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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Application of positive matrix factorization to on-road measurements for source apportionment of diesel- and gasoline-powered vehicle emissions in Mexico City" *by* D. A. Thornhill et al.

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We thank the three reviewers for their valuable and insightful comments and suggestions. In general, they find the work to be novel, interesting, and of good quality, but they are concerned about the small size of the data set. Major changes to the revised manuscript include a new paragraph reviewing the results of previous comparisons between independent estimates of the motor vehicle emission inventory and the official one and new caveats regarding the small sample size used in this study. Below, we address each reviewer's comments individually and describe the corresponding changes

made to the manuscript. The supplemental information contains G-space plots, requested by one of the reviewers.

Reviewer 1

The reviewer finds the work to be "a generally good paper" but criticizes its narrow scope, "relatively routine use of PMF," and "limited results." Below, we address these and other concerns in detail.

1) This is a generally good paper although it is not clear it is of great general interest since it deals with one 75 km drive sampling campaign. A more comprehensive paper would be of more interest. It is a relatively routine use of PMF and obtained rather limited results. It is not clear to me that it belongs in a major international journal.

We recognize that the small size of the data set is a limitation of the research, but we think that the novelty of both the technical approach and the results will be of interest to the readership. We edited the abstract on p. 27573, line 24 to acknowledge the small sample size and now present the comparison to the official inventory more neutrally:

"The resulting fuel-based estimates of emissions are lower than in the official inventory for CO and NO_x and higher for VOCs. For NO_x, the fuel-based estimates are lower for gasoline-powered vehicles but higher for diesel-powered ones compared to the official inventory. While conclusions regarding the inventory should be interpreted with care because of the small sample size, 3.5 hours of driving, the discrepancies with the official inventory agree with those reported in other studies."

The other reviewers agree that the work is novel and should be published in the journal. To our knowledge, this is the first time that PMF has been applied to on-road measurements. There is great value in being able to separate gasoline from diesel exhaust in order to quantify emission factors and to do so without relying on vehicle counts. We anticipate that the method can be extended to other settings, such as tunnel studies and roadside measurements. A more comprehensive analysis will be possible in future

field campaigns, and the results from this manuscript will be important to guide future studies.

2) In addition to lower NO_x emissions when idling, there will be lower BC during that period. During heavy acceleration, there will be still lower NO emissions, but much higher BC since there would be significant fuel rich conditions. This is reflected in the OC/EC results of Shah et al., but they do not have OC values here. Thus, there is some considerable variability in the source profiles between cruising, idling, and accelerating that are not fully reflected in the profiles, but are probably reflected in the uncertainties in the profiles.

Thank you for pointing out the load dependence of NO_x and BC emissions from diesel-powered vehicles. We edited the Discussion section on p. 27591, line 19:

"A second difference is the inclusion of idling in the PMF analysis. Diesel engine NO_x and BC emission factors are lower during idling (Coelho et al., 2009; Huai et al., 2006; Khan et al., 2006; Shah et al., 2004; Zhai et al., 2008), but the influence is expected to be smaller than for gasoline-powered vehicles because the emission factors (fuel-based) vary less as a function of engine load."

The point about variability in driving conditions being reflected in the uncertainties is an excellent one that we have added to the Results section on p. 27583, line 17:

"Uncertainties in the profiles probably reflect variability in emissions with driving conditions and differences between individual vehicles."

3) Unfortunately, the bootstrap method applied in EPA PMF 3 is severely flawed and does not really provide appropriate error estimates. A new approach will be available soon in EPA PMF 4 and it would be better to refrain from any use of the uncertainty estimates from V3.

While we would have preferred to use PMF 4 and its improved error estimation approach, the newer version is not yet available. For the present analysis, having some

estimate of error seems to be a better option than presenting none.

4) Another approach would be to separate the data set into subsets so they look at the idling periods separate from the cruising periods. Then they could examine if there are different numbers of factors involved or different profiles. This would be a better way to explore the potential end members of the profiles.

This is a very good suggestion and in fact, we tried the approach of separating the data into subsets to investigate idling periods separately from cruising periods. The results were not substantially different for each period, probably because measurements during idling periods when the mobile laboratory was stopped at a light were also influenced by emissions from cruising traffic on the cross-streets. This approach might work better with larger data sets in future studies.

Reviewer 2

The reviewer writes, "The paper is well written, polished, novel, and clear. I recommend it for publication. My only criticism of the paper is that the dataset is small. . .. Given the novelty of the author's approach, I don't see this as a barrier to publication." Below, we address the central concern and others in detail.

1) "But using results as a standard of comparison for the official emissions inventory for Mexico is probably not justified. A comparison to the official emissions inventory is a good idea, but I think it should be written in a more neutral way rather than presenting their results as the standard. The authors generally do have sufficient caveats in the text, but I would add additional caveats on this limitation of the data set in the abstract and conclusions."

We acknowledge that the small data set is a limitation of the study and have tried to handle the comparison to the official emission inventory carefully. As the reviewer suggested, we now present the results in a more neutral way, instead of implying that the official inventory may be under- or overestimated, and we have added further caveats

to the abstract on p. 27573, line 24:

"The resulting fuel-based estimates of emissions are lower than in the official inventory for CO and NO_x and higher for VOCs. For NO_x, the fuel-based estimates are lower for gasoline-powered vehicles but higher for diesel-powered ones compared to the official inventory. While conclusions regarding the inventory should be interpreted with care because of the small sample size, 3.5 hours of driving, the discrepancies agree with those reported in other studies."

We made similar changes to the conclusions.

2) Abstract and conclusions: as discussed above, I would mention that this data set represents a sample period of 3.5 hours and thus comparisons to the emission inventory should be interpreted with care (i.e. your sample may not be representative of the vehicle fleet in Mexico).

See previous comment.

3) Pg 27573 line 26. Though not required, it would be interesting for the reader if you'd provide just a little more detail on "autobuses" and "microbuses."

We added a parenthetical definition for "autobuses" to the text on p. 27574, line 26:

"(i.e., large intercity coaches, in contrast to smaller, mostly intracity "microbuses")"

According to the Mexico City Metropolitan Area's mobile source inventory, 95% of "autobuses" run on diesel fuel.

4) Pg 27575 line 4. The distinction you make about gasoline vs diesel emissions being caused by differences in the Otto and Diesel cycles is not totally correct. These are idealized thermodynamic cycles. The distinction between gasoline and diesel engine emissions has more to do with the fact that gasoline engines combust premixed fuel/air mixtures (with a spark plug), and diesel engines use compression ignition of non-premixed fuel and air (i.e. fuel is sprayed directly into the cylinder). Diesel com-

bustion is hotter (i.e. more NO_x) and has more fuel-rich unmixed pockets of fuel (i.e. more soot).

We removed the reference to the idealized thermodynamic cycles and revised the sentence on p. 27575, line 3:

"Differences in combustion conditions for each of the fuels and in their physicochemical properties are the primary cause for the distinctions."

5) Pg. 27578 line 13. The 3953 data points are per instrument, correct? You might want to note this here. The text on PMF makes this point clear, but the text might read easier if you add this detail here.

We deleted the sentence because it was redundant with a clearer explanation of the number of data points on the next page.

6) Pg. 27579 line 18. I don't understand your method for BC given this explanation.

We modified the text to clarify this point on p. 27579, line 17:

"Because the black carbon (BC) analyzer had a slower sampling interval of 2 s, we treated it separately from the other species and calculated its source profile after obtaining PMF results. We ran a multiple linear regression of the measured concentrations of BC against the factor contributions, gik in Eq. 1, which were derived by PMF, to solve for the BC source profiles."

7) Pg. 27582 line 19. You have plenty of discussion of G-space scatter plots but never show one. Would it help to add such a plot to the text?

The G-space plots are shown in new supplemental material accompanying this reply, but in the interest of space, we have decided not to show the G-space scatter plots in the manuscript. Doing so would require three additional figures that would be of interest to a small minority of the manuscript's audience.

8) Pg. 27583 line 15. Fuel-lean conditions of diesel engines do not maximize NO_x.

NO_x emissions are generally at a maximum at stoichiometric conditions (or just lean of stoichiometric). Diesel engines have high NO_x because the non-premixed flame positions itself at a stoichiometric position (even though the overall fuel-to-air ratio is "lean"). I find this discussion to be unnecessary in the text.

We now summarize this topic in a single sentence on p. 27583, line 8 that replaces the discussion:

"The identification of diesel versus gasoline exhaust is based on well-understood differences between the two that produce large contrasts in CO, NO_x, VOC, and particulate emissions."

9) Pg. 27585 line 26. You should add a citation to the statement "3.7 times more gasoline than diesel fuel is consumed in the MCMA"

We added a citation to SMA, 2008a on p. 27585, line 26.

10) Pg. 27586 line 14. Does the fact that pollutants may be confounded by secondary sources point to a limitation of this study? It seems that such a statement should be further discussed.

We are not sure why the formaldehyde and PM results are inconsistent between the PMF and fleet-averaging methods, so we cannot confidently state that the ability to handle pollutants with both primary and secondary sources is a limitation of the study. We raised the possibility of confounding by secondary pollutants because their concentrations can vary substantially during the daytime. We added this idea to the sentence on p. 27586, line 14:

"Results for these pollutants may be confounded by secondary sources, whose concentrations can vary substantially over the day and which. . ."

Thus, assigning them a single concentration, as the PMF approach does, may not be accurate. We now mention secondary pollutants explicitly in the Conclusions section on p. 27595, line 28, where we discuss limitations of the experimental approach and

recommendations for future studies:

"Ideally, the variation in background pollutant concentrations, including those of secondary origin, will be small over the duration of the experiments."

11) Pg. 27590 line 1. Could the high formaldehyde emissions be biased high because of the inclusion of idling in this study? I agree that inclusion of idling is actually realistic, but adding this point once again here when comparing to tunnel and remote sensing studies might be important.

According to Zavala et al. (2009), formaldehyde emissions from gasoline-powered vehicles are not significantly different between idle, stop-and-go, traffic, and cruise conditions. Therefore, it seems unlikely that the formaldehyde emission factors determined in this study are biased high due to idling, as the NO_x emissions appear to be. We added a new sentence on p. 27590, line 1:

"Fuel-based emission factors of formaldehyde do not vary significantly with driving conditions (Zavala et al., 2009), so this species is not expected to be subject to bias associated with the inclusion of idling."

12) Pg. 27591 line 29. Again, I would add a brief statement here at the end of the statement ". . .AML's drive are representative of the MCMA's fleet". Something to the effect of . . . "and thus our estimates are approximate"

We added the suggested text on p. 27591, line 29.

13) Pg. 27592 line 20. In this section, I would compare your results to the official inventory without suggesting which one is correct. A more neutral comparison is probably appropriate given the short duration of your data set.

We reworded the discussion beginning on p. 27592, line 20, removing suggestions that the official inventory is over- or understated, to make the comparison more neutral:

"Compared with the official mobile source inventory (SMA, 2008a), shown in Table 4,

our estimates of emissions of CO and NO_x are lower while our estimates of VOCs are higher."

14) Pg. 27593 line 21. Since you are now discussing a new dataset (2003), it would help to write one sentence describing what was measured (i.e. is this comparison of vehicle exhaust, ambient background, or ?).

We edited the text on p. 27593, line 20 to emphasize that the 2003 measurements were ambient ones collected during the morning hours (6:00-9:00):

"While total VOC results are not yet available from 2006, ambient urban measurements during the morning hours from the MCMA-2003 field campaign (Velasco et al., 2007) can help illuminate the conditions."

15) Pg. 27595 line 3. I would add a sentence about interpreting your results with caution since it's a 3.5 hour dataset. Line 12. Again, using your results as the standard for comparison may be unjustified.

At the end of the first paragraph of the Conclusions section on p. 27595, line 2, we added the following sentence:

"Because of the small sample size in this study, the conclusions presented below apply to the fleet sampled during 3.5 hours of driving and may not necessarily pertain to the MCMA's fleet as a whole."

Following the comparison of our and the official inventories, we added a caveat on p. 27595, line 14:

"While conclusions regarding the inventory should be interpreted with care because of the small sample size, the discrepancies agree with those reported in other studies."

Reviewer 3

This reviewer found the manuscript to be "a novel application of PMF and an interesting approach for evaluating emission inventories." The reviewer also thought the work has

"value from a methodological perspective" and recommends publishing it. We like the reviewer's suggestions regarding other evaluations of Mexico City's inventory, uncertainty, and species with high background contributions. Below, we address these and other concerns in detail.

1) There have been other evaluations of the Mexico City Inventory. My read of the literature is that others have suggests that, for example, VOC emissions are underestimated (Molina, L. T. and Molina, M. J. (Eds.): Air Quality in the Mexico Megacity: An Integrated Assessment, Kluewer Academic Publishers, 384 pp., 2002 or Lei et al. ACP 2007). It would be good to compare your results to these previous evaluations of the Mexico City Inventory (the authors do present some comparisons to other receptor modeling studies). My sense is the biases in VOCs are similar to those estimated by others. Presumably there also have been assessments of CO, NO_x and other emissions considered in this paper. Although the authors focus on mobile sources, these are the dominant sources in the Mexico City inventory for many of the pollutants considered here.

Comparing the results of our evaluation of the official inventory to other studies is an excellent suggestion. We added a new paragraph in the discussion section on p. 27594, line 2 that summarizes other on-road, ambient, and modeling studies that evaluate the inventory. We found that the results of the present work are in agreement with the other studies.

"Employing a variety of techniques, other studies have also evaluated the MCMA's emission inventory. Most agree that CO and VOCs are understated in the official inventory and that NO_x may be overstated. Historically, the official inventory has been a moving target because of updates in methodology (Molina and Molina, 2002), so conclusions may depend on the specific year used for comparison. For CO, whose emissions are dominated by motor vehicles, roadside remote sensing measurements of vehicle exhaust produce emissions estimates that are 48% lower than the official 1998 inventory (Schifter et al., 2005). On-road measurements using the AML suggest

that the official inventories in 2002 and 2006 also overestimate CO by 20-38% (Jiang et al., 2005; Zavala et al., 2009b). However, modeling results using the 2002 inventory suggest that it is correct (de Foy et al., 2007). For VOCs, on-road measurements using the AML produce estimates of mobile source VOC emissions that are 1.3-1.9 times higher than in the 2002 inventory. Obtaining agreement between ambient concentrations and emission inventory ratios and between photochemical air quality modeling predictions and observations requires increasing total VOC emissions in the 1998 and 2002 inventories by factors of 2-3 (Arriaga-Colina et al., 2004; West et al., 2004) and 1.7 (Lei et al., 2007), respectively. For NO_x, measurements by both remote sensing and the AML result in estimates of vehicle emissions that are comparable to or up to 26% lower than the 1998, 2002, and 2006 official mobile source inventories (Jiang et al., 2005; Schifter et al., 2005; Zavala et al., 2006; Zavala et al., 2009b). In spite of the small sample size in the present work, comparisons to the official emission inventory for these three pollutants are in agreement with results from other studies."

2) Uncertainty analysis – The paper needs a more comprehensive discussion of uncertainty, including adding quantitative estimates to various source apportionment values that appear throughout the text. For example in the discussion section, the paper states gasoline engine exhaust accounted for 12% of the NO_x. There needs to be uncertainty estimates added to these sorts of values. In Table 4 some confidence intervals are presented. It is not clear where these came from. Based on the sensitivity studies performed with PMF described on page 27579? How the confidence intervals are estimated need to be described and the results of the analysis need to be added to the discussion.

We added an explanation of how the confidence intervals were obtained on p. 27591, line 29:

"In the table, the ranges shown in parentheses are the 95% confidence intervals, based on propagation of uncertainties associated with the emission factors shown in Table 3."

We also added uncertainty estimates to the list of percent contribution of gasoline engine exhaust to total vehicle emissions in the discussion on p. 27592, line 6 and in the conclusions on p. 27595, line 7:

"Results from the present study suggest that gasoline-powered vehicles are responsible for 97% (58-98%) of mobile source emissions of CO, 22% (18-57%) of NO_x, 95-97% (59-100%) of each aromatic species, 72-85% (43-100%) of each carbonyl species, 74% (44-100%) of ammonia, negligible amounts of particle number, 26% (0-84%) of $PM_{2.5}$, and 2% (0-10%) of BC, where the values in parentheses indicate the 95% confidence interval associated with each value."

3) The approach indicates that the official inventory overestimates $PM_{2.5}$ mass from diesels by a factor of almost 5 with wide uncertainty limits. However, $PM_{2.5}$ is mainly background. One might expect that there are significant uncertainties in the estimated mobile contributions to $PM_{2.5}$ because small changes in background apportionment would have disproportionate effects on the residual available for mobile sources. This issue should be discussed a bit more in the text. Ambient concentrations of several other pollutants are also dominated by the background factor (Figure 2). Do similar issues apply to those?

The $PM_{2.5}$ emissions estimates should be taken with a grain of salt because of large uncertainties in the measurement technique, as we described in the manuscript. However, the reviewer raises an excellent point, that the emission factors of those species with large background apportionments will be very sensitive to small changes (uncertainties) in the background concentration. Species that are apportioned mostly to the background factor include carbon dioxide, ammonia, formaldehyde, acetaldehyde, acetone, and $PM_{2.5}$. Carbon dioxide is constrained well by knowledge about the expected background concentration, but the others are less so. We now address this issue immediately after highlighting discrepancies in formaldehyde and $PM_{2.5}$ emission factors on p. 27586, line 17:

"Additionally, these two pollutants, along with ammonia, acetaldehyde, and acetone, are dominated by their background concentrations. Therefore, the concentrations assigned to the vehicle exhaust factors are especially sensitive to uncertainties in the background factor because small changes in its concentrations would have disproportionate effects on the residual available for mobile sources."

In the Conclusions section on p. 27595, line 25, where we provide recommendations for future study, we added a suggestion related to this point:

"We also suggest focusing on those species whose on-road concentrations are not dominated by the background, unless expected background concentrations are well constrained by independent measurements."

4) Abstract – You compare relative gasoline and diesel apportionment. For example, you state that 26% of $PM_{2.5}$ is apportioned to gasoline. This is 26% of the motor vehicle $PM_{2.5}$ which is only 11% of the total $PM_{2.5}$ based on the text. You should considered rewording this to make sure the basis of comparison is clear.

In the original sentence on p. 27573, line 17, we modified "mobile source" to terminology that will be more familiar to readers, "total vehicular."

"In the fleet sampled during AML driving, gasoline-powered vehicles are responsible for 97% of **total vehicular** emissions of CO, 22% of NO_x, 95-97% of aromatics, 72-85% of carbonyls, 74% of ammonia, negligible amounts of particle number, 26% of $PM_{2.5}$, and 2% of BC; diesel-powered vehicles account for the balance."

5) Abstract – You use qualitative words like "overstated" and "understated" in the abstract, but in the discussion section (page 27592) you are quantitative about bias. CO is 25% low, VOC are off by a 50%, etc. It would be good to be quantitative in the abstract too. My perception is the errors do not seem that large given the uncertainty in the inventory.

Based on this and other reviewers' comments, we have edited the comparison of the

emission inventories to present them more neutrally. We simply quantify the differences between the two and no longer assume that one is more correct, so we have removed the terms "overstated" and "understated." Because of the small sample size that may not be representative of the entire fleet, we have elected not to present the difference between the inventories in quantitative terms in the abstract.

6) Page 27574 – I thought the statement that gasoline powered vehicle emissions vary by day of the week was confusing? Certainly gas-diesel split varies. Maybe reword.

We changed the sentence on p. 27574, line 28 to emphasize that activity patterns vary temporally:

"Emissions from gasoline- versus diesel-powered vehicles differ enormously by pollutant, and activity patterns of the two vehicle types differ by time of day and day of week (Marr et al., 2002)."

7) Given the limited extent of the dataset (one 3.5 hour drive) one could present this as an initial application or test of the idea.

We added a sentence in the last paragraph of the introduction on p. 27577, line 2, where we describe the objectives of the study. The new sentence immediately follows mention of PMF applied to fast, on-road measurements as a novel approach.

"Given the small size of the data set, this work can be considered an initial application or test of the approach."

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/9/C11639/2010/acpd-9-C11639-2010-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 27571, 2009.