**Atmospheric
Chemistry
and Physics
Discussions**

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.

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This paper by Christian and co-workers reports on a unique study in which the emissions from several air pollution sources common in developing countries but relatively uncommon in the developed world are studied using advanced techniques. The results of this study will be very useful to help characterize these sources (which disproportionately affect poor people) in future studies and I hope they motivate further research funding and additional work by this and other groups. I certainly support publication of this paper in ACPD after the authors consider the issues below.

I have no doubt that garbage burning can be a strong particle source at certain times

and locations and perhaps even globally. I witnessed the burning of trash by villagers first hand near the Santa Ana site during the Mexico City MCMA-2003 campaign, and the resulting emissions overwhelmed the ambient concentrations measured by the AMS at that site for the short periods in which it was active. I also found a paper by Garcia et al. (Chemosphere, 65, 2018-2027, 2006) that investigates the sources of air pollution at communities near the US-Mexico border and reports in its abstract that "the evening high PM2.5 is associated with burning-activities occurring to the south of Sunland Park, and these emissions are characterized by elevated Sb, Cl-, and elemental carbon; similar to 68% of the PM2.5 mass can be attributed to this source." And later "The source related to burning-activities at Colonia Anapra is likely associated with waste burning and the firing of open and closed-top brick kilns in the outskirts of that neighborhood. Low-cost, combustible, waste materials such as agricultural waste, sawdust, scrap wood, waste plastics, and scrap tires (often impregnated with toxic resins and varnishes) are commonly used for firing brick kilns." The characteristics of this source seem to match the source profiles of Christian et al., suggesting the importance of garbage burning in some areas of Mexico.

However I do have concerns about two of the estimates that are presented by Christian et al.

(1) First it is stated (and highlighted in the abstract and conclusions) that primary PM from garbage burning (GB) may contribute a third of the total measured PM2.5 in Mexico City. The estimate is somewhat qualified but the current wording is confusing and many readers could take the conclusion at face value. However I do not think that either of the methods to arrive at this estimate are sound and I recommend that they are significantly qualified or removed from the paper.

(1.1) The first method uses measurements of Sb in emissions from GB from this study, together with ambient measurements of Sb and PM2.5 from Querol et al. (2008). The problem with this estimate is that it assumes that 100% of the Sb in the atmosphere of Mexico City is arising from garbage burning. This appears to be quite an extreme

assumption for such a complex region with so many pollution sources, which include many small industries. X. Querol has already submitted a short comment to this discussion in which he points out some flaws of that assumption, and that I fully agree with.

I do want to point out two other problems with the estimates of the GB contribution to PM2.5:

(1.2) A similar estimate of a garbage burning contribution of 1/3 of the PM2.5 is presented on page 10130. Again it is assumed that 100% of the aerosol chloride present in the Mexico City atmosphere is due to GB, and from this it is concluded [P10128-9] that "Thus, the PILS data is consistent with our Sb-based estimate that garbage burning could contribute about one-third of the PM2.5 in the MC airshed. However, the PILS chloride may also reflect a contribution from agricultural fires and brick making kilns (Table 4) and volcanoes (e.g. Burton et al., 2007)."

Again, although qualified, this estimate could also be easily misinterpreted. The estimate of a contribution of 1/3 of the PM2.5 is flawed for similar reasons as described for Sb. There are clearly other large sources of chloride in Mexico City besides agricultural fires, kilns, and volcanoes. These include:

- During the MCMA-2003 campaign large plumes of ammonium chloride were detected at the CENICA site and by the Aerodyne Mobile Lab at different locations in the city, which reached up to 40 μg am-3 (57 μg sm-3) (see Figs. 5, 14, and 15 in Salcedo et al., ACP 2006 and the associated discussion). Quoting from the Salcedo paper: "[A simultaneous increase in organics] was observed only during two (out of about 17) of the strong plumes (with chloride concentration > 4μg m-3) during MCMA-2003. Possible sources of chloride without organics include drinking water and waste water treatment facilities (Tanaka et al., 2003). Refuse burning was observed to produce both chloride and organics with another AMS in mobile sampling mode, so it cannot produce the majority of the plumes observed here were a chloride spike was detected

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without an organic increase."

- Wildfires, which are clearly an important source of fine chloride in the MCMA region (DeCarlo et al., 2008).

- Waste incineration (Moffet et al., ACP 2008, ES&T 2008) in industrial facilities as opposed to the uncontrolled garbage burning studied here. Moffet et al. report that "Incineration is not currently listed in the emissions inventory for the MCMA; however, multiple waste incinerators exist in the northern part of Mexico City."

- Dust from the dry lake bed and other sources (which contributes to PM2.5 and contains NaCl, see e.g. Moya et al., Atm. Env. 2004; Querol et al., 2008).

- In addition a significant fraction of the fine PM chloride in Mexico City is present as ammonium chloride (Salcedo et al., 2006; Johnson et al., ES&T 2008) which is a semivolatile species (e.g. Huffman et al., AS&T 2008) and indeed a significant fraction of the chloride evaporates under mild heating in the MCMA (Huffman et al., ACPD 2009). Thus the ratios of other species to Cl from different emission sources may not be conserved.

Given the influence of multiple large chloride sources, there is no evidence at present to suggest that garbage burning is the overwhelmingly dominant source of aerosol chloride in Mexico City. In fact I am not aware of any piece of evidence that confirms that GB is a major contributor to ambient chloride levels (or to Sb levels). Thus assuming that near 100% of the PM2.5 chloride is due to GB is not justifiable in my opinion, and would leads to a significant overestimate of the GB influence in the MC airshed.

1.3) Finally such high estimate of about 1/3 of the PM2.5 being due to garbage burning is inconsistent with a simple mass balance of what is known from multiple previous and ongoing studies on the composition and sources of PM in Mexico City. I will separate this calculation into several steps to reduce confusion:

(1.3.1) Particles from GB are composed mostly of OM with some EC and with lit-

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tle amounts of inorganic species (other than chloride) according to Table 4 of Christian et al. This is consistent with our recently published measurements of emissions from trash burning surrogates (Mohr et al., Environ. Sci. Technol., 43, 2443-2449, doi:10.1021/es8011518, 2009).

(1.3.2) Multiple studies such as Querol et al. (ACP 2008), Chow et al. (Atm. Env. 2002), Salcedo et al., (ACP 2006), and Aiken et al. (ACPD 2009) are quite consistent about the contribution of different chemical components to the fine PM in the MCMA. I will use the average values for the ground-based studies in Figure S-7 of Aiken et al. 2009 which summarize several of the studies (http://www.atmos-chem-phys-discuss.net/9/8377/2009/acpd-9-8377-2009-supplement.pdf). Fine PM in the ground in the MCMA is about 50% organic as the average of those studies.

(1.3.3) About 1/2 of the OM in the MCMA during MCMA-2003 and MILAGRO is of secondary origin as concluded by multiple studies using several different techniques (e.g. Volkamer et al., GRL 2006; Kleinman et al., ACP 2008; Stone et al., ACP 2008; Herndon et al., GRL 2008; Hennigan et al., ACP 2008; de Gouw et al., ACP 2009; Aiken et al., ACPD 2009). Thus we are left with about 25% of the fine PM as primary OA (POA) to apportion among all the POA sources.

We note primary PM emissions from GB would indeed be apportioned as POA by the AMS-PMF method (Aiken et al., 2009), as the high-resolution mass spec. signatures of paper and plastic burning are very similar to the AMS signatures of POA and very different from those of OOA/SOA (Mohr et al., 2009).

(1.3.4) There is strong evidence that vehicle emissions are an important source of POA in Mexico City. For example Stone et al. (ACP 2008) report that "Motor vehicles, including diesel and gasoline, consistently accounted for 49% of OC in the urban area and 32% on the periphery."

(1.3.5) Wildfires are also an important source of POA during the warm dry season as documented during multiples studies (Bravo et al., 2002; Salcedo et al., 2006; Molina et

al., 2007; Yokelson et al., 2007; DeCarlo et al., 2008; Aiken et al., 2009). For example Stone et al. report that biomass burning contributed on average 12% of the OC at T0, while Aiken et al. (ACPD 2009, and ACPD, in preparation) report that wildfires contributed ~15-20% of the OA at T0.

(1.3.6) In summary, 25% of the PM which is POA. This amount has to include at least two large known POA sources from vehicles and wildfires. Clearly primary PM from GB (which is mostly POA) cannot possibly account for 1/3 of the PM2.5 in the MCMA. If it did, it would imply that there are no vehicle or wildfire emissions of POA affecting Mexico City. Thus GB must contribute a significantly smaller fraction.

Given the arguments in (1.1)-(1.3) above in addition to those from X. Querol, I think the estimate of the contribution of GB as 1/3 of the PM2.5 in Mexico City is too high. Since it is not clear how to obtain a more quantitative estimate, short of a multi-element source apportionment analysis that takes into account the many sources of the different elements in the Mexico City airshed (as suggested by Christian et al.), I suggest that these quantitative estimates are removed from the paper or substantially qualified. Qualifying the estimates as 'crude' while still retaining them in their present form would not be acceptable in my opinion.

I do strongly agree however that the authors should retain the call for further attention and quantitative research on the contribution of garbage burning in Mexico City and other developing world cities, using the useful composition and tracer results reported in this work. I do not wish to minimize the importance of this source, but I think it is important to be careful about putting forward estimates which are not fully supported and which may create confusion about the PM sources in the MCMA.

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Two additional points about GB:

First, the potential formation of secondary species and in particular SOA from sources

such as GB has not been studied at all to my knowledge. Thus the contribution of this source may be larger than those estimated from primary ratios, when secondary PM formation is taken into account. However Christian et al. are using ratios of primary GB PM to other GB primary tracers, together with ambient ratios of total PM to tracers in their estimates. Thus their estimate has to be interpreted as the contribution of primary PM from GB to total PM in the MCMA.

Second, the PM concentrations (ug m-3) at which the filters were collected for each source should be reported, as these determine the partitioning of semivolatile species between the gas and particle phases (e.g. Donahue et al., ES&T, 2006). Fig. 1 shows concentrations in the range 20-100 ppm CO and using the ratios of Table 3 I estimate that the PM concentrations were of the order of 2000-10,000 ug m-3 for one of the cooking fires. If the concentrations were also so high concentrations for the GB sampling, a very large fraction of organic semivolatiles would be present in the particles during sampling that would be likely to evaporate upon dilution in the atmosphere. E.g. using the results of Robinson et al. (Science 2007) for woodsmoke one would estimate that 2/3 to 3/4 of the organic material present in the particles at these source concentrations would be in the gas phase at atmospheric OA concentrations of $\sim$10-20 ug m-3 typical of Mexico City. Interestingly much of this material may come back to the particle phase as SOA after a few generations of gas-phase oxidation (Robinson et al., 2007; Dzepina et al. ACPD 2009). Thus the emission ratios of e.g PM to Sb determined by Christian et al. may not be biased high (and may be perhaps biased low) once SOA has had time to form.

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(2) I have a separate concern regarding the estimates of cooking contribution to total PM emissions in the country of Mexico presented in P10127 and Table 7. If the results of this work are confirmed, they show that the cooking fires are likely to be a major PM source that deserves immediate attention from the Mexican authorities. However the comparison to urban PM is misleading. Table 7 does not consider the underestimation

of primary PM by the MCMA inventory recently reported by several studies (Aiken et al., ACPD 2009; Zavala et al., ACPD 2009), or the formation of secondary PM, which is very large relative to primary PM for urban emissions, in part due to low urban emission factors for primary PM. Aiken et al. (2009 ACPD) conclude that "The 2006 Mexico City emissions inventory underestimates the urban primary PM2.5 emissions by a factor of $\sim$4, and it is $\sim$16 times lower than afternoon concentrations when secondary species are included." Christian et al. estimated that cooking fires were $\sim$18 times larger than urban emissions calculated from the MCMA inventory. Additional formation of secondary species will occur for urban air past the levels observed in the afternoon (e.g. DeCarlo et al., 2008), and secondary species will likely also be formed from the emissions of the cooking fires (which however are not expected to be an order-of-magnitude larger than the primary PM from cooking since the initial primary emission factors are much larger). Thus urban and cooking PM will most likely of the same order-of-magnitude in Mexico within the uncertainty of these estimates.

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