

## ***Interactive comment on “Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico” by T. J. Christian et al.***

**T. J. Christian et al.**

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We thank Referee #1 for timely, detailed, and helpful suggestions. Our responses to each point follow:

**Ref1:** In addition to Table 1, a map of the site/study locations would be useful (perhaps in supporting material)?

**Auth1:** We have produced a map of central Mexico with the site locations indicated and will make it available as supplementary material. On page 10106, line 1, after “Table 1” we added the text: “and shown on a map available as supplementary material (link).”

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Then we changed the start of the next sentence from “These” to “The sources”

**Ref2:** Just to clarify, the authors present total NMOC emissions (e.g., Table 5). I am assuming that the NMOC is the sum of all of those compounds measured with the FTIR?

**Auth2:** Yes. We changed the last footnote to Tables 3 and 5 to read: “NMOC-the sum of non-methane organic compounds measured by FTIR.”

**Ref3:** Page 10106, line 24-25: Does this mean that people only cook every few days? The detailed descriptions of the kilns studied could be removed from the main text and provided in supporting material.

**Auth3:** The cooking schedule varies with season, availability of ingredients and firewood, how many family members are present, etc. We have changed “A typical food preparation regimen begins with . . .” to “In the homes that we visited a typical food preparation regimen began with . . .”

We considered moving the detailed kiln descriptions, but to our knowledge this is the first refereed publication with source descriptions and detailed trace gas and speciated particle emissions data for this type of charcoal-making kiln and for brick kilns of any type. The emissions likely depend on kiln design and fuels, which are apparently extremely variable throughout the world. Since there is no guarantee that a reader will look at the supplement we thought the descriptions were perhaps important enough to warrant inclusion in the main body of the paper.

**Ref4:** Page 10108, line 20-23: What is a typical size of these kind of kilns? It seems like there is a fairly large range in potential sizes.

**Auth4:** We are not sure what constitutes a “typical” brick kiln size for central Mexico. However, our Mexican colleagues did spend several months before the measurement campaign identifying targets (including kilns) representative of central Mexico. In addition, none of the ~40 kilns we happened to observe during our measurement phase

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were significantly outside the size range of the kilns we sampled. However, we don't know the average size.

**Ref5:** Page 10108, line 26: How do these "exemptions" work? Are they commonly allocated?

**Auth5:** When we arrived at the site, the Director of the Atmospheric Division of CENICA was under the impression that there was a burning ban in this part of Mexico and speculated that this site might have obtained an exemption. Because we did not follow up and verify the circumstances, we have removed all mention of a "no burn" policy and a possible exemption.

**Ref6:** Page 10110, line 23: The detection limit of the FTIR is ~50-200ppb for most gases. What concentrations are typically observed in fire plumes?

**Auth6:** The mobility of our rolling FTIR system allows us to get within a meter or so of small fires and introduce high concentrations of smoke into the cell. "Typical" levels are many times greater than the detection limit. For example, the study average plume-sample mixing ratio (above background) for methanol was ~2700 ppb. CO and CO<sub>2</sub> were present in much greater amounts.

To clarify we added to the end of the sentence in question on page 10110 line 23:

" , while typical analyte mixing ratios were in the thousands of ppb or larger." We then changed the beginning of the next sentence to refocus better. We changed "These gases" to "The above gases"

**Ref7:** Page 10111, line 1-4: At what point did the HCl and ammonia losses occur? By adjusting the results upward, doesn't that assume that the loss of detection occurred at the beginning of the study? Is this realistic?

**Auth7:** Past work (Yokelson et al., 2003) has shown that each time a fresh smoke sample is introduced into the FTIR optical cell, some of the HCl and NH<sub>3</sub> molecules initially present in the gas-phase are "lost;" most likely due to sticking to the cell walls. By

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whatever process, the gas-phase mixing ratio of these two species slowly decreases during the one-minute interval that each sample is temporarily stored for signal averaging. After the campaign, using a more powerful (but less portable) data acquisition system, we quantified the decay rate for these gases at 1 Hz time resolution over the course of a one-minute sample storage period so we could correct for it. We then applied the appropriate correction to the field data. We also verified that flushing the cell with background air, for the same time period that was used in the field brought the ammonia and HCl levels below the detection limits. Thus, there was no measurable cross-contamination between smoke samples.

To clarify this we first adjusted an earlier sentence on lines 15-16 of page 10110:

Original:

"Sample air is trapped in the cell temporarily using manual Teflon valves while IR spectra are collected."

New:

"Each sample was held in the cell for one minute using manual Teflon valves while IR spectra were co-added to increase the signal to noise ratio."

Then on page 10110 line 27 we changed the text as follows:

Original:

After the campaign we checked for analyte losses in the FTIR cell due to adsorption or other reasons (Yokelson et al., 2003).

New text:

After the campaign we checked for changes in analyte concentrations that might occur during the one-minute storage period in the FTIR cell due to adsorption or other reasons (Yokelson et al., 2003).

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**Ref8:** Page 10111, lines 5-14: Was the impactor homemade? For the analysis of the sugars-how were the samples extracted?

**Auth8:** The impactor and the filter sampler were manufactured by Thermo MIE Corporation. We changed “basic filter sampling system” to “commercial filter sampling system (Thermo MIE Corp.)”.

Anhydrosugars were extracted with deionized water, as described in Engling et al. 2006.

**Ref19:** Page 10112, line 4-5: How was this uncertainty determined?

**Auth9:** The uncertainty is just an estimate that spans the range between the two study means.

**Ref10:** Page 10112, lines 6-14: Just a question- would one expect the composition of the trash burning PM emissions to be different than what was observed from other forest and vegetation fires? Is it reasonable to expect that sulfate and ammonium is only a few percent?

**Auth10:** The Referee's question is about composition and it refers to lines 6-14. We note that lines 6-7 contained a statement about unspecified “particle differences” that may have contributed to the Referee's question. Thus our response addresses all these lines.

Regarding lines 6-7. We found that using the mass scattering efficiency for cooking fire aerosol to determine a  $PM_{2.5}$  for garbage burning and some of the other sources led to an estimated  $PM_{2.5}$  considerably lower than the sum of the species measured on the quartz filters. Preliminary lab experiments suggest that the size distribution of the  $PM_{2.5}$  in the garbage burning aerosol may be shifted towards larger sizes and, if so, the particles could scatter the 530 nm radiation in the nephelometer less efficiently.

Thus, we changed the text on lines 6-7 from:

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“The particles from the other fires were different enough that we did not estimate a total  $PM_{2.5}$  for these sources based on light scattering”

To:

“The light scattering by the particles from the other combustion types could be very different so we did not estimate a total  $PM_{2.5}$  for these sources from the nephelometer data.”

Regarding line 11-14:

Sulfate and ammonium account for only a few percent of the mass of fresh  $PM_{2.5}$  from BB sources. Trash burning did not have EF for  $NH_3$  or  $SO_2$  that were significantly larger than the EF for these species from BB. Thus, sulfate and ammonium probably account for only a few percent of the mass of fresh  $PM_{2.5}$  for trash burning as well. We have conservatively stated that the sum of species measured on the quartz filters may be 10-30% lower than total  $PM_{2.5}$  mostly because we used a conservative (low) scaling factor to convert organic carbon to total organic mass.

**Ref11:** Page 10114, line 18: The authors state that the measurements agree “reasonably well.” With what?

**Auth11:** We have changed the sentence to read “. . . but the study-average values agree reasonably well with each other.”

**Ref12:** Page 10115, line 1 and Figures 2 & 3: How was the MCE determined from the Andreae and Merlet (2001) paper? And which EF  $CH_4$  was used in this Figure? For Biofuel Use (EF  $CH_4$  = 6.1 +/- 2.2)? The point on Figure 1 looks higher? Along those lines, which EF was taken for Figure 3? EF  $PM_{2.5}$ ? EF TPM? It would be useful to be clear if all studies were measuring  $PM_{2.5}$ ,  $PM_{10}$ , TPM? I realize that there may not be too much difference in these, since the bulk of the mass emitted is typically  $PM_{2.5}$ , but it would still be useful.

**Auth12:** Originally; the emission factors from other studies that assumed a different

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percentage carbon in the fuel than us were recalculated assuming 50% C to be “consistent.” That caused, for example, a 10% increase above the published values for the Andrea and Merlet EF. But we now think it is preferable to use the original values from the other studies and we have reverted to those in the revised Figures 2 and 3. On page 10114, lines 14-15, we removed the parenthetical sentence describing the scaling factor. We have also modified the Figure 3 caption to reflect the PM cutoff for each study as follows:

**“Fig. 3.** Variation of the particle emission factor with MCE for open wood cooking fires. (This work and Andreae & Merlet 2001 - PM<sub>2.5</sub>, Roden et al. 2006 - PM<sub>4</sub>, all others TPM.)”

**Ref13:** Page 10115, line 27; Page 10116, line 5: Could examples of “smoldering compounds” be provided when this phrase is first mentioned?

**Auth13:** We caution that the differences and similarities between flaming and smoldering are not simplistic, and these terms are sometimes used in misleading ways. We hope readers will consult the references provided for detailed discussions of flaming versus smoldering, but we provide examples here, as requested, rather than lengthen the paper.

We have changed the sentence on page 10115 line 27 to read: “. . . not surprisingly the EF for the smoldering compounds (most of the gases measured excluding CO<sub>2</sub> and NO<sub>x</sub>) in Bertschi et al. are generally about 2–4 times higher.”

**Ref14:** Page 10116, line 19: Why were Particle EFs not measured from the Patsari chimney?

**Auth14:** The FTIR is quite mobile so it was easy to access both the kitchen and the roof simply by rolling the instrument outside. But the nephelometer, LICOR, and filter sampler were not as mobile and required more time to rearrange than was available during the Patsari stove measurements.

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**Ref15:** Page 10118, line 12: The authors state the results imply a 3:1 flaming/smoldering fuel consumption in the trash-burning fires, which “does not seem unreasonable.” Based on what?

**Auth15:** We thought that 75% by flaming sounded reasonable based on observation of the fires, but have not done a study of the average flaming to smoldering ratio for garbage fires so we now just clarify the implications of the way we averaged the data at this point and below. We have changed the sentence to read: “For the trace gas EF this is equivalent to assuming that ~75% of the fuel is consumed by flaming combustion and the remainder by smoldering.”

**Ref16:** Page 10118, lines 16-18: It is not clear why, just because 3 out of the 4 fires had filter data, that the average of the filter results is “equivalent to 1/3 of the fuel being consumed by smoldering.” This sentence should be reworded to more clearly state a point here. Also, the authors already state that there is an assumed 3:1 flaming/smoldering ratio in these fires. Is this all consistent?

**Auth16:** The sentence now reads: “Since we only have filter data for two flaming and one smoldering garbage fire, an average of the filter results is equivalent to assuming that two-thirds of the fuel was consumed by flaming.”

Thus, averaging all the available data for particles and gases results in slightly different implicit assumptions about the relative importance of flaming and smoldering.

**Ref17:** Page 10119, line 14: how much of the total Cl is expected to be soluble Cl-? What else

besides PVC could contain Cl?

**Auth17:** We don’t know how much insoluble Cl might be present in garbage burning particles. However, we note that Kyotani and Iwatsuki (2002) found that essentially all the chlorine present in particles in urban Japan was soluble. We cite the study by Costner that suggests that PVC could account for essentially all the chlorine in landfills.

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Kyotani, T. and Iwatsuki, M.: Characterization of soluble and insoluble components in PM<sub>2.5</sub> and PM<sub>10</sub> fractions of airborne particulate matter in Kofu city, Japan, *Atmos. Environ.*, 36, 639-649, 2002.

**Ref18:** Page 10119, lines 28-29: is it still assumed here that 10-30% of the PM<sub>2.5</sub> mass is

not measured? How did the authors determine this percentage for the garbage? (e.g., how did they come up with EF PM<sub>2.5</sub> of 10 +/- 5 g/kg?)

**Auth18:** The sum of measured species on the quartz filters is  $8.74 \pm 7.35$ . Incrementing that by 20% (to account for unmeasured species and the low assumed ratio of organic mass to organic carbon) gives  $10.5 \pm 8.8$ . We corrected the text here, in the abstract and later in the discussion to reflect this.

**Ref19:** Page 10120, lines 1-7: The authors compare EF PM to EF PM<sub>2.5</sub>. It may be worth mentioning how much of the EFPM<sub>2.5</sub> is expected to contribute to the total EFPM.

And why mention EF SO<sub>2</sub> and EF NO<sub>x</sub> when they weren't measured here, and aren't discussed?

**Auth19:** We added a sentence after the period on line 4. "This may be low since EF<sub>PM</sub> is typically ~20% larger than EFPM<sub>2.5</sub> for combustion sources."

The EF for NO<sub>x</sub> and SO<sub>2</sub> are included because they are important emissions and including them completes an overview of the total amount of emissions data available for this under-studied source.

**Ref20:** Page 10124: What fuels were used in the Zambian charcoal-making kiln? Is there a

Reference about the Tannins in Oak compared to other woody species?

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**Auth20:** The woods used in the Zambian kiln - as given in Bertschi et al. - were *Julbernardia* sp. and *Brachystegia* sp., which are hardwoods. While oak has a fair amount of tannins, it turns out that other plants do also. The situation is further complicated by the existence of 2 major types of tannin whose abundance and chemistry vary quite a bit. Since we are now less suspicious that tannin content underlies the observed variability we have removed that speculation throughout the paper.

**Ref21:** Page 10124, line 10: In Table 1 of Andreae and Merlet (2001), the EF for charcoal making is for EF TPM, not PM<sub>2.5</sub>

**Auth21:** Thank you. We have changed the text to reflect this.

**Ref22:** Page 10127: This analysis is a bit confusing. Why are the MCMA emissions multiplied by 75/20 to get the emissions for Mexico? I understand that 75 million people are living in urban areas. (am I missing something?) There are urban emissions inventories for all of Mexico developed for the MILAGRO campaign. Are these available for the analysis? I think it's worth noting here that the Emissions Inventories are highly uncertain, and the results from this analysis can be skewed depending on which EI is used. Also, is it worth noting the difference in the species associated with the NMOC emissions from cooking fires versus anthropogenic emissions?

**Auth22:** 75/20 is the ratio of the urban population of Mexico to the urban population of Mexico City and so we used this ratio to scale the Mexico City urban emissions to national urban emissions. We did this because we felt that the Mexico City Emissions Inventory, which has received by far the most work, was likely the most accurate and so we scaled that. In this sense we are agreeing with Fast et al., who tentatively concluded that the National Inventory may be less accurate than the MCMA inventory.

Citation: Fast, J. D., Aiken, A. C., Allan, J., Alexander, L., Campos, T., Canagaratna, M. R., Chapman, E., DeCarlo, P. F., de Foy, B., Gaffney, J., de Gouw, J., Doran, J. C., Emmons, L., Hodzic, A., Herndon, S. C., Huey, G., Jayne, J. T., Jimenez, J. L., Kleinman, L., Kuster, W., Marley, N., Russell, L., Ochoa, C., Onasch, T. B., Pekour,

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M., Song, C., Ulbrich, I. M., Warneke, C., Welsh-Bon, D., Wiedinmyer, C., Worsnop, D. R., Yu, X.-Y., and Zaveri, R.: Evaluating simulated primary anthropogenic and biomass burning organic aerosols during MILAGRO: implications for assessing treatments of secondary organic aerosols, *Atmos. Chem. Phys. Discuss.*, 9, 4805-4871, 2009.

Our main goal here is not a high-accuracy, species-specific comparison, or even a discussion of the high uncertainties that characterize all the estimates here, but simply that cooking fires are likely a significant source of emissions at the national scale as indicated by a rough comparison to the urban source, which has an acknowledged significance.

We changed the sentence on line 10 to: "These estimates are highly uncertain, but indicate that a switch to cleaner burning and more fuel-efficient stoves (Sect. 3.1) could provide a significant reduction of emissions on the national scale."

**Ref23:** Page 10127, line 22-23: garbage burning could still be an important source here, since it sounds like there are still a lot of modern sources of C being burned in the landfills (Page 10109).

**Auth23:** We agree and modified the sentence beginning on line 16 to read: "Garbage burning consumes some modern carbon, but also a large amount of plastics derived from fossil fuels."

We added. "Some studies suggest a higher proportion of food waste for Mexican dumps than we estimated (Buenrostro and Bocco, 2003; Ojeda-Benitez et al., 2003), which, if true, would not affect our %C, but could increase the fraction of modern carbon. However, indications are that much of the food waste may decompose before burning (Bernache-Pérez et al., 2001)."

The last sentence in this paragraph now reads: "Possibilities include cooking fires and industrial biofuel use in addition to garbage burning."

Buenrostro, O., and Bocco, G.: Solid waste management in municipalities in Mexico:

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goals and perspectives, *Resources, Conservation and Recycling*, 39, 251-263, 2003.

Ojeda-Benitez, S., de Vega, C. A., and Ramírez-Barreto, M. E.: Characterization and quantification of household solid wastes in a Mexican City, *Resources, Conservation and Recycling*, 39, 211-222, 2003.

Bernache-Pérez, G., Sánchez-Colon, S., Garmendia, A. M., Dávila-Villarreal, A., and Sánchez-Salazar, M. E.: Solid waste characterization study in the Guadalajara metropolitan zone, Mexico, *Waste Management and Research*, 19, 169-176, 2001.

**Ref24:** Page 10128, lines 15-21: While I think this discussion of HCl sources and chemistry is interesting, I do not think it's necessary for this paper and is one section I recommend removing. And again, Page 10129, lines 7-12).

**Auth 24:** We thought that high HCl from garbage burning was one of the key results of the study. Thus, we would prefer to retain this level of discussion.

**Ref25:** Page 10128, lines 25-26: What are "typical" levels of Cl<sup>-</sup> in particles?

**Auth25:** Chloride was less than 0.01  $\mu\text{g}/\text{m}^3$  in smoke haze layers in the Yucatan in March of 2006. We are not sure what the typical absolute levels are for urban areas and it may depend on the measurement location. The collaborator that provided the PILS data used the word "significant" to characterize the levels that they observed and we reported here. We recycled that adjective, but have now removed the phrase "significant levels of" as our main interest is in the ratio of chloride to total  $\text{PM}_{2.5}$ . The rest of the paragraph has been modified to include additional relevant information. (Reff et al., 2009) list a number of source profiles with high Cl/ $\text{PM}_{2.5}$  including solid waste combustion, agricultural burning, various types of metallurgy, and other (less common?) industrial processes. Moffet et al (2008) assign much of the particulate Cl in the MCMA to waste incineration based partly on a lack of correlation between particle Cl and  $\text{SO}_2$  that often accompanies metallurgy and partly on a similarity of the overall observed profile with that of waste incineration, which is known to occur in northern

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Mexico City. None of the new information is conclusive, but it is worth adding to the discussion. We will also better emphasize that this and the Sb-based estimate are highly uncertain estimates that would tend to also be an upper limit due to the many other Sb or Cl sources. We have not been able to obtain any information on the specific location or abundance of other potential Sb or Cl sources in MCMA. Thus we can only better stress the qualitative nature of our discussion.

Reff, A., Bhave, P. V., Simon, H., Pace, T. G., Pouliot, G. A., Mobley, D., and Houyoux, M.: Emissions inventory of PM<sub>2.5</sub> trace elements across the United States, *Environ. Sci. Technol.*, 43, 5790-5796, 2009.

Moffet, R. C., Desyaterik, Y., Hopkins, R. J., Tivanski, A.V., Gilles, M. K., Wang, Y., Shutthanandan, V., Molina, L. T., Abraham, R. G., Johnson, K. S., Mugica, V., Molina, M. J., Laskin, A., and Prather, K.: Characterization of aerosols containing Zn, Pb, and Cl from an industrial region of Mexico City, *Environ. Sci. Technol.*, 42, 7091-7097, 2008.

**Ref26:** Conclusions: How much were these emissions relative to other fires burning in the region during that time?

**Auth26:** We have a separate publication in progress where we plan an integrated assessment of the relative importance of the various types of combustion in different parts of Mexico. On a national scale the other types of fires are thought to consume 100-180 Tg of biomass fuel per year, which is more than our estimate of 68 Tg biomass burned in cooking fires. However, detailed study is needed to focus on any particular region.

**Ref27:** Table 4: The measurements of K<sup>+</sup> from IC and K from ICP are given. However, the results from either methods are pretty different. Could you comment on this? (Also with Ca).

**Auth27:** The IC extraction is basically a soak in deionized water for an hour with shak-

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ing. This treatment dissolves ionic salts of K and Ca (e.g. KCl). The ICP extraction is a total digestion in an acid mixture (HNO<sub>3</sub> and HF) with microwaving. ICP is expected to have higher yield since it will dissolve ionic salts but also more tightly bound forms of K and Ca (e.g. K or Ca in mineral particles).

**Ref28:** Figure 5 (and Page 10126): Why is it that dry season cooking fires that contribute at least 33% to the total dry season burning emissions have larger annual emissions? Wouldn't it be 50%? Could this be explained with a bit more detail?

**Auth28:** A dry season cooking fire emission that is 33% of the total constitutes 1 part in 3, with the corresponding savanna emission making up 2 parts in 3. If you double the cooking fire emission to account for year round use while holding the savanna emission constant because it is a dry season emission only, the cooking fire emission now makes up 2 parts in 4 on an annual basis. We have modified the text as follows:

"For 11 of the 17 species, the dry season cooking fire emissions are at least 33% - or 1 part in 3 - of the total dry season pyrogenic emissions. By doubling the emissions of those 11 species to account for year round use, they now constitute at least 50% - or 2 parts in 4 - of the total annual emissions."

**Ref29:** Page 10111, line 28: Change comma to period after (0.267)

**Auth29:** Thanks.

**Ref30:** Page 10116, line 27: I recommend changing "significant" to "noticeable"

**Auth30:** Agreed.

**Ref31:** Page 10119, line 9: Define PVC when first used.

**Auth31:** Yes, thanks. Page 10119 line 9 now reads: "Lemieux et al. (2000) reported a strong dependence on poly vinyl chloride (PVC) content . . ."

**Ref32:** Page 10125, line 12: I suggest replacing "they were probably" with "they could have

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been”.

**Auth32:** We changed the text as suggested.

**Ref33:** Table 3: the text is very small and difficult to read.

**Auth33:** This problem is common and can be overcome in the electronic version, at least, by expanding the display size. For the print version, we will ask if any of Tables 3-5 can be rotated to landscape layout or if the Table entries can be enlarged slightly if the footnotes are downsized.

**Ref34:** Figs. 2 and 3: The symbol used for the Andreae and Merlet (2001) point is pretty

similar to the symbol for Johnson et al. (2008) results. Could these be changed?

**Auth34:** We have changed it to a “plus” sign.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10101, 2009.