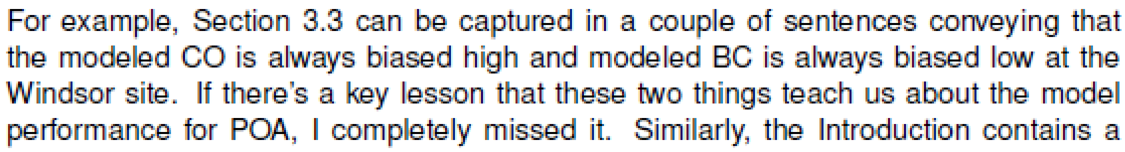
Authors Response to Reviewer Comments

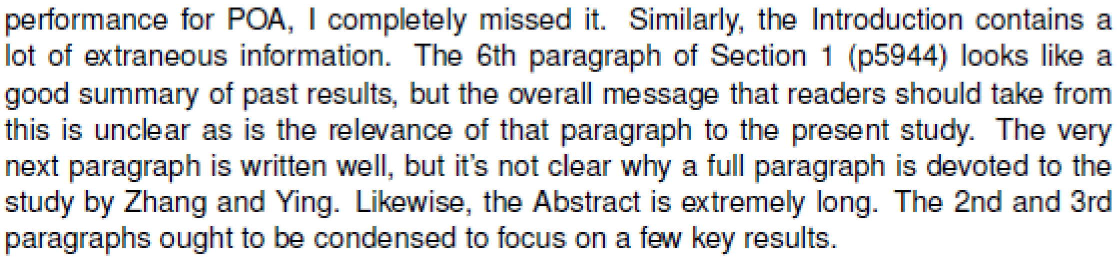
We would like to thank both reviewers for their very thoughtful comments. We feel their comments have helped us to greatly improve the focus of the paper and the readability of the text in terms of reducing its length. We have more clearly stated several model improvement recommendations in the abstract. We have also tried to state more precisely our key results throughout the paper and how they support our story for what factors result in the model biases for POA, CO and BC.

Response to Reviewer #1



For example, Section 3.3 can be captured in a couple of sentences conveying that the modeled CO is always biased high and modeled BC is always biased low at the Windsor site. If there's a key lesson that these two things teach us about the model performance for POA, I completely missed it. Similarly, the Introduction contains a

We have considerably shortened section 3.3, as suggested. An explanation for the model CO and BC biases cannot be based just on the results in section 3.3. Given the evidence presented in all of the sections put together (biases at Harrow, Bear Creek and Windsor, bias trend plots as a function of concentrations and indicator ratios, emission inventory calculations), a clearer picture emerges for the sources of the biases, as described in the new Discussion section and the Conclusions section.



performance for POA, I completely missed it. Similarly, the Introduction contains a lot of extraneous information. The 6th paragraph of Section 1 (p5944) looks like a good summary of past results, but the overall message that readers should take from this is unclear as is the relevance of that paragraph to the present study. The very next paragraph is written well, but it's not clear why a full paragraph is devoted to the study by Zhang and Ying. Likewise, the Abstract is extremely long. The 2nd and 3rd paragraphs ought to be condensed to focus on a few key results.

We have shortened the Introduction to include only the most pertinent material. For example, we have removed the paragraph that describes the prior AURAMS model applications, as the studies do not report on general conclusions relevant to the atmospheric chemistry and atmospheric science community but rather specific studies relevant to Canada and policy applications.

Paragraph 6 of section 1 was also shortened to include only the prior studies that are relevant to this study, namely Zhang et al., 2005; Zhang et al., 2007; Lanz et al., 2007 and Mohr et al., 2009. The paragraph now more clearly emphasizes what source information can be extracted from unit resolution AMS PMF analysis. The paragraph now reads as follows:

"OA data acquired by the Aerosol Mass Spectrometer (AMS) instrument have been deconvolved into hydrocarbon-like OA (HOA) and oxygenated OA (OOA) components (Zhang *et al*., 2005). HOA has been linked to primary emissions such as liquid fuel combustion. Zhang *et al*. (2007) performed factor analysis on AMS data from 37 field campaigns and found that HOA represented 36% and 17% of OA at urban and suburban sites, respectively. There has been discussion in the literature about whether HOA includes other sources such as food cooking and biomass burning. A positive matrix factorization (PMF) analysis of AMS data in Zurich, Switzerland during the summer (Lanz *et al*., 2007) ascribed a 10% contribution from liquid fuel combustion and a 10-15% contribution from local food cooking to OA in which both sources loaded onto the HOA factor with a 2-component solution (HOA, OOA) but were separated with a 3-component solution (HOA, food cooking, OOA). Mohr *et al*. (2009) analyzed the unit resolution AMS spectra from meat cooking, plastic burning, paper burning, and wood burning and concluded that meat cooking and plastic burning grouped with the HOA factor, whereas paper burning and wood burning grouped on a unique factor (termed BBOA). In general, with the unit resolution AMS and a limited number of PMF factors chosen, biomass burning will load on its own factor for air masses sampled near biomass burning sources, but will load mostly onto the HOA factor for a smaller regional biomass burning influence (Slowik et al., 2011)."

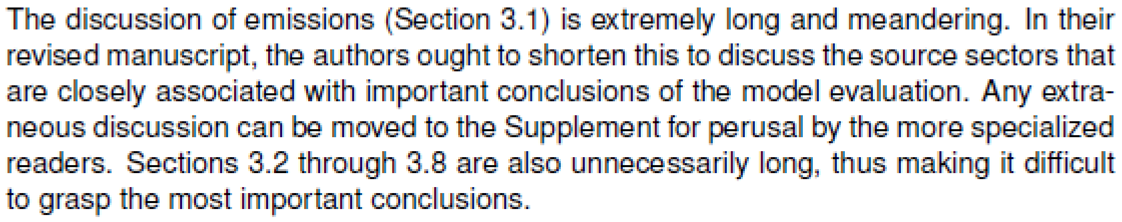
We have shortened the discussion from Zhang and Ying (2010) to the most relevant material (e.g. predicted POA from diesel and gasoline combustion in Houston, TX agreed well with observationally-derived HOA) and included it in the paragraph with the other prior CTM results.

We have also restructured the Abstract to better convey the novel aspects of our analysis (1st paragraph), the key results that support our hypothesis for the model biases (2nd paragraph), and the recommendations for future work (3rd paragraph). The Abstract now reads as follows:

"Observations from the 2007 Border Air Quality and Meteorology Study (BAQS-Met 2007) in southern Ontario (ON), Canada, were used to evaluate predictions of primary organic aerosol (POA) and two other carbonaceous species, black carbon (BC) and carbon monoxide (CO), made for this summertime period by Environment Canada's AURAMS regional chemical transport model. Particle-component-based factor analysis was applied to aerosol mass spectrometer measurements made at one urban site (Windsor, ON) and two rural sites (Harrow and Bear Creek, ON) to derive hydrocarbon-like organic aerosol (HOA) factors. A novel diagnostic model evaluation was performed by investigating model POA bias as a function of HOA mass concentration and indicator ratios (e.g., BC/HOA). Eight case studies were selected based on factor analysis and back trajectories to help classify model bias for certain POA source types. By considering model POA bias in relation to co-located BC and CO biases, a plausible story is developed that explains the model biases for all three species.

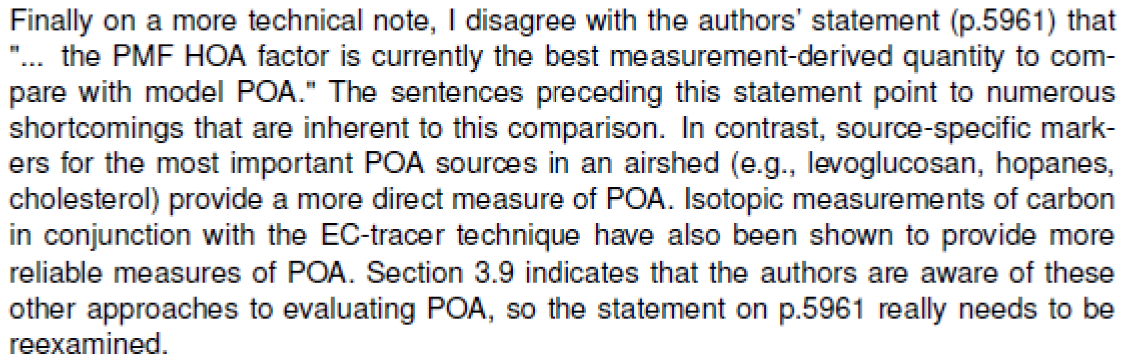
At the rural sites, daytime mean PM$_1$ POA mass concentrations were under-predicted compared to observed HOA concentrations. POA under-predictions were accentuated when the transport arriving at the rural sites was from the Detroit/Windsor urban complex and for short-term periods of biomass burning influence. Interestingly, the daytime CO concentrations were only slightly under-predicted at both rural sites, whereas CO was over-predicted at the urban Windsor site with a normalized mean bias of 134 %, while good agreement was observed at Windsor for the comparison of daytime PM$_1$ POA and HOA mean values, 1.1 μg/m^3 and 1.2 μg/m^3, respectively. Biases in model POA predictions also trended from positive to negative with increasing HOA values. The POA over-prediction was further exaggerated at the urban site on calm nights due to an overly-stable model surface layer. This model behaviour can be explained by a combination of model under-estimation of vertical mixing at the urban location, under-representation of PM emissions for on-road traffic exhaust along major urban roads and highways, and a more structured allocation of area POA sources such as food cooking and dust emissions to urban locations. A downward trend in POA bias was also observed at the urban site as a function of the BC/HOA indicator ratio, suggesting a possible association of POA under-prediction with under-representation of diesel combustion sources. An investigation of the emission inventories for the province of Ontario and the nearby US state of Indiana also suggested that the top POA area emission sources (food cooking, organic-bound dust, waste disposal burning) dominated over mobile and point sources.

We conclude that more effort should be placed at reducing uncertainties in the treatment of some POA emissions sources, in particular food cooking, fugitive dust, waste disposal burning, and on-road traffic sources, and especially their spatial surrogates and temporal profiles. This includes using higher spatial resolution model grids to better resolve the urban road network and urban food cooking locations. We also recommend that additional sources of urban-scale vertical mixing in the model, such as a stronger urban heat island effect and vehicle-induced turbulence, would help model predictions at urban locations, especially at night time."



The discussion of emissions (Section 3.1) is extremely long and meandering. In their revised manuscript, the authors ought to shorten this to discuss the source sectors that are closely associated with important conclusions of the model evaluation. Any extraneous discussion can be moved to the Supplement for perusal by the more specialized readers. Sections 3.2 through 3.8 are also unnecessarily long, thus making it difficult to grasp the most important conclusions.

We have considerably shortened the Results sections (3.1 to 3.8) to only include the observations that are relevant to our hypothesis to explain the model biases for POA, CO and BC. For example, we have moved the time series analysis (Sec. 3.4) to the SI section, as we felt it did not provide any additional information that could not be seen in the tables and scatter plots (although it does provide insight into the importance of predicting nighttime vertical mixing near surface and a model POA over-prediction in SO_4 rich plumes). We have moved the lengthy discussion of two case studies (transport from the southwest and transport from the northwest) to the SI section while briefly highlighting results for these two cases in the main text. We have tried to make each paragraph in the Results section have a clear purpose that supports our story to explain the model behaviour.



Finally on a more technical note, I disagree with the authors' statement (p.5961) that "... the PMF HOA factor is currently the best measurement-derived quantity to compare with model POA." The sentences preceding this statement point to numerous shortcomings that are inherent to this comparison. In contrast, source-specific markers for the most important POA sources in an airshed (e.g., levoglucosan, hopanes, cholesterol) provide a more direct measure of POA. Isotopic measurements of carbon in conjunction with the EC-tracer technique have also been shown to provide more reliable measures of POA. Section 3.9 indicates that the authors are aware of these other approaches to evaluating POA, so the statement on p.5961 really needs to be reexamined.

We agree with the reviewer that the statement, "PMF HOA factor is currently the best measurement-derived quantity to compare with model POA" is too strong. We have added a Discussion section comparing our model results to other receptor-based results. We state that a weight-of-evidence approach using various receptor model approaches (PMF, CMB, Isotope, EC-tracer correlation) is needed, and we discuss previous receptor-model results that are relevant to our study, especially the Zhang et al. (2009) paper on using PMF of molecular markers for Detroit and a rural Illinois site. The Zhang et al. (2009) study supports our conclusions that our modelled ORM emissions are under-represented for the Detroit/Windsor urban air shed. The text now reads as follows:

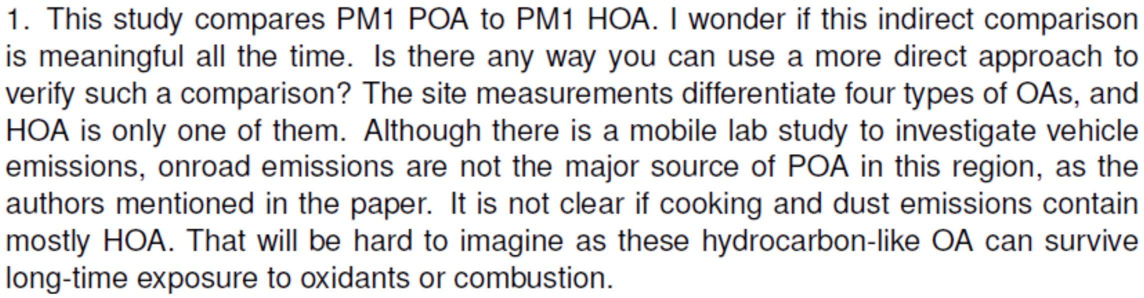
"Other receptor-oriented models have been used to estimate POA contributions to $PM_{2.5}$. Pachon *et al*. (2010) compared four methods to estimate POA and SOA contributions to long-term filter measurements of $PM_{2.5}$: BC tracer; regression; carbon mass balance (CMB); and PMF. In Atlanta over several years, the CMB method gave the lowest estimate of the relative contribution of POA (54%) and PMF gave the highest (74%). Williams *et al*. (2010) performed hourly measurements of source marker species at Riverside, California during the summer and their PMF analysis showed that primary contributions to OA were 11% from fuel combustion, 10% from food cooking, and 7% from forest fires. Dreyfus *et al*. (2009) used organic molecular composition measurements for an autumn period in Wilmington, Delaware in a PMF analysis to identify six factors linked to specific sources (diesel exhaust, road dust, meat cooking) or types of compounds (alkanes/alkanoic acids, phthalates, PAHs). For the POA sources, ~1/3 was contributed from fuel combustion (largely diesel) and ~2/3 was from non-combustion sources (dust, meat cooking). Each of these receptor modeling approaches has its advantages and overall a weight of evidence assessment using various approaches to source apportionment is favourable.

The most geographically relevant prior receptor-orientated analysis was reported by Zhang *et al*. (2009). They used monthly measurements of eight individual particle-phase organic marker species as well as $PM_{2.5}$ BC and OA mass over a one-year period in Detroit with PMF analysis to estimate the POA component. Three factors were derived, representing (1) urban primary sources (food cooking, road dust), (2) ORM sources, and (3) other combustion sources (coal). These three POA sources accounted for 57% of OA mass. In Detroit, in the summer, POA concentration from ORM combustion was estimated at 0.6 $\mu g/m^3$ (60% of POA). This receptor-based ORM contribution is much larger than the emission inventory and processing for the Detroit grid cell presented in section 3.2 (28% ORM). Furthermore, our results for POA bias as a function of HOA mass loading and as a function of BC/POA ratio point to an under-prediction in mobile emissions, especially diesel. This is also consistent with the Ying et al. (2007) study that concluded BC and POA levels were underpredicted in Los Angeles due to low diesel emissions in the California emissions inventory.

In the Zhang et al (2009) study, at a rural midwestern U.S. site, on the other hand, the ORM-source-dominated factor was negligible compared to the other urban primary sources (food cooking, road dust) and other combustion sources (coal). Their results are similar to the emission inventory percentages for Indiana presented in section 3.1."

Response to Reviewer #2

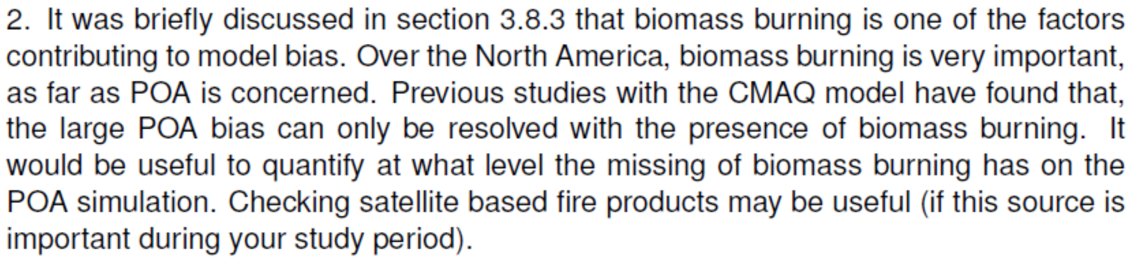
General Comments


1. This study compares PM1 POA to PM1 HOA. I wonder if this indirect comparison is meaningful all the time. Is there any way you can use a more direct approach to verify such a comparison? The site measurements differentiate four types of OAs, and HOA is only one of them. Although there is a mobile lab study to investigate vehicle emissions, onroad emissions are not the major source of POA in this region, as the authors mentioned in the paper. It is not clear if cooking and dust emissions contain mostly HOA. That will be hard to imagine as these hydrocarbon-like OA can survive long-time exposure to oxidants or combustion.

POA source apportionment for Windsor is complex with many local and regional sources. Undoubtedly, there are times when the HOA measurement-derived factor is excluding some POA sources in the NEI and model. We had acknowledged this in the original manuscript with the following statement: "Comparing model-derived POA with measurement-derived HOA must be done carefully and with the knowledge that HOA and POA are not identical quantities under all situations."

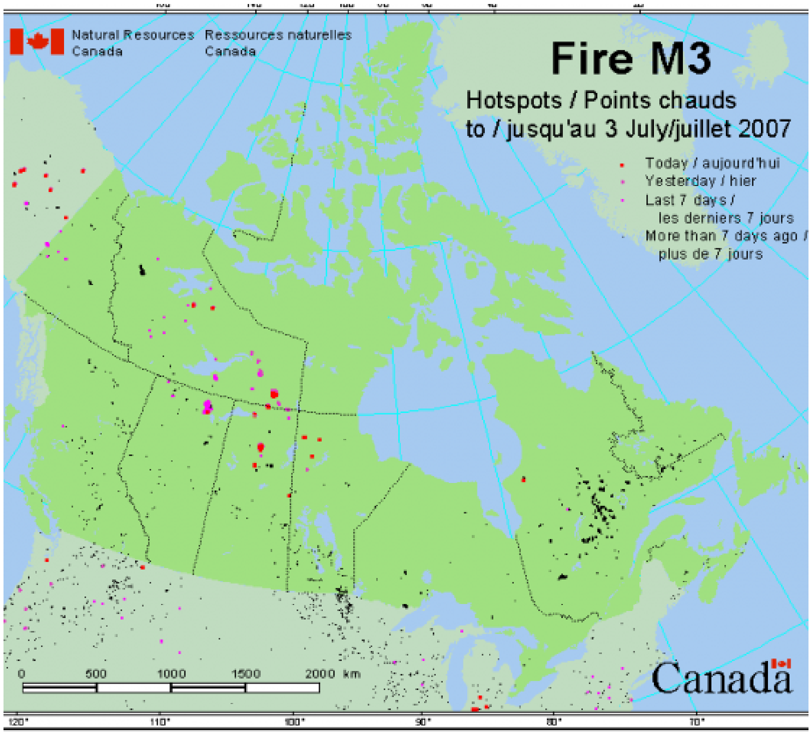
Organic-bound to dust is a good example. As the reviewer notes, organic-bound to dust is likely aged and thus oxygenated and would not load onto the HOA factor. In discussing the AMS PMF method with several experts, it was noted that for a location with many sources it is common for some sources with indistinct spectra to “load” onto another source factor. The two AMS groups that participated in the BAQS-Met field study (Slowik at Harrow and Bear Creek, Brook at Windsor) each performed their own PMF analysis and could not identify a food cooking factor. The McGuire et al. (2011) study, using single-particle AMS spectra from Harrow, also could not identify a unique food cooking source. These experts thought it was very likely that the food cooking source was loading onto the HOA factor. This is consistent with literature references, as the manuscript noted in the Introduction - meat cooking will only present as a unique factor if the cooking source is very local to the instrument sampling site (Mohr et al., 2009; Lanz et al., 2007). We have clarified this issue in the paragraph on AMS PMF in the Introduction section.

Literature studies have also found that biomass burning can result in a unique PMF factor (Mohr et al., 2009), but it depends on the magnitude of the event and the number of solutions selected in the PMF. The McGuire et al. study for Harrow was able to derive some short time periods with a unique biomass burning factor, and we have identified those periods as unique case studies. There were no molecular-marker measurements made during BAQS-Met; however, with which to perform POA source apportionment.



2. It was briefly discussed in section 3.8.3 that biomass burning is one of the factors contributing to model bias. Over the North America, biomass burning is very important, as far as POA is concerned. Previous studies with the CMAQ model have found that, the large POA bias can only be resolved with the presence of biomass burning. It would be useful to quantify at what level the missing of biomass burning has on the POA simulation. Checking satellite based fire products may be useful (if this source is important during your study period).

It is difficult to quantify at what concentration biomass burning may impact the POA results since we do not have biomass burning sources in the model. We have, however, looked at satellite-derived forest fire counts analyzed by the Canadian Forest Service and there were no large fires in southern Ontario during the 3-week study (http://cwfis.cfs.nrcan.gc.ca/en_CA/fm3maps/tri/20070624?fullwidth=0). There is also no evidence of smoke plumes over southern Ontario from the AQUA MODIS cloud cover data and GASP MODIS aerosol optical depth during the study. The Hazard Mapping System fire and smoke product (http://www.osdpd.noaa.gov/ml/land/hms.html), as reported on the US Air Quality Weblog (USAQ, http://alg.umbc.edu/usaq/), does not show any long-range transport of forest fire plumes into southern Ontario during the period of interest. There are some smaller fires that do appear in the fire counts data in south-central Michigan on July 3, 2007 and these may be a source of the biomass burning events seen in the single-particle AMS PMF results on July 6 and 7, although back trajectories suggest that air came from northern Michigan during these case study times. As shown in Table 12, short-duration case study times when the single-particle PMF analysis suggests significant biomass burning is consistent with the model POA being significantly smaller than the unit resolution AMS HOA factor.



There is one relevant study that estimates background summertime POA from forest fires of 0.14 μgC/m^3 over a 2001-2004 period (Park, R.J., Jacob, D.J. and Logan, J.A., 2007, *Atmos. Environ*., 41 (35) 7389-7400) in the northeastern U.S. This may give an indication of the magnitude of the impact of biomass burning on the campaign-averaged results reported in Tables 4 and 7 (minor but not insignificant at Windsor and Harrow, more significant at Bear Creek).

> Specific Comments:
>
> Throughout the text: change “spatial and temporal surrogates” to “spatial surrogates and temporal profiles”.

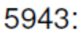
We agree with the suggestion and have made the changes.

> 5942,
>
> L11-12: These health studies do not differentiate primary or secondary aerosols when linking total mass concentration to health endpoints.

We have looked into the health-related references in more detail and have included the references that are not specific to primary vs. secondary aerosol in the first sentence and the reference that is specific to primary aerosol in the second sentence.


L21. the Earth system;

Done.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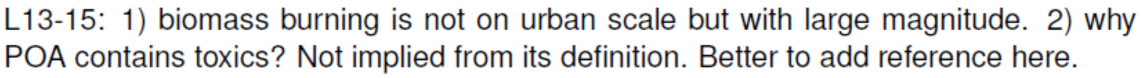
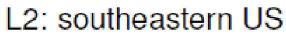

L13-15: 1) biomass burning is not on urban scale but with large magnitude. 2) why POA contains toxics? Not implied from its definition. Better to add reference here.

We have changed the text as follows:
"Primary organic aerosol (POA) is defined as directly emitted organic aerosol (e.g., traffic emissions, biomass burning). POA has received less attention in the literature than secondary organic aerosol (SOA). However, POA is important because it can act as a seed for organic vapour condensation and it is believed to contain some toxic materials (e.g., dioxins: Lohmann and Jones, 1998; Lee *et al.,* 2007)."


5944


L2: southeastern US

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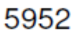
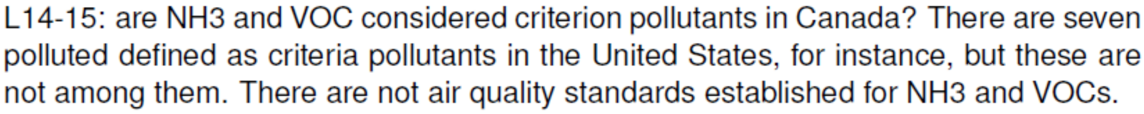
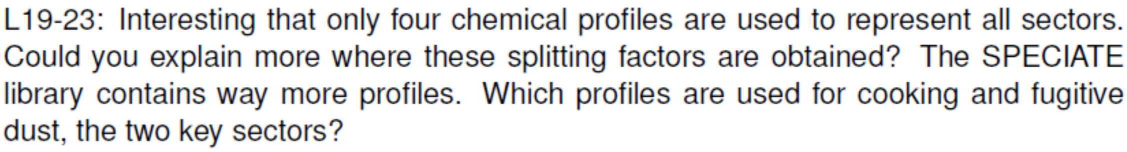
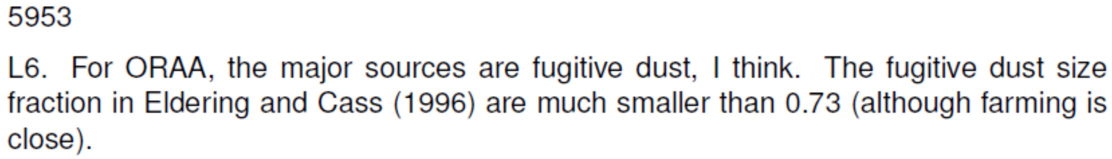

5952


L14-15: are NH3 and VOC considered criterion pollutants in Canada? There are seven polluted defined as criteria pollutants in the United States, for instance, but these are not among them. There are not air quality standards established for NH3 and VOCs.

The criterion pollutant list referred to are the species that must be reported in the U.S. and Canada National Emission Inventories (NEIs). We agree that the word "criterion" is confusing. We have changed the text as follows:
"Point sources are larger sources that emit at least 100 tonnes (Canada) or 100 tons (U.S.) per year of at least one of the following pollutants: SO_2, NO_x, CO, VOC, NH_3, $PM_{2.5}$, or PM_{10}."


L19-23: Interesting that only four chemical profiles are used to represent all sectors. Could you explain more where these splitting factors are obtained? The SPECIATE library contains way more profiles. Which profiles are used for cooking and fugitive dust, the two key sectors?

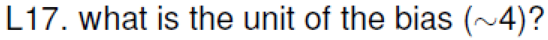
The entire 2001 U.S. NEI was used by one of us (Makar) to create the PM species allocation splitting factors. Each chemical profile in the US EPA SPECIATE database was weighted by the sum of the annual mass emissions with the same source classification categories (same SCCs) divided by the sum of mass emissions for all SCCs. Of course this is an assumption with some errors, especially for urban to regional locations with a different proportion of emitted pollutants than the average proportion for the entire U.S. The meat-cooking profile in SPECIATE4.2 assigned in U.S. EPA version of SMOKE is #92015 (Charbroiling – Simplified, OC 81%, BC 4%, PM other 15%). The paved road fugitive dust profile is #92053 (9.7% OC, BC 1%, PM other 89%). The unpaved road fugitive dust profile is #92088 (OC 5.5%, BC 0.097%, NO3 0.13%, SO4 0.23%, PM other 94%). These percentages are listed in Section 3.1.



5953

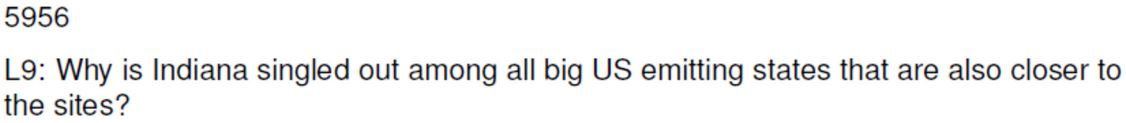
L6. For ORAA, the major sources are fugitive dust, I think. The fugitive dust size fraction in Eldering and Cass (1996) are much smaller than 0.73 (although farming is close).

Similar to the PM chemical speciation, the PM size profiles by category were derived using all of the source sectors from the 2001 U.S. NEI. The ORAA category is a weighted average from a combination of liquid fuel exhaust, wood combustion, natural gas combustion, charcoal grilling and dust sources, among others.



L17. what is the unit of the bias (∼4)?

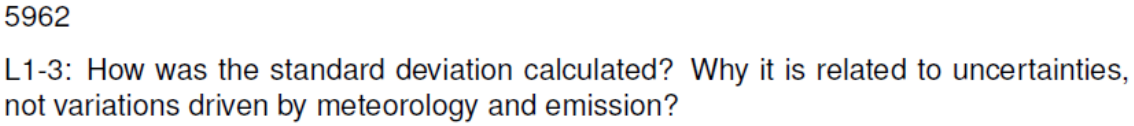
Factor of ~4 is in mass concentration. We have made the text more clear on this point.



5956

L9: Why is Indiana singled out among all big US emitting states that are also closer to the sites?

We were interested in understanding the model POA underpredictions for air masses with trajectories from the southwest. The model had reasonable POA bias for air masses from the northwest. Michigan is a large state with most land mass to the west of the study area. Ohio is also a large state with significant land mass to the south of the study area. Indiana was the nearest state that best aligned with the southwesterly back trajectories. We have added a sentence to the text to state the rationale for the choice.



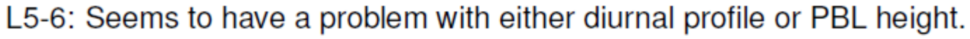
5962

L1-3: How was the standard deviation calculated? Why it is related to uncertainties, not variations driven by meteorology and emission?

The standard deviation is calculated as the ±1σ width from the mean value. We agree that it is not likely related to measurement uncertainties but rather a measure of atmospheric variations driven by meteorology and emissions spatial allocation. We have clarified this in the text.

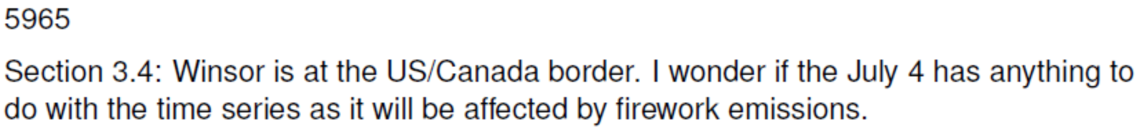
L13: what is HOA solution?

The “HOA solution” refers to the PMF calculation of the HOA factor. We have clarified this in the text.



L5-6: Seems to have a problem with either diurnal profile or PBL height.

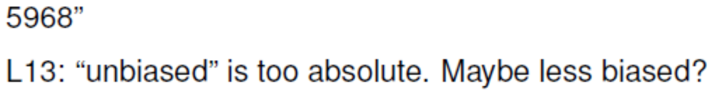
We agree that the difference in POA diurnal pattern between model and measurements suggests large uncertainties in either the diurnal profile or PBL height. The diurnal profiles are the standard options for SCCs in the U.S. EPA SMOKE program. Given the large CO over-predictions for urban locations and the very large POA over-predictions at low wind speed on cool nights, it suggests that near-surface pollutant vertical mixing is a key area for model improvement.



5965

Section 3.4: Winsor is at the US/Canada border. I wonder if the July 4 has anything to do with the time series as it will be affected by firework emissions.

Yes, the impact of the July 4 firework celebrations was seen in the single-particle AMS PMF analysis in the early morning of July 5 at Harrow (McGuire et al., 2011). Back trajectories from Harrow were also consistent with an air mass originating from the Detroit River. The analysis from the single-particle AMS suggests that fireworks particles are largely inorganic in composition. Furthermore, the PMF analysis of the unit resolution AMS also did not identify any spikes in any of the organic factors (HOA, OOA-1, OOA-2, UNKN) during the time of the cation-marker (K+, Cu+, Sr+, Ba+, BAO+) spikes indicative of fireworks. Thus, we conclude that particles originating from fireworks do not have a large organic content.



5968”

L13: “unbiased” is too absolute. Maybe less biased?

We have made the recommended change. Thanks.