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Atmospheric
Chemistry
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Discussions

Interactive comment on "Inferring ozone production in an urban atmosphere using measurements of peroxynitric acid" *by* K. M. Spencer et al.

K. M. Spencer et al.

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We thank the reviewers for their comments. We have made changes to the manuscript to address these comments. In particular, we have modified former Fig. 8 to more clearly demonstrate the underprediction of P_{O3} at high NO. Specific comments are addressed below.

Reviewer 1: Response to major comments:

1.) Page S369, lines 7-9: The authors conclude that the model and measurements can be brought into agreement by including the reaction of NO_2^* with H_2O as a HO_x

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source, reducing the rate of $HO + NO_2$ or both.

Response: We have changed the text to clarify that these two processes are two possible sources of error in the prediction of HO_2NO_2 levels. Their inclusion leads to better, but not perfect, agreement between the observed and modeled values of HO_2NO_2.

Text revision: Increased levels of calculated HO_2NO_2 are in better agreement with observations. These two recently suggested ideas lead to better, not perfect, agreement between observed and calculated HO_2NO_2.

Reviewer 1: Response to specific comments

1.) Page 2801: Is the atmosphere at steady-state? Comparing HO_2NO_2 calculated from the full diurnal equilibrium model to that calculated in steady state modeled HO_2 and NO_2 does not fully address the question of whether the sampled airmass is truly in steady state with respect to HO_x sources and sinks. The fact that the slope of the correlation (Fig. 3) is close to 1 indicates that the time constant for the box model to converge is primarily limited by the time required for HO_2NO_2 to reach steady state. However, the atmosphere might be out of steady-state with respect to HO_x or NO_x sources and sinks because the plume sampled is too close to the source and is still exhibiting effects of dilution and mixing? Other studies (e.g. Thornton et al., 2002) have found the assumption of photostationary state at high NO_x levels to be questionable because the parcels in question were still mixing into the background atmosphere. Presumably chemical processes (e.g HONO formation and photolysis) are also introducing effects that slow the approach to photochemical steady state. One partial test would be to evaluate whether there is a bias in the deviation of the

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$NO : NO_2$ ratio from photostationary state at high NO_x? If there is excess NO then it might indicate the measurements are too near the source. There are probably other steady-state relationships in the C-130 data set that could serve as additional checks.

Response: To verify the validity of the photochemical steady state assumption with respect to HO_2NO_2, the model was run in a non-steady state mode. A large, polluted perturbation was introduced into the model and allowed to decay over several days. A second set of calculations was performed in which each point was solved along the decay of the plume using steady state assumptions. While some species were not in equilibrium during this model run, the mixing ratios of HO_2NO_2 were consistent with the steady state run. This is attributed to the very short lifetime of HO_2NO_2 (five minutes) for the temperature range in the dataset. NO_x is directly input into the model while HO_x varies rapidly enough to represent the instantaneous precursor condition.

Text revisions: Due to the short lifetime of HO_2NO_2 with respect to thermal decomposition for the conditions experienced during the MILAGRO flights, photochemical steady state of HO_2NO_2 was assumed. To verify the validity of this assumption with respect to HO_2NO_2, the model was run in a non-steady state mode. A large, polluted perturbation was introduced into the model and allowed to decay over several days. A second set of calculations was performed in which each point was solved along the decay of the plume using steady state assumptions. While some species were not in equilibrium during this model run, the mixing ratios of HO_2NO_2 were consistent with the steady state run. This is attributed to the very short lifetime of HO_2NO_2 for the temperature range in the dataset. NO_x is directly input into the model while HO_x varies rapidly enough to represent the instantaneous precursor condition.

For the conditions experienced during the MILAGRO flights, the median lifetime of HO_2NO_2 with respect to thermal decomposition was five minutes while the lifetimes

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with respect to reaction with OH and UV/IR photolysis were on the order of 10 hours and 6 days, respectively.

2.) Page 2804 and Fig. 8: Are the correlations among the major factors controlling HO_2? While using CH_2O as a proxy for HO_x production is reasonable, it appears that the CH_2O and NO_x are correlated and we presume that VOC reactivity is also strongly correlated with NO_x. Given these correlations, it would be more straightforward to first identify the size of an additional HO_x source, the additional VOC reactivity or the excess HO_x sink (presuming all are about equally correlated with NO_x) and express each of these as a fraction of the total source/sink. It should also be confirmed that the analysis used a VOC reactivity that is not averaged over a different time window than the HO_2NO_2.

Response: Although it is certainly the case that the mixing ratio of CH_2O does increase with NO_x, there is considerable variation of CH_2O at all NO_x levels. Although it is certainly possible that the difference in P_{O3} between the model and that inferred from HO_2NO_2 arises from uncaptured HO_x sources at high NO_x levels, as seen in the third panel of revised Fig. 7, at low NO_x and high CH_2O, the model accurately captures the rate of ozone production derived from observations while at high NO_x, the model underpredicts the rate of ozone production (as inferred from HO_2NO_2) at both high and low CH_2O. This suggests that the error in the model description of HO_2NO_2 at high NO_x likely reflects error in both HO_x sources and possibly sinks. The 1-minute merged data set was used for this analysis to provide consistency in averaging periods.

3.) Page 2806. The Caltech group made important contributions to our understanding of the products of the $OH + NO_2$ reaction. It is unclear how our understanding of the products affects the discussion about this rate in this paper. It would help the reader who is more familiar with the primary literature than the JPL evaluations if the paper described the rates in the JPL evaluations and the assumed products with additional details, so that the reader can understand the arguments in question without going back to the two JPL reviews.

Response: The manuscript has been revised to discuss the inclusion of the $OH + NO_2 \rightarrow$ HOONO channel for the $OH + NO_2$ reaction in the 2006 JPL critical evaluation. It has also been reworded to emphasis that Okumura and Sander (2005) concluded that the 2000 recommendation for the $OH + NO_2 \rightarrow HNO_3$ reaction may be closer to the true rate than the 2006 recommendation, which is used in current atmospheric models.

Text revision: In addition, a recommended rate constant for the reaction of OH and NO_2 to form pernitrous acid (HOONO) is included for the first time in the 2006 JPL critical evaluation. Recent laboratory work at Jet Propulsion Laboratory and California Institute of Technology suggests that the 2000 JPL critical evaluation recommendation (Sander et al., 2000) may be closer to the true rate of R8 (Okumura et al., 2005) than the current recommendation (Sander et al., 2006).

4.) The paper should note that the problem with the HO_x budget at high NO_x appears to be distinct from the problem of excess HO_x correlated with isoprene; although if the problem is a missing source molecule (and not excited state NO_2) perhaps the issues are more related than has been described to date.

Response: The manuscript has been revised to discuss the correlation between excess HO_x and isoprene in light of Ren et al. (2008).

Text revision: It should be noted that the discrepancy between observed and modeled values of HO_2NO_2 at high NO_x found in this study appears to be distinct from the underprediction of HO_x values correlated with isoprene. Ren et al. (2008) found the observed-to-modeled OH ratio in the boundary layer to be strongly dependent on isoprene during the INTEX-A summer 2004 campaign, with divergence occurring at isoprene levels greater than 100 pptv. Isoprene mixing ratios were well below 100 pptv for the vast majority of the data used in this analysis.

5.) Fig. 7: It is not entirely clear what additional information the reader received from this figure. It appears that perhaps the model fails to capture the hot sports but the figure is never referenced in the text and could possibly be omitted without diminishing the discussion or conclusions.

Response: Figure 7 and page 2803, lines 10-12 have been omitted.

6.) Fig. 8: The differences between the two panels are not readily apparent in the figure as presented. They seem to span the same range of P_{O3} and it is difficult to see whether or not the Langley model P_{O3} turns over more than the P_{O3} implied by the observations. Perhaps if you added a panel showing the ratio of the measured to modeled P_{O3}.

Response: We thank the reviewer for this suggestion. Revised Fig. 7 (formerly Fig. 8) has been modified to include a third panel of the ratio of derived P_{O3}, based on observations to P_{O3} calculated by the NASA LaRC photochemical box model as a function of NO. The third panel more clearly indicates the enhanced P_{O3} calculated from observations compared to that calculated by the photochemical box model.

7.) Fig. 9: This figure would be easier to read if it were reformulated so that agreement

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between a model and the observations gave a value of 1. Then the reader would be better able to judge whether the successive model changes make improvements to the analysis or not. The figure would be easier if the first panel showed the ratio of observed to model for the base model and then the next ones showed the other models, again as a ratio to the observations.

Response: Although Fig. 9 was reformulated such that the ratio of observed HO_2NO_2 to different model calculations of HO_2NO_2 was presented, the trend in increased calculated HO_2NO_2 was less apparent than in the original figure due to insufficient precision and a lack of data points.

Reviewer 2: Response to major comments

1.) S698-S699: Details on such vital information as the temperature and water vapor are missing, as are specifics about NO, OVOC, OH, etc, which would make it easier to interpret the paper. The temperature is not given for the measurements (only a 50-degree range).

Response: Details regarding NO, OVOC, OH, H_2O, CH_2O and temperature measurements have been added to the manuscript.

Text revision: NO and NO_2 mixing ratios were measured by photofragmentation / chemiluminescence. The precision of these measurements is ~ 15 pptv and the overall uncertainties are $\pm$(15+7% of the mixing ratio) pptv and $\pm$(15+10% of the mixing ratio) pptv, respectively (Campos et al., 1998, Weinheimer et al., 1998). CH_2O mixing ratios were measured by tunable diode laser absorption spectroscopy with an uncertainty of 15% (Fried et al., 2003, Wert et al., 2003). HO_2 mixing ratios were

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determined by chemical-conversion / chemical ionization mass spectroscopy with an uncertainty of 35% (Cantrell et al., 2003). Non-methane hydrocarbons (NMHC) were measured using whole air sampling (WAS) and subsequent analysis was conducted by gas chromatography/ mass spectrometry/ flame ionization detection/ electron capture detection (Colman et al., 2001, Blake et al., 2003). H_2O mixing ratios were calculated using the ambient water vapor pressure and corrected static pressure. These measurements and the ambient temperature measurements are included in the NCAR C-130 standard airborne scientific measurements and are discussed in RAF Bulletin No. 9 (Miller et al., 1985). The full details of measurements taken during MILAGRO from the NCAR C-130 aircraft platform can be found at http://mirage-mex.acd.ucar.edu/Measurements/C130/index.shtml.

In this study, we limit the analysis to those points that include direct measurement of NMHCs.

Reviewer 2: Response to specific comments

1.) Page 2798 and Fig. 2: It looks to me like the slope of the fit line is around 0.75 (380/500), not 0.90 as stated. This means that transitioning from wet air to dry air could introduce an uncertainty of 25% into the measurements. This could play a role in the low altitude flights mentioned above. Interestingly, the data on March 29th (red dots) all lie closer to the 1:1 line than to the robust fit line.

Response: Figure caption and manuscript have been corrected. slope = 0.76. intercept = 0.90. The reviewer makes a good point. There are uncertainties associated with transitioning between dry and wet air (transfer ion m/z 98 and cluster ion m/z 164) when determining HO_2NO_2 mixing ratios. We have reason to believe, at high

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waters, the cluster ion provides a more accurate measurement of HO_2NO_2 than the transfer ion due to increased acetic acid interference. However, if we go to the limit of the uncertainty pointed out by the reviewer and use the transfer ion, it would result in a 25% increase in HO_2NO_2 mixing ratio. This would make the discrepancy in Fig. 5 larger, especially at high NO_x. The discrepancy between the derived production of ozone, based on observations and the production of ozone calculated by the NASA LaRC box model has been evaluated and is independent of H_2O. Although there are uncertainties related to the two product ions, these uncertainties do not change our results.

2.) A brief look at the Shon et al. paper in the same Special Issue of ACPD suggests that the March 29th data had anomalously high photostationary states compared to other Boundary Layer runs. Does that impact the ozone production rates here at all?

Response: This is an interesting question. The effect of photostationary state, as described by Shon et al. (2008), on ozone production rate was investigated. Photostationary state was calculated as

$$\mathrm{PSS} = (k_1[\mathrm{O_3}] + k_3[\mathrm{HO_2}] + k_4[\mathrm{RO_2}])/J_{NO_2}$$

(Shon et al., 2008), where k_4 is the coefficient corresponding to the reaction between NO and CH_3O_2. The rate of ozone production does not appear to be influenced by the photostationary state of the system. Also, photostationary state does not appear to depend on NO mixing ratio.

3.) Box model: How was acetaldehyde treated in the model? It is thought to be one of the major contributors to OH reactivity, and probably also to HO_x production. Was the concentration allowed to be governed by the chemistry of larger alkanes, or was it

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constrained by in-flight measurements? This could affect the modeled concentration of HO_2 dramatically. How is propene treated? It is not mentioned explicitly in the list on page 2800, but is a major precursor of acetaldehyde, and a contributor to OH reactivity.

Response: Acetaldehyde (CH_3CHO) is calculated in the model. 49% of the subset of data points used in this analysis (as described in the text) have CH_3CHO observations available. In general, the model predicts significantly less CH_3CHO than was measured. When the model is constrained to CH_3CHO observations, there is a 5-10% decrease in OH and a slight decrease in calculated HO_2 (less than 3% in the median value). The relative impacts appear to be somewhat larger at high NO_x, but in general, the correction for HO_2, in particular, is minimal. The measurement of CH_3CHO is quite difficult to make, and questions regarding its precision and accuracy remain. Given the uncertainty of the CH_3CHO observations and small impact on HO_2 expected from constraining CH_3CHO to observed values, we do not think the impact from CH_3CHO affects the conclusions of this study. We are confident in the model-predicted values of HO_2 for this study. Coincident with the MILAGRO campaign was INTEX-B, in which the NASA DC-8 made several flights in the vicinity of Mexico City. HO_2 measurements on that aircraft were made with the ATHOS instrument (Faloona et al., 2004). These measurements were generally within 10% of model predictions. Observations were generally larger than the model by a factor of 1.1 for altitudes below 2 km and smaller than the model by a factor of 0.9 for altitudes above 2 km. The differences between observed and calculated CH_3CHO and their effects on OH and HO_2 mixing ratios are presented in the table below. Median values are presented.

NO_x	Obs CH_3CHO (pptv)	Calc CH_3CHO (pptv)	OH mixing ratio when constrained to CH_3CHO obs / OH mixing ratio when using calculated CH_3CHO	HO_2 mixing ratio when constrained to CH_3CHO obs / HO_2 mixing ratio when using calculated CH_3CHO
$<$ 100 pptv (176 points)	229	81	0.95	1.0
100 - 500 pptv (66 points)	1135	492	0.91	0.97
$>$ 500 pptv (48 points)	3006	1861	0.90	0.97
Overall median (all NO_x)	480	159	0.94	0.99

Propene is included in the C_3 and higher alkenes. The reactions for the lumped alkenes are based on Lurmann et al. (1986). Reactions of lumped C_3 and higher alkenes are assumed to be predominantly propene. The assumed aldehyde product is CH_3CHO and reaction rates are based on those for propene. The manuscript has been revised to address these concerns.

Text revisions: While a discrepancy between calculated and observed values of acetaldehyde (CH_3CHO) does exist and has the potential to impact HO_x levels, constraining the model to observed CH_3CHO values suggests that this uncertainty propagates to impact OH mixing ratios by 5-10% and HO_2 mixing ratios by less than a few percent.

Reactions of lumped C_3 and higher alkenes are assumed to be predominantly propene. The assumed aldehyde product is CH_3CHO and reaction rates are based on those for propene.

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4.) Page 2802 and Fig. 5: To play Devil's Advocate, the observed HO_2NO_2 at high NO_x lies very close to the 1:1 line, while the majority of measurements lie closer to the 0.8:1 line. So it is hard to justify the statement that the model underpredicts HO_2NO_2 concentrations at high NO_x, when these measurements are in fact closer to the model than the majority. As I commented earlier, there is a possible 25% discrepancy between measurements obtained at low and high H_2O, and these discrepancies clearly fall into that range.

Response: The reviewer's point is well taken. The NO_x dependence of HO_2NO_2 is not accurately captured by the model. Below 1 ppbv of NO_x, the uncertainty of the HO_2NO_2 measurements, $\pm$ (30% + 30 pptv), contributes significantly to the discrepancy between observed and modeled values. Between 1 and 10 ppbv of NO_x, observed and modeled HO_2NO_2 are in agreement. Modeled HO_2NO_2 values for $NO_x > 10$ ppbv are underpredicted compared to observations, indicating the NO_x dependence of HO_2NO_2 is not fully captured in the photochemical box model. This underprediction of observed HO_2NO_2 at high NO_x translates into underprediction of the rate of ozone production. This is more clearly shown in the revised figure than in the original manuscript. Per Reviewer # 1's suggestion, revised Fig. 7 has been modified to include a third panel of the ratio of derived P_{O3}, based on observations to P_{O3} calculated by the NASA LaRC photochemical box model as a function of NO.

5.) Page 2802, line 14-17: Clarify for the reader that you are referring to the instantaneous rate of photochemical ozone production, not the net rate.

Response: Added “instantaneous rate of photochemical ozone production".

6.) Page 2803, lines 14-23. This paragraph is not particularly relevant (or correct).

It seems to imply that HO_2 cycling mostly occurs through alkanes, where there is an alpha-hydrogen attached to the carbon bearing the alkoxy radical. As was shown in the TEXAQS campaigns, the most potent sources of ozone are typically alkenes. Here the OH adds to the hydrocarbon, leading to alkoxy radicals of the form $HOCH_2CH_2O$, which decompose to form CH_2OH, and then give HO_2. Conversely, for many alkanes, despite the presence of an alpha hydrogen atom, the alkoxy radical decomposes. This process tends to lead to 3 (NO to NO_2) conversions. So, I am not sure where that paragraph is leading. If all the RO_2 are being accounted for explicitly, it does not matter whether they have alpha-hydrogen atoms or not. However, if you are trying to predict the number of NO_2 formed per OH produced, then the number of conversions matters, for the above reasons. Also, I am not sure what tertiary aldehydes are, or how that fits in.

Response: The reviewer's point is well taken. The paragraph has been removed.

7.) Fig. 8: There does seem to be a slight tendency for the P_{O3} values to fall off in the model, but I am not convinced that it is much different from the observations, or that you can be sure that the production rate of HO_x is constant in reality, since the relative amounts of secondary carbonyls can change. Looking at Fig. 8, it seems like the largest discrepancies actually occur at low NO_x, where the measured values of P_{O3} span two orders of magnitude. Again, on page 2804, line 16, it is stated that the observed HO_2NO_2 levels are greater than the model at high NO_x, whereas in fact they lie close to the 1:1 line in Fig. 5.

Response: Per Reviewer #1's suggestion, a third panel was added to revised Fig. 7. The ratio of derived P_{O3}, based on observations to P_{O3} as calculated by the NASA LaRC model is presented as a function of observed NO and colored by observed CH_2O in the third panel. The enhanced P_{O3} derived from observations compared to that calculated by the photochemical box model is clearer than in the original figure. Also see response to Reviewer #2, comment 4.

8.) Page 2806: These are good tests as to the sensitivity of the ratios to different kinetic parameters. It is not clear how HOONO was treated, since the 2006 JPL evaluation treats this as an explicit channel. Depending if HOONO regenerates HO_x or serves as a sink, it can affect the overall HO_x loss rate. Please give more explicit details about this.

Response: The model does not include the HOONO branch of the $OH + NO_2 + M$ reaction. The explicit rate for HNO_3 formation given in the JPL critical evaluation is used. Due to the short lifetime of HOONO of a few seconds to a few minutes for the tropospheric temperatures and pressures under consideration, the formation and breakdown of HOONO is considered to be a null cycle that can be neglected (Fry et al., 2004). The manuscript has been revised to include these details.

Text Revision: The explicit rate constant for HNO_3 formation was used in the model. The model does not include the HOONO branch of the OH + NO_2 + M reaction due to the short lifetime (seconds to minutes) of HOONO under MILAGRO conditions. The formation and breakdown of HOONO is considered to be a null cycle under these conditions (Fry et al., 2004). A reduction in the rate constant for R8 leads to an increase in OH and NO_2 mixing ratios, leading to an increase in HO_2NO_2 levels. To test the importance of this modified rate constant on HO_2NO_2 levels, the 2000 JPL critical evaluation recommended rate constant for R8 was substituted into the model.

9.) Fig. 9: Caption could be more complete. It needs to say what is plotted on the y-axis, i.e., ratio of calculated values of HO_2NO_2 using different values of the following parameters.

Response: The caption has been revised to more clearly state what is being presented.

10.) Page 2805, line 8: “where" should be “were".

Response: Corrected.

11.) Page 2810. Lurmann et al. reference. Page numbers should be 10905-10936.

Response: Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 2791, 2009.

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