Atmos. Chem. Phys. Discuss., 8, S8041–S8044, 2008
www.atmos-chem-phys-discuss.net/8/S8041/2008/

Atmospheric Chemistry and Physics 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.

Anonymous Referee #2

Received and published: 8 October 2008

General comments:

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 over-interpretation 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.

Specific concerns about accuracy and validity of assumptions made are outlined in the "Specific Comments" section below.

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.

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%.

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?

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 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?

p. 15749: the point made about CO mixing ratios being proportional to the quotient of

ACPD

8, S8041–S8044, 2008

Interactive Comment

emission factors and PBL height needs to be demonstrated by a plot. 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?

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?

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?

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.

p. 15753/4: what are the assumed HO2 radical mixing ratios and the ozone deposition velocity based on? How good are your NOz measurements given the huge uncertainty

ACPD

8, S8041–S8044, 2008

in HNO3 and the unknown fraction of particulate nitrate measured?

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?

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.

Section 3.3.3: 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.

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.

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).

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?

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

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