height dynamics, so unfortunately this not definitive.

p. 15753/4: what are the assumed HO2 radical mixing ratios and the ozone deposition velocity based on?

The sum of [HO2] and [RO2] is based on the observed P(Ox) and measured [NO], as now described at the end of section 3.2. A reference for the O3 deposition velocity has been added (Wesely, M. L., and Hicks, B. B.: "A review of the current status of knowledge on dry deposition", Atmospheric Environment, 34, 2261-2282, 2000.)

How good are your NOz measurements given the huge uncertainty in HNO3 and the unknown fraction of particulate nitrate measured?

The uncertainty in the HNO3 measurements in no way affects the NOz measurements - they are separate instruments (see experimental section). Similarly, the size cut-off in particulate nitrate of the AMS does not affect the NOz measurement either. The following sentence has been added for clarification: "NOz was calculated using the

NOy, NO, and NO2 measurements (i.e., NOz = NOy - NO - NO2)"

p. 15755: how were all these calculations performed without actual measurements of VOC from canisters during this time period? If these calculations are not made for the time period of 12:15 and 13:15, how do they relate to this time period?

It is unfortunate that VOC canister measurements were not available on that afternoon, but we believe we have made a reasonable estimate with an honest (±50%) uncertainty. In response to one of reviewer 1'ss comments requesting clarification of the uncertainties, the sentence now reads:

"This quantity is estimated as 0.4 ± 0.2 pptv/s, based on the ozonolysis rates calculated from other afternoon samples at PTP with comparable values of concentrations of O3, CO, aromatic VOCs, and photochemical age values calculated using a C3-benzene photochemical clock (Herndon et al., 2008)."

The arguments in section 3.3.2 are extremely hard to follow. This section needs to be rewritten and the significance of changes in species ratios and concentrations at the different time periods need to be clarified.

We assume that the most confusing part of 3.3.2 was the paragraph that discusses P(HNO3)/P(RONO2). In the revision this paragraph has been removed since it did not contribute greatly to the manuscript and obviously had the potential to confuse.

Section 3.3.3: (Estimate of OH) What is the variability of NO2 between 12:15 and 13:15? As much of the following discussion is based on the 12:15-13:15 period, a blow-up time series is needed so the reader can have an impression of the variability in the data. figure 2 is too small and coarse to allow this.

For the 20 NO2 data points within this hour (3 minute data), the mean mixing ratio is 11.0 ppb with a standard deviation of 2.3 ppb. This standard deviation is the result of instrumental noise, atmospheric variability, and the result of a small sample size. Since this manuscript focuses on the photochemical analysis and not the instrument noise and performance, and since the figures are of high resolution and can be enlarged by a reader, we do not think an additional figure portraying this time period is necessary.

p. 15763: it is interesting that the authors declare the ROx budget "closed" without having made actual measurements of ROx nor having made exhaustive measurements of sources and sinks for ROx.

In the revised manuscript we have clarified that describing the ROx budget as "closed" means that the overall sources and sinks of ROx have been shown to be equal, but with no analysis of ROx cycling (i.e., interconversions among OH, HO2, and RO2):

"The comparison of the calculated P(ROx) value (1.7 ± 0.5 pptv/s) and L(ROx) inferred from P(NOz) (2.1 ± 0.4 pptv/s) indicates both that the budget of ROx sources and sinks is "closed" within the methodological uncertainties (i.e., P(ROx) has been shown to equal L(ROx)) and that ozone production is indeed VOC-limited since P(NOz) is roughly equal to L(ROx)."

and

"We note that this analysis of the calculated ROx production rate and the inferred ROx loss rate does not provide information on the interconversion between OH, HO2, and RO2; actual measurements of those species would be required for that analysis."

We do not have actual measurements of ROx (OH, HO2, and RO2), but such measurements cannot be used to quantify sources of ROx! Though we have not described our measurements of O3, H2O, HCHO, acetaldehyde, acetone, and alkenes as exhaustive, they are not insignificant either. The 2 most important species we are missing are (arguably) HONO and oxygenated VOCs beyond the ones measured, though estimates of the range of possible values (described in the manuscript) show that even the highest possible conceivable concentrations would not affect the conclusions greatly.

The traditional method of quantifying ROx sinks is to calculate them from measurements of OH, HO2, RO2, NO2, etc, and the relevant rate constants (e.g., OH + NO2

=> HNO3, RO2 + HO2 => ROOH). Measurements of OH and HO2 are to this day quite challenging and not fully validated, measurements of speciated RO2 radicals are almost non-existent, and the uncertainties in the relevant rate constants are extremely large. It is therefore evident that though this "standard" approach is important and useful, it is far from perfect and there is a need to investigate alternate approaches to quantifying ROx sinks. Our method of calculating ROx-NOx sinks is quite different: we have instead focused on the observed formation rate of the products of these reactions (using the observed NOz production rate) rather than the calculated reaction rate of the reactants. This method of quantifying ROx-NOx sinks is not perfect either, but given the uncertainties in the traditional approach our method does have merit. For ROx-ROx sinks, our estimates (based on reasonable estimates of OH, HO2, and RO2) are uncertain, but would have to be unreasonably high to alter the conclusions presented in this section of the manuscript.

p. 15767: data from 0900-1600 hours on the 11th and 12th of March is used for the calculation of the ozone production efficiency. Does this make sense given that PTP is not within the PBL before 11 am? If, for example, in figure 6, much of the data below 100 ppbv Ox was eliminated because it was measured before 11am (see Ox time series figure 2), the slopes would be very different (e.g., smaller).

As described in section 3.1, upslope winds transport PBL air to PTP before the T1 measurements show that the BL has reached the elevation of PTP. That is, air that has undergone photochemistry reaches PTP before the BL height over T1 reaches the elevation of PTP. Thus, it is appropriate to use data from 0900 to 1600.

Section 3.5.2: It does not make sense to use data from 0900 to 1700 hours on March 12 for reasons given above. It is not explained how delta-t[OH] is actually calculated. How were the Ox and CO backgrounds of 45 and 130 ppbv determined and how do they vary from day to day?

For the reasons above, we believe it is appropriate to use data from 0900 to 1700. The

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calculation of the photochemical age has been clarified in the following sentence in the 2nd paragraph of section 3.5.2:

The calculation is described in Herndon et al (2008).

The following sentence in the 3rd sentence of 3.5.3 has been added to explain the choice of background values:

"Background values of 45 ppbv for Ox and 130 ppbv for CO are based on observations at night, when PTP was well above the nocturnal boundary layer."

Technical comments: p. 15741 line 8: "US. EPA" should read "U.S. EPA"

This has been corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15739, 2008.

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