Atmos. Chem. Phys. Discuss., 9, S2058–S2071, 2009
www.atmos-chem-phys-discuss.net/9/S2058/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Biomass burning and urban air pollution over the Central Mexican Plateau" *by* J. D. Crounse et al.

J. D. Crounse et al.

Received and published: 12 May 2009

Reply to Anonymous Referee #1

We thank referee #1 for the time s/he invested in careful review of this paper. The comments have been very helpful in our manuscript revision. Original comments are shown in **bold** and responses are given beneath in normal fontweight.

1. P2702, lines 20-25. I recommend that a sentence or two be added to give the reader an idea of the cause of these pine forest fires. Are they ignited for forest management (controlled burns), ignited by people for other reasons, accidental, etc. (Since it is the dry season lightning is probably not the major factor.) Then the reader can decide perhaps how easy it would be to reduce the number of fires during this season (re the conclusions of this paper and

mitigation).

The following sentence has been added to the manuscript:

"These fires are virtually all of human origin. Primarily they originate from accidental means (escaped agricultural/land maintenance fires, escaped campfires, smoking, fireworks, vehicles, etc), with a smaller number originating from intentional ignition (Ernesto Alvarado, private communication)."

2. Suggest P2703, line 20: (3×3 degree box centered on MC, shown in Fig. 2, and termed . . .)

Done.

3. I would recommend that Figure 3 (a very nice presentation summarizing a lot of work) be accompanied by a new Fig. 3b showing the aircraft flight track (with time markers) superimposed on a standard topographical map of the region (preferable) or an enlarged version of one of the MODIS images. Including the standard box used for the analysis would also be appropriate (I realize the box is given in the current Figure 2). The track should be color coded by altitude. This would help the reader better understand some of the variations in the time plot and allow them to know where the aircraft was relative to Mexico City, the mountains, the fires, the box of emphasis, etc. (The present figure has black circles around data within the box of interest, but that really does not give the reader a good perspective of where all the substantial variations in the time plot occur.)

A new figure (new number 4) has been created to include the flight track for this flight as suggested above.

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The following sentence has been added to the text:

"Figure 4 shows the flight track corresponding to Figure 3 on top of the MODIS - AQUA image for March 8th."

4. Figure 3a as currently given (without flight track) does not really explain why in Figure 2 the C_2H_2 and HCN are (not "appear") geographically coincident. The coincidence is quite unexpected. Are there other reasons that you can give to offer some understanding? Is a contributor that emissions from fires on the city side of the mountains collect within the basin at night and morning? And also that the aircraft usually sampled in the noon to afternoon period when venting (to the northeast usually) of the basin occurred to various degrees?

While HCN and C_2H_2 may appear geographically coincident in Figure 2, the HCN is more diffuse than the C_2H_2 (which is more centrally located over the metropolitan center of MC). The populated area of the basin goes right up to the ring of mountains which defines the basin. Smoke from the fires on the mountainsides can be blown over the basin. Figure 2 does not depict the vertical distribution of the pollution (see Figure 9).

5. P 2703 line 27: in the study-needs clarification-do you mean for the seven flights and within the box of Figure 2?

Yes, this is for data collected within the 3×3 box, over the 7 flights considered for the study. We have clarified this sentence:

"The mean mixing ratio of HCN in the study area (7 flights considered, within

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the 3×3 box) was measured to be 530 pptv, about 390 pptv higher than the background values observed in clean air encountered above the plateau pollution."

6. One of the major products of the analysis (Table 1, and [missing text])
The NOy converter should sample nitrate aerosol (if size less than a few microns) other than crystalline aerosol nitrate. But there is no description of the NOy inlet, whether isokinetic, whether at right angles to the flow, or whether particle amplification might occur. Some related words would help the reader. MILAGRO also had a number of instruments measuring aerosol composition so some idea of the kind and magnitude of aerosol nitrate should be available at least for the MC air parcels. Also there were fair amounts of ammonia in the MC area, and ammonium nitrate should be measured by the NOy converter/instrument. The statement in the appendix that aerosol nitrate was added to the observed/measured NOy (double counting, etc.) seems quite at odds with most NOy measurers. Some clarification and expansion of the NOy treatment is absolutely required.

There seems to be some missing text at the beginning of this comment, but we assume it relates to the NOy instrument and its description, and the treatment of the NOy data.

Additional information has been added to the appendix further describing the NOy instrument (see response to comment #10).

The reviewer's suggestion that the NOy instrument probably samples some aerosol nitrate is well-taken. The fit has been conducted with and without adding the aerosol nitrate. The correlation is much better, as stated in the appendix, when the aerosol nitrate is added. Because the NOy instrument samples a portion, but not all, of the aerosol nitrate, the appropriate sum is in-between adding the aerosol nitrate and

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assuming it is completely sampled by the NOy instrument. Unfortunately, because we don8217;t have a good constraint on the aerosol sampling characteristics of the NOy instrument, we cannot constrain this better. The discussion of the assumptions and uncertainties in the NOy treatment (A4) has been modified.

7. I had problems with the present ordering (and quality of some) of the Figures and suggest that some reorganization be made. Figure 1 is repeated by Figure 10 (admittedly in the Appendix). The text could easily be changed to include all of the MODIS images (currently Figures 10, 11, 12 in the Appendix) or a subset of them where the present Figure 1 occurs. (Consider whether they are all necessary even if you decide to leave the remaining ones in the Appendix). Even more important, current Figures 10-12 are the antithesis of what figures are supposed to be. It is impossible to see the red fires in all of the print-friendly version. Even in the on-line version the plots have to be zoomed individually by 200-400.

In Figure 1, two MODIS images from two days are shown to highlight several points. 1). Fires during this period do have an important impact on regional air-quality (i.e. they and their emissions are visible from space), and 2). Not all fires are detected as thermal anomalies by MODIS. We do not feel it is nessisary to include additional MODIS images to make this point. Rather, we include the complete set of MODIS images in the Appendix (and in the revised manuscript, we include these at higher resolution in the supplementary material see below).

We concur in that most detected fires in figures 10, 11, and 12 are cannot be identified without zooming. The overall weather pattern is discernable in the print version without zoom. The main issue with depicting larger images is the number of pages required for display. Using 2 pictures per page requires 15 pages for in total. This seems excessive. Our solution is to leave Figs. 10-12 unchanged in the main

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manuscript, and attach a supplementary addition which contains the MODIS images from both Terra and Aqua satellites at higher resolution.

8. P2704, line 25: you call the Fy scalars (fine) but then on P2706 line 21 you call them emission ratios. Why not call them what they are right up front. In fact the paragraph beginning on P2706, line 21 to P2707 line 2 might be better placed beginning on P2704 directly after the equations presented. And then say you determine some things essentially from the slopes of correlation plots as given in Figures 4, 5, 7, 8 etc. At present the discussion of the equations (model) is interrupted by discussion of details (gasoline, diesel, etc) and backgrounds, before finishing the basic description of the application of the model (TLS etc.). (Just a suggestion to improve the flow.)

The term 'scalar' is used to emphasis that the Fy's remain constant across the entire analysis. Typically, the term 'emission ratio' carries a specific meaning, defined as emissions of a pollutant relative to concomitant emissions of CO or CO_2. The introduction via the term 'scalar' may help avoid some misunderstanding, as these 'emission ratios' are not relative to CO or CO_2, but rather relative to HCN and C_2H_2.

As suggested the TLS description has been moved to just before the background and cross-term discussion.

9. Page 2705, lines 28, 29: How does the reader infer from ("see Table 1") that the contribution of biomass burning to C_2H_2 accounts for less than 10%.

The reference to Table 1 has been removed.

10. Page 2706, lines 20-25. Don't errors in the measurements (or shouldn't errors in the measurements) contribute to the weighting? Since the HCN

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measurement by CIMS is new, the Appendix at least needs to have a statement of the calibration procedure, the precision and the estimated accuracy of the instrument. Same for all the other instruments. Currently only CO has a precision and estimated accuracy statement.

The following sentences have been reworded to more clearly describe the procedure:

"We weight [HCN]* and [C_2H_2]* by estimates of their error comprised of the uncertainties in the backgrounds levels and estimates of measurement accuracy. We estimate the uncertainties in the derived emission ratios using a bootstrap method (Efron and Tibshirani, 1993)."

A brief description of the HCN measurement technique by CIMS has been included in the Appendix, as well as precision and uncertainty estimates for the other instruments.

11. P2706, lines 10-11: Background at the top of P2705 is defined as "the amounts of these tracers advected into the region from afar". More explanation is required on why the background for HCN or C_2H_2 would be different for the aerosol analysis versus other gas analysis for a given flight. Other backgrounds (CO) are derived from corrections to a model. Others from higher altitude or clean air. No background is discussed for NOy. Does not seem like a very consistent procedure. As well, it all begs the question of how sensitive the derived quantities are to the various backgrounds. No discussion is given but there should be a few words added.

In our analysis, the 'background' for a tracer (HCN or C_2H_2) with respect to another pollutant, is taken as the amount of the tracer present when the specific

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pollutant concentration is zero, and is obtained using a linear fit to the scatter plot for the tracer versus the pollutant. Pollutants with different lifetimes thus can give different backgrounds for the tracers. In practice, the gas phase pollutants give very similar backgrounds for each tracer. The HCN background with respect to gas phase pollutants shifted with the weather on March 21. Two background values are used for HCN with respect to gas phase species (one for flights before and the other for flights after the weather shift). The C_2H_2 background (derived from scatter plots) for the gas phase pollutants was close to zero for all flights, so 0 was used for the C_2H_2 background for this analysis.

Aerosols have a highly variable lifetime in the atmosphere. We find that the tracer backgrounds with respect to organic aerosol mass and submicron aerosol scattering are quite variable from flight to flight (as derived from scatter plots). Because of this, the per flight background values for each tracer (i.e. amount of each tracer present (HCN, C_2H_2) at 0 aerosol organic mass or scattering) were used for the organic aerosol and scattering analyses as derived from the scatter plots.

Background values for CO (atmospheric lifetime $\sim$ 1-2 months) were derived from the chemical transport model MOZART, because CO transport into the region is significant. While CO background could have been attained through means similar to the trace gas backgrounds, taking this from the model was considered superior as the model can better account for temporal and spatial variations.

Backgrounds (the amount transported into the region) for the other pollutants are considered to be negligible, as the atmospheric lifetimes of benzene, NOy, and aerosol are relatively short (less than 2 weeks).

12. P2707, line 12: Please clarify: You say all observations made from the C-130 during MILAGRO for CO. Do you mean all flights for the entire campaign

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or are you talking about the 7 flights?

We show all data from all flights for MILAGRO campaign in figure. The portions of the 7 flights within the 3×3 degree study area are used for the calculation the percentage of fire impact for the various pollutants as reported in the text. The 2-component model however, works well for all data collected throughout the campaign. This sentence has been clarified.

13. CO background. It is essentially constant in Figure 3. Why do you need to invoke a model (MOZART) and a bias (between MOZART and observations) to arrive at the background. Why was the procedure not the same as used for other gasesi.e. "clean air" coming into the region or higher altitudes, etc.

See reply to #11. The use of the model helps capture the variability in the background.

14. P2708, line 4: Why re the aerosol discussion do you now skip a couple of Figures and refer to Fig. 8. (Relates to earlier discussion of reorganizing some of the paper.)

Figs 7 and 8 actually are contained in the Appendix, the numbering scheme for ACPD does not allow for distiguishing figures in the main text from those contained in the Appendix. We reference them here because they are analogous to Figs. 4 and 5.

15. Regarding Figures 4, 5, 7, 8: As written, the authors seem to say that the correlations are high or good. Certainly true for some, but Fig 4c, 4f, Fig 5b, 5c, Fig 8c give poor to bad correlations. Often the points with the highest toluene to acetylene ratios are well displaced from the correlation line, and very often these are the data within the box (i.e., circled in black). There is very little discussion of the poor correlations. A few sentences need to be added-and how

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these poor correlations relate to or control the uncertainties given in Table 1. Indeed, in the smaller panels of the figures, the correlations seem to be often controlled by the large number of points external to the box of interest and points within the box (often fresher air parcels) are well off the correlation line. Some additional discussion would serve the paper well. If the correlations were restricted to data within the box what would the numbers be?

The idea behind these figures is to demonstrate that the correlation for a pollutant with the total model (urban+fire, large panels) is superior to that with either individual component (urban or fire, small panels). One would not expect to have a good correlation for a pollutant with an individual component across air-masses which are affected significantly by both biomass burning and urban components. The optimized 'emission ratios' do not originate from the small panels (ie correlations with individual components), but rather from the best fit to the total model (large panels). The small panels are shown to give the reader an idea for the improvement which is achieved using the two component model. The beauty of the method is that in considering both fire and urban sources, one can account for most of the variation in several important pollutants.

The suggestion that the derived emission ratios are driven primarily by data outside the box, while interesting, does not appear to be true. Only considering data within the box yields emission ratios quite similar to those obtained using all data. Emission ratios relative to HCN for CO, benzene, NOy, OA, and scattering change by +3%, +10%, +11%, +6%, and -3%, respectively, relative to the original case. It is our opinion that using all for deriving the emission ratios is a more robust approach.

16. Table 1 footnote (and several places in the text) says that the median values are from the Yokelson et al. (2007) paper (part of this special issue). The Yokelson paper does not give median values but only gives mean values. I think

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there should be consistency between this paper and the Yokelson paper unless you add some text as to why you want to use medians instead of means.

Given the anomalously high modified combustion efficiency (MCE) of the 'March 17-Planned fire' (anomalously low CO emissions) and the non-uniform weighting in the reported mean emissions (ie March 6, fires 1-4 are give a 1/4 of the weight of the remaining fires) given in the Yokelson paper, it is our (JDC & POW) opinion that the median is a better representation of the average emissions for the fires around MC than the mean of these numbers. The comparison with the mean values, while not quite as good as that with median values, is still reasonable and does not alter the conclusions.

Revised text Pg 2708, ln 14:

"Note, while Yokelson et al. 2007b report emission factors for up to 5 fires (or groups of fires) as well as the geometric mean of the reported individual emission factors, we report the median value of the individual emission ratios calculated from the emission factors given in Yokelson et al 2007b Table 1. Median values are reported here because of the high variability of the individual emission factors, and the non-uniform weighting in the geometric mean calculation. In particular, the unusually high modified combustion efficiency (MCE) of the 8216;March 17-Planned Fire8217; and the group of fires reported 'March 6-Fires 1-4' are given 25% of the weight as the remainder of the fires in calculating the geometric mean."

17. Further on Table 1-the Yokelson paper does not give (measure) a NOy fire emission ratio. They do give a NOx as NO ratio but your listing it as a NOy emission ratio requires some assumptions. Some explanation is necessary in the main text.

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Given that Yokelson sampled very fresh fire plumes (usually directly over the fires and generally $\leq$ 5 minutes old), we have assumed that for his samples $NO_x \approx NO_y$. This is now stated as a footnote to Table 1. The freshest fire sampled by the C-130 during MILAGRO was over the Yucatan Peninsula, and is discussed in Yokelson et al. (2009) as 'C-130 fire 1'. At the time the smoke from this fire was sampled by the C-130, NO_x/NO_y = 0.77. Most of the remaining NO_y likely exists in the form of HONO, aerosol nitrate, and PAN.

18. Figure 6: Robust least squares (add a reference and a few words about the difference from regular least squares please). Is the correlation coefficient the same for the (regular?) least squares and the Robust least squares? Only one is given in the figure.

Robust least squares is an iterative algorithm using reweighted least squares and a bisquare weighting function, where data which lie far from the best fit (ie outliers), are given less weight in successive iterations. The regular method (all data given equal weight) for calculating the correlation coefficient is used to for the r^2 values listed on all figures. This has been explained in the figure caption.

19. Figure 9: Top and bottom mean values at 1.5 km and 5.5 km look odd. Why are the altitude bins chosen to cover where there is no data below about 2 km or above about 5.3 km. Or at least plot the means at the mean altitude of the points within that altitude bin. It seems that if the bins were 2-3, 3-4 and 4-5.3 km the altitude dependence would be much less and you would need to revise the discussion. Why are mean values used here, when most of the rest of the paper uses medians (see earlier comments)? Perhaps show means and medians.

For readability the plot had been zoomed to a small viewing window. There were data included in the mean calculation which resided outside the viewing window.

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The figure has been improved (view window resized to show more data, altitude bins changed for better resolution, and mean and median averages shown at mean altitude of data).

20. P. 2700: two asterisks on now at: AAAS Science and Technology.

This error was detected and reported during the proofing process, but apparently never got corrected. The problem seems unique to the 'print' version of the paper.

21. 2704 line 3: should be Figure 2b not 2c.

Corrected.

22. 2705 line 12: text says 0.054 (mol/mol) in two places in the paragraph, Table 1 lists 0.056.

The value in Table 1 is correct. The text has been modified to match Table 1.

23. 2705 line18: grammar-should be on 29 March from other days, not on 29 March than on other days.

Corrected.

24. Figures 5a and 7a do not have any numbers on the x-axis.

Corrected.

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Interactive Comment

25. Figures 4 b,c,e,f, 5 b.c, 7 b,c, 8 b,c-please clarify. The y-axes are labeled observed C_2H_2 or observed HCN while the captions state they are C_2H_2* or HCN*. Which is it? If they are really the asterisked variable then shouldnt "observed" be deleted.

The y-axes for the figures listed above are the asterisked values. The axes were mislabeled. This has been corrected.

References

Yokelson, R., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem. Phys. Discuss., 9, 767–835, 2009.

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