

Response to Co-Editor Comments

1) The title talks about "Improving Air Quality predictions using...". The first sentence of the abstract suggests the same, assessing the impact of revised VOC and OA emissions estimates on air quality predictions for...". Most readers would then expect like me to find a paper reporting improved air quality predictions but that is not what we get. Instead, you merely report how the use of top down emission estimates better constrains the fugitive emissions in the OS region. That is a much more restricted objective, I would expect to read how air quality predictions on things like oxidants (ozone) and particles in the air were improved by using those better constrained emission data. The actual results reported in the paper are extensively discussed which may of interest and merit publication, but then say so up front.

The manuscript focuses on air quality model predictions for VOCs and PM2.5 organic aerosol. As recommended, we have changed the title to be more specific to this focus, "Improving Air Quality **Model Predictions of Organic Species** using Measurement-Derived Organic Gaseous and Particle Emissions in a Petrochemical-Dominated Region". We have also changed the first line of the abstract to specifically mention the paper discusses air quality model predictions for organic species.

2) The paper is also overly long, as mentioned by referee 1 (who also made some comments about the original title). You mention that you shortened the paper upon referee 1's comments. Well that sounded odd to me so I counted: the original paper had an abstract of 34 lines, 7 lines shorter that the revised version. The original main text runs from lines 50-603, the revised version runs from lines 43-628... So I feel there is work to do.

One of the things that makes the paper so long is the amount of detail. I do not know the Zhang et al. paper, now accepted for ACP, but I suspect that there is quite some overlap with section 2.1, so reference to that paper should be possible. Similarly section 2.3 may well include a lot of the details already reported in the Li et al. and Liggio and al. papers, so again, references to those papers should be possible. In short, only describe what is new and refer for the rest to those earlier papers.

A lot of space is used for detailed case studies. I am wondering whether it would not make sense to move most of the case studies to the supplement (lines 207-338, figures 2-3; lines 359-386, figures 6-8; lines 403-444, figure 10; lines 486-543, figures 14-16), and only write a few paragraphs in the main body of the text summarizing these case studies

Thank you for your suggestion in moving the case study analysis to the SI. We have moved 9 figures illustrating case study results to the SI. We have also added a few paragraphs in the main text summarizing the case study results. This reduces the length of the paper from 552 lines to 484 lines. The original abstract was 445 words and the revised abstract is now 351 words. The original text was 7484 words and the revised text is now 5946 words. The main part of the manuscript now has 7 figures. This length should help to make the paper more readable by the air pollution research community.

The Zhang et al. (2018) paper is a comprehensive summary of all the emissions projects under JOSM, of which the measurement-derived organic emission project is only a subset. I have taken the main points from the comprehensive Zhang et al. paper relevant to this paper and summarized them in the Methods section. The first reviewer also requested MORE detail in the emissions method section to understand the paper, without having to read another long paper. As a result, we have not changed the emissions method section, apart from rewording one sentence and removing one sentence that is redundant with the sentence already in the Table 1 caption.

We have removed a couple sentences in the Observation section that are unnecessary detail.

3) One further comment: lines 169-171 mention that the PM_{2.5} emissions in Table 1 are derived only for the summer months which seems eminently sensible. But it makes me wonder whether the same should be true for the gaseous VOCs. Are there wintertime aircraft observations for these VOCs suggesting that fugitive emissions are more or less the same?

We do not have wintertime aircraft VOC observations from the JOSM 2013 field study. The Li, S.M. et al. (2017) paper reports the annual measurement-derived VOC emission totals for each facility. For the plant emissions this was scaled up using the monthly and annual oil production yields reported by the facilities. For the mine face and tailing pond emissions, the emissions were estimated considering surface-to-atmosphere mass transfer calculations using ambient temperature and wind speeds. In this paper, we refer to this previous published work. We agree that there is considerable uncertainty in these annual VOC totals. The results from the April 2018 aircraft study with snow cover will be interesting to compare. We have added the following caption to Table 1. For comparison, Table 1 includes the annual VOC emission totals reported from the bottom-up inventories.

“VOC revised-emissions are based on annual estimates, derived in Li *et al.*, (2017). The estimates for the plant stack emissions consider monthly and annual oil production yields reported by facilities. For the tailing ponds and mine faces, the VOC estimates are calculated using a surface-to-atmosphere mass transfer model considering ambient temperature and wind speed.”

4) Chapter 4, Discussion, only pertains to the results in chapter 3.4. Therefore make current chapter 3.4 into 3.4.1, and chapter 4 into chapter 3.4.2.

We agree that the logic of your suggested section numbering makes more sense. We have made the changes.

5) Finally, among the conclusions (should now be Chapter 4!) I note your comment on the especially large increases in the ALKA compounds at the facilities that use paraffins for bitumen extraction. That seem to me like an important observation that should also be mentioned earlier (in chapter 2).

We have added a sentence to the emissions method section to emphasize this large change in ALKA emission and decrease in aromatic emission for the facilities that use paraffins for bitumen extraction.

“Interestingly, the facilities that use paraffinic solvents for bitumen extraction (e.g. Shell Muskeg/Jackpine) were associated with the largest ALKA emission increases and aromatic decreases.”

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Improving Air Quality Model Predictions of Organic Species using Measurement-Derived Organic Gaseous and Particle Emissions in a Petrochemical-Dominated Region

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Abstract

This study assesses the impact of revised volatile organic compound (VOC) and organic aerosol (OA) emissions estimates in the GEM-MACH (Global Environmental Multiscale–Modelling Air Quality and CHemistry) chemical transport model [on air quality model predictions of organic species for the Athabasca oil sands region in Northern Alberta, Canada, driven with two different emissions input datasets, using observations from the 2013 Joint Oil Sands Monitoring \(JOSM\) intensive field study](#). The first emissions dataset [that was evaluated](#) (base-case run) makes use of regulatory-reported VOC and particulate matter emissions data for the large oil sands mining facilities, ~~in northeastern Alberta, Canada, while~~ [the second emissions dataset \(sensitivity run\) uses total facility emissions and speciation profiles derived from estimates based on](#) box-flight aircraft observations around specific facilities. ~~(Li *et al.*, 2017, Zhang *et al.*, 2017) and a mass balance analysis (Gordon *et al.*, 2015) to derive total facility emission rates. The preparation of model-ready emissions files for the base case and sensitivity run is described in an accompanying paper by Zhang *et al.* (2017).~~ [The large increases in some VOC and OA emissions in the revised emissions data set for four large oil sands mining facilities and decreases for others](#) were found to improve the modeled VOC and

OA concentration maxima in facility plumes ~~from these facilities~~, as shown with the 99th percentile statistic and illustrated by case studies. The results show that the VOC emission speciation profile from each oil sand facility is unique and different from standard petrochemical-refinery emission speciation profiles used for other regions in North America. A significant increase in the correlation coefficient is reported for the long-chain alkane predictions against observations when using the revised emissions based on aircraft observations. For some facilities, larger long chain alkane emissions resulted in higher secondary organic aerosol production, which improved OA predictions in those plumes. A feedback between larger long-chain alkane emissions and higher secondary organic aerosol (SOA) concentrations was found to be significant for some facilities and improved OA predictions for those plumes. Overall, ~~t~~he use of the revised emissions data resulted in a large an improvement of the model mean OA bias; however, a decrease in OA correlation coefficient and a remaining negative bias suggests the need for further improvements to model ~~organic aerosol-OA~~ emissions and formation processes. ~~Including intermediate volatile organic compound (IVOC) emissions as precursors to SOA and spatially allocating more PM₁ POA emissions (primary organic aerosol of 1.0 µm or less in diameter) to mine face locations are both recommended to improve OA bias and correlation further. A systematic bias in the background OA was also predicted on most flights, likely due to under-predictions in biogenic SOA formation.~~ Overall, ~~t~~he weight of evidence suggests that the top-down emission estimation technique helps to new aircraft observation-derived organic emissions help to better constrain ~~better~~ the fugitive organic emissions in the oil sands region, which are a challenge to estimate given the size and complexity of the oil sands operations and the number of steps in the process chain from bitumen extraction to refined oil product. ~~in the~~ creation of bottom-up emission inventories. This work shows that the use of facility-specific

~~emissions, based on direct observations, rather than generic emission factors and speciation profiles can result in improvements to model predictions of VOCs and OA. This work shows that top-down emissions estimation techniques, such as those used to construct the inventories in our study, may therefore help to constrain bottom-up emission inventories in have beneficial impacts when applied to other industrial regions of the world with large sources of VOCs and OA.~~

1 Introduction

Chemical transport models (CTMs) are useful tools to support clean energy policy decisions because they can be used to assess the impact of past and future pollutant emission changes on air quality (e.g., Schultz *et al.*, 2003; Kelly *et al.*, 2012; Rouleau *et al.*, 2013; Lelieveld *et al.*, 2015). CTMs can also be run in forecast mode with their output being used to support air quality forecasts (Moran *et al.*, 2010; Chai *et al.*, 2013). CTMs require pollutant emission inputs, typically at hourly intervals, at the model grid spatial resolution (Dickson and Oliver, 1991; Houyoux *et al.*, 2003; Pouliot *et al.*, 2012, 2015; Zhang *et al.*, 2017). The pollutant emission input files are based on the processing of emission inventories compiled for all emission sectors, usually at some geopolitical spatial resolution (e.g., county, province/state, or country), and may thus require the application of spatial disaggregation factor fields to allocate emissions to the model grid. North American emission inventories are typically derived from bottom-up approaches, where representative pollutant emission factors (e.g., pollutant mass emission per volume of fuel burned) are multiplied by activity factors (e.g., volume of fuel burned per unit time). In developed countries, industrial facilities are usually required to report estimates of their pollutant emissions to national inventories such as the National Pollutant Release Inventory (NPRI) in Canada (<https://www.canada.ca/en/environment-climate-change/services/national->

~~[pollutant release inventory.html](#)~~(Government of Canada, Canada Gazette, 2018) and the National Emissions Inventory (NEI) in the United States (~~<https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei.html>~~(Office of the Federal Register, Protection of Environment, 2015)). Updates of these inventories occur under a regulatory framework on a regular basis. -However, reporting requirements may be limited to aggregated mass emissions on an annual basis (e.g., a total bulk mass of VOC emitted rather than a detailed and observation-based emissions of individual speciated VOCs), with the subsequent use of VOC speciation profiles (splitting factors) to determine the relative contribution of the individual VOCs to the total VOC emissions. -Uncertainties in the availability and assignment of appropriate VOC speciation profiles, spatial and temporal allocation factors (Mashayekhi *et al.*, 2016), and/or unaccounted-for emitting activities, result in the need to evaluate the impact of these assumptions through the comparison of CTM predictions with ambient observations.

The Athabasca region of northeastern Alberta, Canada has one of the largest reserves of oil sands (OS) in the world. The OS deposits are composed of bitumen, minerals, sand and clay. Oil sand near the surface is mined by open-pit mining techniques. The oil sand is then transported by heavy hauler trucks to crushers, followed by the addition of hot water to make the oil sand flow through pipelines to a bitumen extraction facility. Here, the bitumen is separated from the sand and clay by the use of organic solvents. The product is ~~used either directly, then~~ upgraded on-site to crude oil or transported to a remote upgrader facility. Volatile organic compounds from the bitumen have the potential to escape into the atmosphere as fugitive emissions during the mining, extraction, processing, or tailing discharge steps. - The complexity and vast size of the oil sands operations make generating pollutant emission input files for CTMs a challenge (Cho *et al.*, 2012; ECCC & AEP, 2016).

Organic compounds in the atmosphere are oxidized over time and, in the presence of sufficient levels of oxides of nitrogen, are important precursors to ozone formation (Seinfeld and Pandis, 1998). VOCs and semi-volatile organic compounds (SVOCs) are also precursors to secondary organic aerosol (SOA) formation (Griffin *et al.*, 1999; Kanakidou *et al.*, 2005; Robinson *et al.*, 2007; Kroll and Seinfeld, 2008; Slowik *et al.*, 2010; Stroud *et al.*, 2011; Gentner *et al.*, 2017). If the organic compounds have sufficiently low saturation vapor pressures, then upon release into the atmosphere they remain particle-bound and are classified as primary organic aerosol (POA). Many specific organic compounds can also be toxic to human health and require explicit reporting in emission inventories (Stroud *et al.*, 2016).

The Joint Oil Sands Monitoring (JOSM) program was developed by the federal government of Canada and the Alberta provincial government with input and consultation from the local indigenous population and industry stakeholder groups to monitor the potential impacts of pollutant emissions. During JOSM, top-down approaches to estimate emissions based on atmospheric observations provided a unique opportunity to compare with bottom-up calculated emissions for the . One such approach has recently been applied for Athabasca OS facilities in Alberta, Canada (Gordon *et al.*, 2015; Li *et al.*, 2017). The mass-balance approach that was used is based on using box-shaped aircraft flight patterns around a facility and measuring pollutant concentrations and meteorological variables (wind speed and direction, air density). In this approach, the difference in pollutant mass fluxes entering and leaving the box is used to determine the total facility-wide emission rate, subject to assumptions such as minimal losses due to chemical oxidation between the emissions location and the nearby aircraft observations. This emission estimate can then be compared with the reported bottom up emission total.

~~The Joint Oil Sands Monitoring Program (JOSM) was developed by the federal government of Canada and the Alberta provincial government with input and consultation from the local indigenous population and industry stakeholder groups.~~ Environment and Climate Change Canada (ECCC)'s chemical transport model, GEM-MACH (Global Environmental Multi-scale-Modelling Air quality and CHemistry) is being used in JOSM to assess the impact of current emissions and future emission changes on local air quality and downwind regional-scale acid deposition (Makar *et al.*, 2018). Evaluations of the model performance in different configurations and with respect to other pollutants may be found elsewhere in this special issue (Makar *et al.*, 2017; Akingunola *et al.*, 2017). In this model study,
~~—Here~~ we make use of both regulatory-inventory-based and aircraft-observation-derivedbased emissions data for VOCs and primary particulate emissions for six large OS mining facilities as inputs to GEM-MACH in order to assess the impact of these two different emission data sets sources of information on model predictions of VOC concentrations and organic aerosol (OA) formation. ~~The base case inventory, which was derived from regulatory reporting, and updates for point sources, spatial and temporal allocation, and measured top-down, facility total aircraft measurement based emission rates are described in detail for VOCs in Li *et al.* (2017) and for particulate matter (PM) in Wang *et al.* (2015) and Zhang *et al.* (2017).~~

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2 Methods

The GEM-MACH model uses the ECCC operational weather forecast model (GEM) as the core operator for dynamics and microphysical processes (Côté *et al.*, 1998a,b; Girard *et al.*, 2014). GEM-MACH is an “on-line” CTM - the chemistry, vertical diffusion, and pollutant deposition routines exist as a set of subroutines contained and called from within GEM's meteorological physics package (Moran *et al.*, 2010, Makar *et al.*, 2015a,b). The gas-phase

chemistry scheme is based on the ADOM-II mechanism, originally developed for continental boundary-layer oxidant formation. The VOC lumped species used in GEM-MACH are described in Stroud *et al.* (2008). The focus here is on evaluating volatile aromatic and alkane species of anthropogenic origin. The aerosol size distribution is described by a 12-bin sectional approach based on the Canadian Aerosol Module (CAM) (Gong *et al.*, 2003; Park *et al.*, 2011). The SOA scheme is based on a two-product fit to smog chamber data using the SOA yield equations derived from gas/particle partitioning theory (Pankow 1994; Griffin *et al.*, 1999; Barsanti *et al.*, 2013). In the GEM-MACH model's current SOA formation algorithms, after initial particle formation, the organic compounds in the particle phase are assumed to be converted rapidly to non-volatile mass, as observed by recent studies (Cappa and Jimenez, 2010; Cappa *et al.*, 2011; Lopez-Hilfiker *et al.*, 2016) and recommended by modelling studies (Shrivastava *et al.*, 2015). However, other recent observation studies suggest that SOA 'chemical aging' over hours to days is quite complex, and involves further gas-phase oxidation and fragmentation reactions (Jimenez *et al.*, 2009; Donahue *et al.*, 2014), as well as potential particle-phase oxidation and oligomer reactions (McNeill *et al.*, 2015). The particle oligomer reactions are rapid, often acid-catalyzed, and can result in conversion to non-volatile mass (Liggio *et al.*, 2005; Kroll *et al.*, 2005). We discuss below the evidence from this work on the likelihood that these additional missing processes are still impacting our model organic aerosol bias.

2.1 Emissions

The Canadian base-case emissions were derived ~~by combining several emission from a hybrid~~ inventor~~iesy~~, targeting 2013 as the base year, ~~as described by Zhang *et al.* (2017)~~. This base year was chosen to align with the JOSM 2013 intensive field study period, which provided the observations for the model/observation comparisons that follow. Canadian emissions for

industrial facilities, including the Athabasca OS mining facilities, were obtained from the 2013 NPRI. The U.S. base-case emissions were obtained from the 2011 U.S. NEI Version 1 (Eyth *et al.*, 2013).

These base-case, bottom-up emissions inventories were processed with the SMOKE emissions processing tool (<https://www.cmascenter.org/smoke>), which includes three major steps corresponding to spatial allocation, temporal allocation, and chemical speciation (for NO_x, VOC, and PM). The base-case VOC speciation profiles used by SMOKE for the OS surface mining facilities were obtained from the CEMA (Cumulative Environmental Management Association) inventory (Davies *et al.*, 2012; Zhang *et al.*, 2015).

For the sensitivity run, speciated VOC emissions from the base case for four OS mining facilities (Suncor Millenium/Steepbank, Syncrude Mildred Lake, Shell Canada Muskeg/Jackpine, and CNRL Horizon) were revised by replacing them with the top-down emission rates estimated by Li *et al.* (2017) while primary PM emissions were revised for six oil sand facilities (Suncor Millenium/Steepbank, Syncrude Mildred Lake, Shell Canada Muskeg/Jackpine, CNRL Horizon, Syncrude Aurora North, and Imperial Oil Kearn) (Zhang *et al.*, 2018⁷). The VOC and PM chemical speciation profiles used for these facilities were also revised using the aircraft-observed VOC speciation (Li *et al.*, 2017) and ground-based PM filter analysis (Wang *et al.*, 2015), respectively. The set of emissions input files making use of these revisions is hereafter referred to as the “revised emissions”, while the original emissions input files without these changes is referred to as the “base-case emissions”. A detailed description of the development of the emission inventory and emissions processing steps to create the model-ready files (hourly gridded emission fields for the same domain and grid spacing as the model) for the base case and revised version are described in Zhang *et al.* (2018⁷). [Table 1 compares](#)

the facility emission rates for four species for the base case and revised-emissions case. The changes are not consistent from species to species and are not uniform across facilities. Interestingly, the facilities that use paraffinic solvents for bitumen extraction (e.g. Shell Muskeg/Jackpine) were associated with the largest ALKA emission increases and aromatic decreases. The SI section includes figures illustrating the emission difference maps for the oil sand region (absolute and relative difference) showing the spatial distribution of emission changes between revised and base case. The changes are largest over the surface mines and tailing ponds.

Depending on whether bitumen extracted from the oil sand is upgraded on site or not, the OS mining facilities can be classified into two broad types: (1) integrated extraction and upgrading facilities (Suncor Millennium/Steepbank, Syncrude Mildred Lake, and CNRL Horizon) and (2) extraction-only facilities (Shell Canada Muskeg/Jackpine, Syncrude Aurora North, and Imperial Oil Kearl). -Table 2S4 shows a comparison of the CEMA plant-specific VOC speciation profiles used in the base case for the two types of OS plants facilities compared to two standard VOC speciation profiles for petrochemical facilities (#9012 “Petroleum Industry – Average”, #0316 “Fugitive Emissions, Pipe/Valve Flanges”) that were used by SMOKE for the base case to speciate more than half of the U.S. refinery emissions in the Houston area, the largest petrochemical cluster in the U.S. There are significant differences between the base case OS plant aircraft-observation-based OS VOC speciation profiles and the two commonly used standard oil refinery-reference profiles. The OS integrated extraction and upgrading plant facilities profiles are higher in long-chain alkenes, toluene, and other aromatics than the standard-reference profiles, while the extraction-only plant facilities profile has ve the highest long-chain alkane fraction. -The other two standard profiles used for the base case and revised

simulation (for speciating U.S. and Canadian refinery emissions) have higher less-reactive species (e.g., propane, acetylene) and formaldehyde (profile #9012), than both the CEMA OS plant-profiles. Note also that these differences in relative fractions result in substantial differences in the absolute emissions of certain groups of VOCs between the standard profiles for oil refineries and the facility-specific oil sand profiles. For reference, the aircraft-measurement-derived facility-specific VOC speciation profiles used for four OS facilities in the revised-emissions case are presented in Zhang *et al.* (2018). The aircraft-measurement-derived profiles in Zhang *et al.* (2018), and used here for the revised case, are composite profiles since they encompass plant, tailing pond and mining emissions. As such, they are not appropriate for comparison with the profiles in Table 2, which are specific to plant emissions.

The primary PM emissions from the OS facilities originate largely from off-road heavy-duty diesel trucks, plant stack emissions, and fugitive and wind-blown dust. The 2009/10 CEMA inventory was used to specify the tail-pipe emissions from the off-road mining fleet and the 2013 NPRI inventory was used for fugitive road-dust emissions. -The base-case inventory did not include wind-blown dust. For the revised inventory, the PM size distribution was measured during the 2013 field study for all six facilities and these data were used to constrain the revised PM emission input data set. Note that the PM emissions estimates based on the aircraft-measured aerosol data included the contribution of wind-blown dust emissions. The aircraft-based PM emissions were re-binned for the 12 GEM-MACH PM size bins. The first eight size bins correspond to mass up to diameter 2.56 μm . Interestingly, the aircraft measured a much higher fraction of particulate mass in bin 8 (bounded by diameters 1.28 and 2.56 μm) compared to the mass fraction in bin 8 from the area-source PM size-distribution profiles used by SMOKE in processing the base-case emissions. In addition, a PM chemical speciation profile specific to OS

fugitive dust emissions was created from an analysis of deposited dust collected from surfaces in the OS region (Wang *et al.*, 2015); this speciation profile replaced the standard fugitive dust profile for unpaved roads from the U.S. EPA SPECIATE v4.3 database

~~(<https://www.epa.gov/air-emissions-modeling/speciate-version-45-through-40>)~~ in the revised emissions processing. The resulting organic carbon fraction in the observation-derived PM speciation profile was higher than that of the base-case emissions by about a factor of 3 (Zhang *et al.*, 2018⁷). In general, significantly higher POA emissions were observed over the open-pit mines for all facilities, except for the Imperial Kearsarge mine. The impact of the revised POA emissions will be discussed further in Section 3.4.

2.2 Modeling

The GEM-MACH model was run in a nested configuration with an outer domain covering the continental U.S. and Canada and an inner domain covering Alberta and Saskatchewan. The continental-scale GEM-MACH model (10-km resolution) and the Canada-wide GEM weather model (2.5-km resolution) were run first. These provided the chemical and meteorological lateral boundary conditions, respectively, for the high-resolution GEM-MACH 2.5-km resolution run, which has a domain covering the provinces of Alberta and Saskatchewan (Figure 1). The two models providing boundary conditions were run on a 30-hour cycle, of which the first six hours were spin-up and discarded, while the remaining 24 hours provided boundary conditions for the 2.5-km GEM-MACH simulation. The initial conditions subsequent to the starting model simulation for each overlapping 24-hour 2.5-km GEM-MACH simulation came from the end of the previous 2.5-km GEM-MACH simulation. This strategy was used to allow the two boundary condition simulations to make use of assimilated meteorological analyses. The sequence of

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model simulations was started for August 10, 2013 and run until September 7 to cover the 2013 JOSM intensive field study period.

2.3 Observations

The NRC (National Research Council) Convair two-engine turboprop aircraft was used to collect air-quality observations during the JOSM 2013 intensive field study. The aircraft was equipped with a suite of instruments to measure air quality over 22 flights (see Li *et al.*, 2017, Figure S1). Most of the flight hours focused on “box” flight paths; these took the aircraft around the periphery of facilities at different heights, with the goal of deriving facility-wide emission rates by using observations of chemical concentrations and winds to estimate the mass of pollutants entering and leaving the box enclosures. Coupled with a mass-conserving flux model (Gordon *et al.*, 2015), these aircraft data were used to estimate emissions from the encircled facilities.

VOC and PM observations were collected by the instrumented research aircraft using different technologies. A proton-transfer-reaction mass spectrometer (PTR-MS) was used to measure a select number of VOCs at high temporal resolution (1-sec) (Li *et al.*, 2017). An aerosol mass spectrometer (AMS) was used to measure PM₁ mass and non-refractory chemical composition (Liggio *et al.*, 2016). A Single Particle Soot Photometer (SP2) was used to measure refractory black carbon aerosol (Liggio *et al.*, 2016). ~~Black carbon is used in our analysis, as a proxy for transport from open-pit mine-face sources.~~ A number of canisters were filled with ambient air on each flight and returned to the lab for GC-FID and GC-MS analysis of VOCs (Li *et al.*, 2017). The canister VOC analysis measured 154 different C₂ to C₁₂ hydrocarbons (Dann and Wang, 1995). ~~Each flight typically filled 30 stainless steel canisters.~~ The resulting observation data were compared to the model output generated as described above. The 2.5-km

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GEM-MACH runs used a 120-s chemistry time step; 120-s model output values were linearly interpolated in time and space to the aircraft observation locations; all comparisons which follow make use of the resulting model/observation data pairs for the two simulations.

3 Results and Discussion

We present our evaluation results for four ~~species~~VOC classes: mono-substituted aromatics in section 3.1; multi-substituted aromatics in section 3.2; long-chain alkane species in section 3.3; and organic aerosols in section 3.4.

3.1 Toluene and other Mono-Substituted Aromatics (TOLU) Evaluation

The aircraft PTR-MS measurement data set was averaged to 10-sec intervals for comparison to ~~the time and spatially linearly interpolated~~ GEM-MACH model output. The ~~interpolated~~ model ~~grid cell~~ output ~~was extracted along the flight track and interpolated linearly between the two minute model output intervals along the flight track was merged with the observations~~ to create a coincident model ~~and~~-measurement time series. The model lumped TOLU species includes toluene and other mono-substituted aromatics with the two most important additional species being ethyl-benzene and propyl-benzene. Therefore, we must derive an equivalent observed lumped TOLU species for a comparison. We used all of the canister VOC data from the field study to create ethyl-benzene vs. toluene and propyl-benzene vs. toluene scatterplots. The corresponding slope, ~~y-intercept~~ and correlation coefficient for both these plots (not shown) were as follows: $m=0.376 \pm 0.006$, $y=0.0328 \pm 0.006$, $R=0.91$ and $m=0.0652 \pm 0.0008$, ~~y-intercept~~ $=0.0011 \pm 0.0008$, $R=0.90$, respectively. Thus, we derived an observed TOLU equal to the PTR-MS C7 aromatic multiplied by the factor 1.4412 (sum of $m=1.0$ C7+ 0.376 C7+ 0.0652 C7). This new observation-derived TOLU was used in the statistical comparison with model output TOLU, which follows.

Histograms of mixing ratio were created using the observed TOLU, the revised-emissions model output, and the base-case model output. Figure 2 ~~S1~~ illustrates the histograms using 20 mixing-ratio bins and an increment of 0.2 ppbv per bin. It is clear that there are more high values (>2 ppbv) produced by the sensitivity model run with revised emissions compared to the base-case model run. The number of observations in the highest value bins lies between the results from the revised and base-case versions. This can be quantified by using the 99% percentile statistic (obs=1.258 ppbv, revised=1.906 ppbv, base=0.934 ppbv). The 99% percentile means that 99% of the data points are lower than the value. The median concentration of the observations (0.061 ppbv) is higher than both the revised (0.038 ppbv) and base-case model (0.019 ppbv) simulated values, but is closer to the revised version. -Table ~~31~~ lists ~~other~~ statistical scores for the TOLU lumped species and the other species considered in this study. The mean bias goes from a negative value with the base-case run to a positive value with the revised emissions. There is little difference in the correlation coefficient for the model vs. observation scatterplot between the base-case and sensitivity run. -The changes to the VOC emissions for the revised-emissions run affected their total mass and speciation, and the observations were made sufficiently close to the sources that there was little time for oxidation. -The main sources for VOCs are the processing plants, tailing ponds, mine faces, and off-road vehicles and their spatial allocation (from CEMA, 2010) did not change significantly between the two model-emission versions. The main differences in the model time series between the two simulations are thus in magnitude of concentrations, and hence relatively invariant correlation coefficients might be expected. -The correlation coefficient is more likely controlled by the meteorological model accuracy in the placement of the plumes (i.e. wind direction).

~~Figure S2 illustrates the difference between the 2.5 km TOLU emissions field over the Athabasca OS mining facilities for the revised base case as a spatial map for one selected time (Friday, August, 18Z). The largest increases in the TOLU emission, between the revised and base case run, are noted for the Syncrude Mildred Lake facility over the tailing ponds and open pit mine faces. The Table 1 shows the changes shown here reflect net changes on a facility-wide level. Notable ~~actual and relative~~ increases are also calculated for the Suncor Millennium/Steepbank and the Canadian Natural Resources Ltd (CNRL) Horizon facilities.~~

~~Figure 2 illustrates the correlation between the sensitivity case TOLU output and the base case TOLU output. The flights on August 14 and 23 have the largest TOLU mixing ratios for the aircraft study, and both flights ~~(blue and green points)~~ correspond to box flights around the Syncrude Mildred Lake facility. The SI section includes the model and measurement time series comparisons for the flights on August 14 (Figure S5) and August 23 (Figure S6). Overall, the magnitude of the mixing ratio maximum in the time series are better represented in the revised-emission simulation. This is also reflected in the better slope statistic in Table 3 for the revised-emission simulation. Figure S3 shows the flight path for August 14, color coded as a function of the difference between the modelled revised and base case concentrations. The background is a satellite map image along with the GEM meteorological model wind barbs predicted for that day at 16 UTC. The largest differences in the simulated concentrations (1.8 ppbv) correspond to a location just downwind of the Syncrude Mildred Lake open-pit mine, as expected based on the emission difference map (Figure S2) and the southerly wind direction.~~

~~—Figure 3 shows the time series for a segment of the August 14 flight corresponding to three flight boxes at different heights (green dotted line). The observations are plotted as open circles and the two lines represent the two model results. The model output with the revised VOC~~

emissions clearly captures the main peak of the TOLU concentrations driven by TOLU emissions from the Synerude Mildred Lake facility. The secondary peak occurs from the aircraft flying over the Suncor Millennium/Steepbank facility while on the east side of the flight box pattern. The direct flyover adds uncertainty to the model comparison, as it depends on predicting accurately the early stage vertical mixing of the plume from the Suncor facility.

—Figure is a time series segment for August 23 corresponding to a fly over of the Synerude Mildred Lake (earlier peak in time) and Suncor Millennium/Steepbank (later peak in time) facilities at a constant altitude of 300 magl. Winds were light on this day with variable swings in direction. A double peak pattern is observed in both the model and observations with a 1-min time shift needed to align the peaks. For this fly over, the magnitude of the peaks is better represented with the revised emission model version. We note also that the one minute lag time of the model peaks illustrates the difficulties in prediction of plume location at high resolution; this corresponds to an error in the forecast position of the plume of 6 km, or 2.4 of the model's grid cells, given the aircraft's typical flight speed of 100 m s^{-1} . Small errors in wind direction, the potential for point sources located near grid cell boundaries to effectively be re-located to the grid centroids, as well as directional errors in the forecasted winds, can contribute to these offsets between observed and simulated concentration peaks.

—For the TOLU lumped species, the overall statistical scores change from a small negative bias to a small positive bias with little change in correlation coefficient, which may be controlled in part by the meteorological model accuracy as noted above. However, for the locations where the absolute difference in emissions has changed the most (see Fig. S2), the model time series for the revised emissions shows improvement and this is reflected in the improvement in the slope statistics in Table 1. The larger deviation between model and observed RMSE for the revised

~~emissions likely reflects the error in positioning of the plumes inherent in both simulations—in the revised emissions simulation, the positioning error noted above likely contributes to the increased RMSE value.~~

3.2 Multi-Substituted Aromatics (AROM) Evaluation

The model lumped AROM species includes all multi-substituted aromatics, with the most important species being the xylene isomers and trimethylbenzene isomers. -These two species match with the PTR-MS C8 and C9 aromatic fragments, respectively. However, the observed C8 aromatic also includes ethyl-benzene and the C9 aromatic also includes propyl-benzene, which are lumped with TOLU in the model VOC speciation. -Thus, we need to subtract these unwanted species from the totals used to compare to the model lumped AROM species. To do this, we use their correlation slopes with PTR-MS C7 aromatic from Section 3.1. -The new observation-derived AROM was calculated from the PTR-MS measurements as follows: $C8 + C9 - 0.376 C7 - 0.0652 C7$.

Figure ~~3S4~~ shows the histograms for the lumped AROM species for 10-sec averaged points along all the flight tracks. The base model has a large number of high value points (> 2ppbv), many more than the model simulations with the revised emissions, and also more than the observations. This can be quantified by using the 99% percentile (obs=0.7607, revised=1.004, base case=2.302). The median value for the observations is 0.0182 ppbv, smaller than both the model versions (revised=0.0236 ppbv, base case=0.0466 ppbv), but closer to the model driven by the revised emissions. Table ~~31~~ lists other statistical scores for the AROM lumped species. The mean bias and RMSE are smaller for the revised emissions run compared to the base case. However, there is a small degradation in the correlation coefficient with the sensitivity run.

The largest decreases in the AROM emission field between the revised and base case emissions Figure S5 displays the difference between the 2.5 km AROM emissions field over the Athabasca OS mining facilities for the revised emissions and base case emissions. The largest ~~decreases~~ are again over the Syncrude Mildred Lake facility (refer to Table 1). There were also notable decreases over the CNRL Horizon and Shell Muskeg/Jackpine facilities, but positive changes in AROM emissions were noted over the Suncor Millennium/Steepbank facility (also refer to Figure S2 for the emission spatial difference map). ~~Figure S6 shows the flight track for the August 23 survey flight, which flew over all the facilities. The background map shows model winds were light and variable on this afternoon. The flight track is color-coded as a function of the difference between AROM from the sensitivity base case. Consistent with the emission changes, negative difference in ppbv were modelled over Synerude, Shell, and CNRL and positive differences in ppbv over Suncor.~~

—Figure 5 shows the time series for a segment of the August 23 survey flight over Synerude Mildred Lake and Suncor Millennium/Steepbank. The largest maxima are for times over Synerude (7:31Z) and, while both runs show an over prediction in plumes, the sensitivity run predictions are closer to observations. Panel B is the time series for a short segment later in the flight for locations over the Synerude (earlier peak in time) and Suncor (later peak in time) facilities. For the Suncor maximum, the sensitivity run with revised emissions has a better prediction for the magnitude of the mixing ratio change.

—Figure S7 shows the box flight track on September 3, which was focused on quantifying emissions from Synerude Mildred Lake facility. The flight path also included some turns over the Suncor Millennium/Steepbank facility. Similar to the August 23 flight, there are negative differences in the predicted AROM mixing ratio between the sensitivity and base runs over

~~Synerude and positive differences over Suncor. The decreases in mixing ratio are as large as 2 ppbv. Figure 6 is the time series for a segment of the September 3 flight. The observed mixing ratios are closer to the predictions from the revised emissions model run compared to the base-case run.~~

~~—The SI section includes the model and measurement time series comparison for the flights on August 23 and September 3. In general, the observed mixing ratio changes are closer in magnitude to the predictions from the revised-emission simulation compared to the base case for the plume intersects. From the overall statistics and the case studies, the revised emissions model run output for lumped AROM species compares better to observations than the base-case emissions run, reducing the mean bias by a factor of three, and the RMSE by a factor of two (Table 1), and giving a better overall performance for the histograms of AROM concentration.~~

3.3 Long-Chain Alkanes (ALKA) Evaluation

The long-chain alkanes (C₄ to C₁₂) were sampled by filling canisters with ambient air on-board the aircraft. Figure ~~4S8~~ presents the histogram for the long-chain alkanes. The mixing ratios are divided into 20 bins each with a width of 3 ppbv. From the observed histogram, there is a wide range to the mixing ratios with a small number of very large concentrations, but also the first bin (0 to 3 ppbv) has a high percentage of the points. The model gas-phase mechanism represents all higher carbon-number alkanes by a single lumped species, with chemical and physical properties derived from C₄ to C₈ alkanes. The base-case run calculates lower ALKA mixing ratios than the model version using revised emissions. The model using revised emissions is much better at reproducing the higher concentration points, particularly above 12 ppbv. This is quantified by the 99% percentile of the data sets (obs=29.9, base=18.0 revised=24.6). Other statistics for the lumped ALKA species are shown in Table ~~34~~. The mean bias went from a small

negative value to +1.98 ppbv. The slope decreased by a small value, but the y-intercept increased, which also increased the RMSE for the run with the revised emissions. The correlation coefficient improved significantly for the model run with revised emissions.

~~Figure S9 shows the difference in emission rate between the revised emissions and the base-case emissions. Interestingly, the revised ALKA emissions are considerably higher for the CNRL Horizon and Shell Muskeg/Jackpine facilities, but have smaller changes for the other facilities (refer to Table 1), possibly reflecting differences in the processing activities between the facilities.~~

~~Figure S10 shows the differences between the two model predictions for ALKA at the observation canister sample locations, for the flight on August 26. On this day, winds were from the northeast and notably Fort McMurray (further to the south, not shown) had quite poor air quality. The largest differences in the modelled mixing ratios correspond to observation locations south of CNRL. Positive differences as large as 20 ppbv were simulated for some points. Figure 7 shows the time series for the observations, revised emissions model results, and base case model results for the Aug. 26 box flight around the CNRL Horizon facility. A clear improvement in ALKA modelling is observed when using the revised emissions for the plume sampled downwind of the CNRL facility.~~

~~There were two other box flights around the CNRL Horizon facility. The flight on August 20 also showed an improvement in ALKA predictions when using the new emission data set. Winds were from the west on this day. The flight on Sept. 2 showed the opposite trend, with more of an over-prediction with the revised emissions. Winds were from the north on this day. The background ALKA on this flight was predicted to be higher for the sensitivity run; however,~~

~~the differences in mixing ratio between background and plume were still over-predicted with the revised emissions and under-predicted with the base emissions.~~

~~—The other facility that had large increases in ALKA emissions with the revised data was the Shell Muskeg/Jackpine facility (Fig. S9). Flight 9 on August 21 was a box flight around the Shell facility. A detailed analysis of this flight showed that for the majority of the data points on this flight, the model run with the base case emissions showed the best results, except for the three highest measured canister samples, where the model run with the revised emissions performed better. This likely reflects an uncertainty in the spatial allocation maps used to distribute the emissions with a higher fraction of emissions needed at the point-specific locations.—~~ Overall, the time series analysis for the aircraft flights (refer to Figures S10 and related discussion in SI) ~~the ALKA statistics showed~~ mixed improvements for ALKA associated with the revised emissions, ~~using the entire data set. The correlation coefficient does improve significantly.~~ The large increases in ALKA emissions in the sensitivity simulation for the CNRL facility did improve the model maxima for the plume intersects on August 26, time-series downwind. The analysis suggests further improvement in spatial allocation for the Shell facility may be needed. The higher ALKA mixing ratios also feeds back to higher SOA formation downwind of these facilities, as discussed below.

The use of aircraft observations to both derive emissions data and evaluate the subsequent model simulations might be taken as circular reasoning. We note first that observation-derived emissions are frequently used in modelling (for example, Continuous Emissions Monitoring System concentration observations are used to generate emissions data for large stack emitters), and second, that the emissions are only one component of the overall modelling system. An improvement in the simulated VOC concentrations using observation-based emissions is only

guaranteed if the emissions dominate the net model error. While our results show that, in general, the new emissions information does improve model performance, the results using that new data are not perfect, indicating other sources of error are contributing to the overall model performance.

3.4 Organic Aerosol (OA) Evaluation

Figure 5 S11 illustrates the histograms for the organic aerosol observations and model results with base case and revised emissions. A clear improvement is shown in the highest concentration bins ($>15 \mu\text{g}/\text{m}^3$) with the revised emissions. This can be quantified with the 99th percentile of the data (obs= $13.4 \mu\text{g}/\text{m}^3$, revised= $9.3 \mu\text{g}/\text{m}^3$, base= $4.9 \mu\text{g}/\text{m}^3$). The median statistics also improved (obs= $2.8 \mu\text{g}/\text{m}^3$, revised= $0.84 \mu\text{g}/\text{m}^3$, base= $0.70 \mu\text{g}/\text{m}^3$). The lower 5th percentile is also significantly under-predicted compared to observations and does not change much between the two model runs (obs= $0.49 \mu\text{g}/\text{m}^3$, revised= $0.036 \mu\text{g}/\text{m}^3$, base= $0.035 \mu\text{g}/\text{m}^3$). This reflects an under-prediction in the background OA predicted by the model, which is likely due to ~~too~~ low ~~a level of~~ biogenic SOA formation and aging in both model versions. The importance of widespread biogenic SOA formation from boreal forests has been reported in other work (Slowik *et al.*, 2010; Tunved *et al.*, 2006).

~~The other Additional~~ statistics are presented in Table 34. The mean bias, RMSE and slope all improve for the revised-emissions run, though the correlation coefficient decreases significantly for this run. ~~The decrease in correlation suggests that the improved bias may not always be the result for the right reasons for some points. To investigate this further, this study looked at the model PM_{10} OA bias as a function of different observed variables. Figure 8a shows the base case model bias as a function of observed PM_{10} sulfate for individual points. Figure 8a is color coded as a function of the model %SOA relative to model OA. There is a trend of increasing negative~~

~~bias in model OA in the base case with increasing observed sulfate aerosol. This suggests that air masses that originate from sources high in SO₂ tend to be under-estimated in simulated organic aerosol. These air masses also tend to have large %SOA in the base model. Figure 8b is the same plot but for the model run using revised emissions. There are a large number of points that are relatively high in observed sulfate (>1 µg/m³) that change from a negative OA bias to a positive OA bias and these points also shift to being dominantly POA in model composition (low %SOA, blue points). The model output confirms that much of the increase in model OA in the sensitivity run originates from the increase in primary PM emissions and from the increase in the mass fraction of that primary PM assumed to be OA (based on Wang *et al.*, 2015). The revised emissions simulation has less organic aerosol bias at high sulfate loading suggesting that the improved results are closely linked to model organic emissions co-located with sources of SO₂.~~

To investigate the variability in the OA bias, we plotted the OA bias as a function of different measured variables. Figure 6 9a is a plot of the OA bias as a function of the observed black carbon (BC) aerosol for the base-case and sensitivity runs. The BC is a marker for petrochemical combustion, particularly diesel. For the base-case run, the OA negative bias is observed to increase in magnitude with observed BC. Points with high observed BC correlate well with emissions from the OS open-pit mines (Liggio *et al.*, 2017), where the BC is likely emitted from the heavy-hauler trucks. ~~This~~ The locations with the largest OA bias ~~was~~ were also consistent with the locations of mines and the transport wind direction. A review of the OS emission inventories suggest that about 70% of the BC comes from the OS off-road diesel fleet. Including all points, the mean bias improves from -2.8 to -2.4 (see Table 34) when using the revised emissions. Figure 69b shows a zoomed plot for points with high observed BC (>0.8 µg/m³). There is a clear improvement in bias for most of these points. The average bias for these high BC

points improves from $-6.8 \mu\text{g}/\text{m}^3$ for the base case to $-2.6 \mu\text{g}/\text{m}^3$ for the revised emissions. For emissions processing the increase in PM emissions was assigned to the processing plants (particle bin $D < 1 \mu\text{m}$) or the surface mines (particle bin $D > 1 \mu\text{m}$). Overall, Figure 6 shows that, while the negative OA bias improves for samples high in BC concentration (i.e. influenced by petrochemical combustion or collocated with petrochemical combustion sources), there still remains an unaccounted for negative OA bias. Note that anthropogenic SOA formation should be minimal for the high BC points close to the emission source, so uncertainties stemming from the model SOA formation mechanism should be reduced. The revised emissions simulation has less bias as a function of observed black carbon, suggesting that the improved results are closely linked to model emissions with similar sources to the black carbon.

Figure ~~7~~ 10 is a scatterplot of the difference in predicted POA between the revised and base-case emissions runs vs. the difference in predicted total OA. A large fraction of the points fall along the 1:1 line, and hence for these points the difference between the two runs is almost completely due to the increased total primary PM emissions, and increased POA fraction of those emissions, of the revised emissions simulations. The points with largest concentrations along the 1:1 line correspond to flights over the Syncrude Mildred Lake facility on Aug. 16, Aug. 23 and Sept. 3. There is a subset of points, however, that lies below the 1:1 line; these correspond to points with significantly enhanced model SOA between the two runs (Aug. 16 flight over CNRL Horizon and Aug. 21 survey flight over Shell Muskeg/Jackpine). The SI section includes the model and measurement time series comparisons for the flights on August 21, August 23 and September 3. Overall, the case studies showed improved predictions for the magnitude of the organic aerosol change for the plume passages with the revised emissions; however, the base line organic aerosol was over-predicted for all case studies.

—The focus of the flight on Aug. 21 was an enclosing box pattern around the Shell Muskeg/Jackpine facility at different altitudes. The approach to this facility, however, also included an overpass of the Synerude Mildred Lake facility. Figure S13 illustrates the flight path color-coded as a function of POA difference (revised emissions—base case) and SOA difference (revised emissions—base case). The corresponding time series for OA observations, the revised emissions model run, and the base case emissions model run OA predictions are shown in Figure 11. There is a clear “hot spot” in POA difference in Figure S13a located over the Synerude Mildred Lake facility. This hot spot corresponds to the first large maxima in the times series in Figure 11 (17:17 UTC). The observations at this time lie between the predictions from the two model simulations, though the overestimate of the revised emissions simulation is closer to the observations than the underestimate of the base case emissions simulation. The aircraft then entered the box pattern at different altitudes around the Shell Muskeg/Jackpine facility, and each successive pass around this facility intersected the observed plume on the north-east corner of the flight box (see hot spot, Figure S13b); the model predicts that the increase in OA is largely due to SOA (as implied by Figure 10), and the revised emissions simulation produces peak OA concentrations that are closer to the observations than the base case emissions simulation. As is clear from Fig. 11, the base case emissions simulation greatly underestimated the OA relative to observations. In examining the time series, it is also clear that both model simulations are underestimating the background biogenic OA concentrations, by about $0.5 \mu\text{g m}^{-3}$. The height of the peaks relative to background is closer to the sensitivity run peaks than the base case run peaks.

—Figure S14 shows the difference between revised emissions and base case model OA predictions for another case study, for southerly winds with a box flight over the Synerude Mildred Lake facility. The flight started and ended with a horizontal zig-zag pattern with

overpasses directly over the facility emissions sources. This corresponds to the initial spikes in the model in the time series shown in Figure 12 (8:30 p.m. UTC). Again, the observed height of the peaks lies between the model peak heights for the base case and revised emissions simulations. For this flight the background OA concentration is under-predicted by up to $2 \mu\text{g}/\text{m}^3$ by the end of the flight. The background air has more measured oxygenated organic aerosol (OOA) (Liggio *et al.*, 2015), with an aerosol mass spectra more reflective of laboratory monoterpene SOA (Han *et al.*, 2017). During the box pattern, the peak heights in the observations more closely match the base model peaks. The PM_{10} emission rates derived from the five box flights around Syncrude Mildred Lake did show more variability than for the other facilities. The average of five aircraft-derived PM_{10} emission rates was used to revise the PM_{10} emissions for Syncrude in the revised emissions data used by the model. Interestingly, the largest observed OA value was measured in the spiral into the free troposphere near the end of the flight. There is no corresponding peak in the model at this time. The model peaks again only after the flight path has dropped into the boundary layer. Note that there was no corresponding increase in acetonitrile observed in the free troposphere so the source of the elevated OA is not likely from biomass burning, but may represent long range transport from other sources.

—The last case study is for the survey flight on August 23. Figure S15 shows the corresponding flight path color-coded by POA difference (revised—base case emissions; panel a) and SOA difference (revised—base case emissions; panel b). From Fig. S15a, we can again see the local maxima in POA difference between runs over the Syncrude Mildred Lake facility. This corresponds to the peaks in time series at 5:50 p.m. UTC (Figure 13). The observed peaks are closer in magnitude to the base case model peaks at this time. The peak at 7:40 p.m. UTC corresponds to another time later in flight over the same location. The peak in SOA difference at

6:20 p.m. UTC is downwind of the CNRL Horizon facility (red points in Fig. S15b). The observations show a more broadly spread out peak at this time than is predicted by the model, perhaps indicating a greater degree of turbulence or wind variability in the observations than predicted by the model. Both modelled and observed meteorology had light wind speeds with a high degree of variability in direction on this day. The variability in the observed winds at the local Mildred Lake weather station was large on this afternoon with hourly averaged wind directions of 40°, 290°, 180°, 20°, 40° from 12–16 UTC and wind speeds all less than 6 km/hr. These light, variable winds result in a more dispersed nature of the observed organic aerosol. The peak in observations at 6:25 p.m. UTC is represented well by the revised model. This corresponds to a location over Shell Muskeg/Jackpine (light blue points in Fig. S15a). Note that Fig. 13 suggests that background OA levels once again seem to be under-estimated in both simulations.

3.4.2 Organic Aerosol Model Recommendations

In summary, the improvement in model PM₁ OA bias due to the use of the revised emissions is encouraging; however, the decrease in correlation coefficient suggests that the spatial allocation of PM₁ emissions may need further refinement. The remaining negative bias suggests that other important processes may be missing or under-represented in the model. Three recommendations emerge from recent and current work:

The under-prediction in background OA was a general finding from the study; the cause is believed to be due to underestimated biogenic SOA, due to the lumping of biogenic monoterpene emissions into the anthropogenic ALKE model species in the model's gas phase mechanism, and the lack of speciated representation of other biogenic SOA precursors such as sesquiterpenes. Biogenic SOA mass yield stoichiometric coefficients, based on more recent chamber

~~experiments that consider vapor wall loss, should also be used for future modeling. Future aircraft observations should include a biogenic emission closure flight, where the aircraft flies a box pattern over a boreal forest location where the tree speciation is uniform and observed and modeled surface emission fluxes are then compared.~~

1) SOA Formation from Fugitive IVOC Emissions

~~Recent publications also suggest that fugitive intermediate volatile organic (IVOC) emissions from the OS open-pit mines are needed to represent SOA formation downwind of the OS region (Liggio *et al.*, 2016). In our emissions revision, only a small portion of the IVOCs (dodecane C₁₂) were added and lumped placed into the long-chain ALKA lumped species. IVOC species with carbon number >13 were not measured by the Li *et al.*, (2017) aircraft study and thus we do not have revised IVOC emissions included in this work. Furthermore, the ALKA lumped model VOC species has an SOA yield more representative of a lower molecular-weight range, and the yield is known to increase with increasing carbon number, so the dodecane SOA contribution would be underestimated. Work is currently underway with GEM-MACH to implement a Volatility Basis Set (VBS) approach to SOA formation. The VBS approach will more adequately represent the intermediate and semi-volatile volatility range and chemical aging of this lower volatility compounds (Robinson *et al.*, 2006). Future work will measure IVOC emissions using box flights around the oil sand facilities and open-pit mines. This will remove current uncertainties in models and help improve the negative bias in plumes. Implementing the VBS scheme will also enable the PM emissions used here (in both data sets) to be distributed into volatility bins.~~

~~Also, while the measurement-derived emissions are missing the IVOCs, the measurement-derived POA emissions may contain some gaseous VOCs, IVOCs and SVOC species that react~~

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quickly and in one oxidation step yield products that condense onto particles. This rapid SOA mass produced would be measured in the box flights and, at least partially, accounted for in the updated OA emissions; however labeled here as POA instead of fresh SOA. Furthermore, there is the potential for double counting if some of the very reactive gaseous precursors react to form SOA and this is accounted for in the measured POA. In this paper, we have tried to minimize this effect by examining the model performance in the “near field” from emission flights close to facilities. This will be the topic of future box modelling work with the new 2018 measurement-derived IVOC and SVOC emissions to determine how much of the measurement-derived POA is derived from the fugitive open-pit mining IVOC and SVOC emissions and their rapid particle formation.

2) Background Organic Aerosol Levels

The under-prediction in background OA was a general finding from the study; the cause is believed to be due to underestimated biogenic SOA, due to the lumping of biogenic monoterpene emissions into the anthropogenic ALKE model species in the model’s gas-phase mechanism, and the lack of speciated representation of other biogenic SOA precursors such as sesquiterpenes. Future work will update the biogenic SOA yield coefficients in the VBS approach using recent smog chamber results which account for gas-phase loss of organic species to chamber walls (Ma *et al.*, 2017).

3) Spatial Allocation of Emissions

Future field studies should also focus on improving within-facility spatial allocation. For example, within-facility data such as the GPS location of the mining trucks would be helpful to derive their activity diurnal profiles and to improve ~~truck~~ their emission spatial allocation within

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a facility. The GPS data would also be useful to define the location of freshly excavated open-pit mines within a facility.

4) Conclusions

Overall, the weight of evidence suggests that the top-down emission estimation technique applied to revised aircraft measurement derived organic emissions for the OS surface mining facilities helps to better constrain reported facility-total organic emissions including for fugitive sources, as shown by improved model results when the revised emissions are employed. We note that emissions from these sources are a challenge to calculate in bottom-up inventories due to the potential for fugitive emissions. For the mono- and multi-substituted aromatics (TOLU and AROM), the emission rates from facilities were more fine adjustments, as some facility totals went up and some went down and the overall biases compared to observations improved for AROM but degraded for TOLU. However, the model's ability to predict very high aromatic concentrations in plumes improved with the revised emissions, as shown by the 99th percentile statistic and the case studies.

For the long-chain ALKA species, the revised emissions may have over-corrected, on average, as shown by the increase in mean bias for the entire aircraft data set. However, the correlation coefficient did improve significantly for the long-chain alkane predictions, suggesting the combination of alkane emission increases for some facilities and decreases for others helped to improve the spatial distribution of ALKA emissions. The results for some facilities suggest that further improvement could be achieved by putting more emissions at extraction processing plant locations (i.e., adjusting within-facility spatial allocation). Interestingly, the alkane emission increases and aromatic emission decreases, derived from aircraft data (Li *et al.*, 2018), were associated with the facilities that use paraffinic solvents for bitumen extraction (e.g. Shell

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Muskeg/Jackpine) and Synerude Aurora North; Li *et al.*, 2017). Overall, the predictions of alkanes in high concentration plumes improved with the revised emission data set, as shown by the 99th percentile statistic.

For PM₁ organic aerosol, the revised emissions improved the mean bias for predictions; however, a negative bias still exists and the improvement was associated with a decrease in correlation coefficient. The increase in predicted PM₁ OA concentration was largely due to the increase in POA emissions in the revised emissions input files. The POA emissions increased because of a combination of larger ~~aircraft~~-measurement-derived PM₁ emissions and the revised ground-observed PM speciation profile having a larger POA fraction. The increase in PM₁ POA emissions were largely allocated spatially to stack locations and this allocation may be a key factor in the degradation of the correlation coefficient, especially if the fine OA originates from mine-face fugitive emissions. Future work should focus on improving within-facility spatial allocation of emissions. The remaining negative bias in plumes likely stems from missing IVOC emissions in both the emission data sets used here, as suggested by Liggio *et al.* (2015). Ongoing field work to measure the IVOC emissions using aircraft box flights is underway in a new 2018 measurement intensive. Upcoming modelling work with GEM-MACH will include the VBS approach to better represent lower volatility compounds.

~~A portion of this aircraft measurement-derived POA emission increase could stem from rapid SOA formation in the interior of the aircraft flight boxes. It was recently discovered that IVOC SOA formation can be important in OA formation downwind of the OS surface mining region and the IVOC emissions came from open pit mine fugitive emissions. GEM MACH does not currently include the IVOC emissions from open pit mines, as the estimation of the IVOC emission rate and SOA aging rate are the subject of ongoing Lagrangian box model studies.~~

~~Furthermore, the increase in PM₁-POA emissions were largely allocated spatially to stack locations and this allocation may be a key factor in the degradation of the correlation coefficient, especially if the fine OA originates from mine-face fugitive emissions. Future work should focus on improving within-facility spatial allocation of emissions.~~

Acknowledgements

The authors are grateful to all of the participants in the 2013 JOSM intensive field study for their commitment. The authors are also appreciative of the ECCC Pollutant Inventory and Reporting Division (PIRD) and the U.S. EPA for developing, maintaining, and distributing each country's national emission inventories. We also appreciate the efforts of George Marson of ECCC in helping to compile the various emissions inventories from Alberta Environment and Parks, and also CEMA. We also appreciate the analysis of the NAPS VOC measurement group. This study was funded by the Joint Oil Sands Monitoring program and the Climate Change and Air Quality Program.

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Table 1. Facility total emission rates for three lumped organic species and PM_{2.5} calculated with the bottom-up, base case inventory, CEMA facility-specific VOC profiles (labeled Base Case) and the top-down measurement-derived rates (labeled Revised Emission case, scaled to tonnes/year for VOCs or tonnes/Aug&Sept for PM_{2.5}). Emission rate increase/decrease of more than ±500 tonnes compared to base case is shown in red/blue.

<u>Species</u>	<u>Suncor – M/S</u>		<u>Syncrude - ML</u>		<u>Shell – MR/J</u>		<u>CNRL - Horizon</u>	
	<u>Base Case</u>	<u>Revised</u>	<u>Base Case</u>	<u>Revised</u>	<u>Base Case</u>	<u>Revised</u>	<u>Base Case</u>	<u>Revised</u>
<u>Mono-Substituted Aromatics (TOLU)</u>	486	1112	806	1539	6.8	72	135	393
<u>Multi-Substituted Aromatics (AROM)</u>	1457	1569	5273	1696	746	88	1125	500
<u>Long Chain Alkanes (ALKA)</u>	5636	13488	12348	10022	1690	14384	2651	23779
<u>Particulate Matter (PM_{2.5})</u>	1251	2537*	1021	3648*	459	2423*	402	1015*

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VOC revised-emissions are based on annual estimates, derived in Li *et al.*, (2017). The estimates consider monthly and annual oil production yields reported by facilities for the plant stack emissions. For tailing ponds and mine faces, the VOC estimates are calculated using a surface-to-atmosphere mass transfer model considering ambient temperature and wind speed.
 * PM_{2.5} revised emissions are based on 2-month emission (Aug&Sept) rather than based on an annual estimate (Zhang *et al.*, 2018) due to uncertainties in calculating dust emissions in the winter months.

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Table 2. Facility-specific VOC speciation profiles (mass fractions) applied to the surface mining facilities in the Athabasca oil sands region compared to standard speciation profiles for Canadian and U.S. petrochemical oil refineries (in ADOM-II chemical speciation). Data are based on Zhang *et al.* (2018) and references therein. All four profiles are used in the base case simulation.

<u>Species</u>	<u>Shell M/J, Syncrude AN, Imperial Kearn Base Case Plant Profile (CEMA)</u>	<u>Syncrude ML, Suncor, CNRL Base Case Plant Profile (CEMA)</u>	<u>CEPS Database Standard Profile #9012 For Oil Refineries in Base Case</u>	<u>SPECIATE Database Standard Profile #0316 For Oil Refineries in Base Case</u>
<u>EC38 (Propane, Benzene, Acetylene)</u>	<u>0.0</u>	<u>0.0</u>	<u>0.247</u>	<u>0.176</u>
<u>EA3 (Alkane ≥C4)</u>	<u>0.90</u>	<u>0.71</u>	<u>0.623</u>	<u>0.781</u>
<u>EA2 (Alkene ≥C3)</u>	<u>0.007</u>	<u>0.069</u>	<u>0.031</u>	<u>0.002</u>
<u>ETOL (Toluene and other mono-aromatics)</u>	<u>0.001</u>	<u>0.057</u>	<u>0.005</u>	<u>0.008</u>
<u>EARO (Multi-functional aromatics)</u>	<u>0.0003</u>	<u>0.099</u>	<u>0.003</u>	<u>0.003</u>
<u>EHCO (Formaldehyde)</u>	<u>0.00001</u>	<u>0.0003</u>	<u>0.110</u>	<u>0.0</u>

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Columns do not add up to unity due to “unaccounted for” or “unassigned species” and/or due to consideration of reactivity weighting for the ADOM-II mechanism.

Refinery Profile #9012 is a profile from the Canadian Emissions Processing System (Moran, M.D., M.T. Scholtz, C.F. Slama, A. Dorkalam, A. Taylor, N.S. Ting, D. Davies, P.A. Makar, S. Venkatesh, An Overview of CEPS1.0: Version 1.0 of the Canadian Emissions Processing System for Regional-Scale Air Quality Models. In Proc. 7th AWMA Emission Inventory Symp., Research Triangle Park, North Carolina, Air & Waste Management Association, Pittsburgh, Oct. 28-30, 1997.)

Table 31. Statistical scores from the model simulations with revised and base case emissions; all statistics are relative to observations.

Lumped Species	Simulation	Mean Bias (ppbv)	RMSE (ppbv)	Slope	Y-intercept (ppbv)	Correlation Coefficient, R
TOLU	Base Case	-0.041	0.277	0.217	0.063	0.32
	Revised Emissions	0.049	0.386	0.426	0.125	0.31
AROM	Base Case	0.152	0.435	0.957	0.154	0.41
	Revised Emissions	0.044	0.227	0.383	0.083	0.37
ALKA	Base Case	-0.123	5.556	0.378	2.028	0.24
	Revised Emissions	1.98	6.403	0.335	4.097	0.34
OA	Base Case	-2.79	3.866	0.186	0.252	0.59
	Revised Emissions	-2.37	3.632	0.292	0.273	0.49

RMSE is the root mean square error. Y-intercept corresponds to the model intercept of a model vs observation correlation plot. Mean bias is the model-observation mean score. The better score for a given pair of statistics is shown in **bold-face** font.

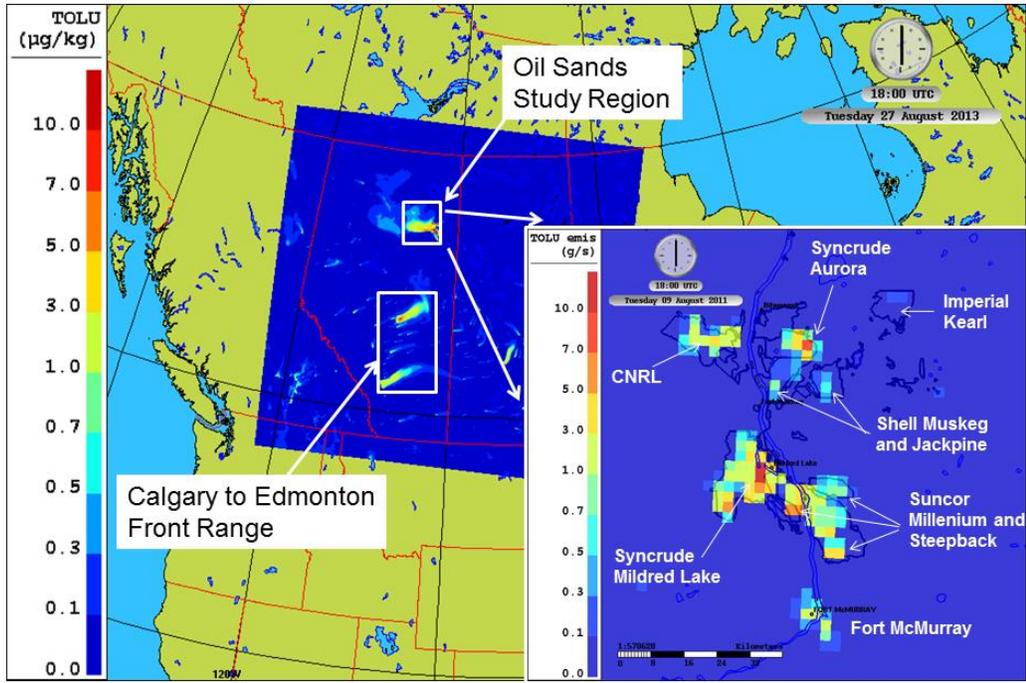


Figure 1. The background image is the nested domain, at 2.5-km grid spacing, covering all of Alberta and Saskatchewan and encompassing the Athabasca Oil Sand study region (white box). The model field shown is for the lumped toluene species (TOLU) mass mixing ratio ($\mu\text{g}/\text{kg}$ air). The inserted image on the right is the TOLU emission map ($\text{g}/\text{s}/\text{grid cell}$) for the Oil Sands study region at the same hour as mixing ratio image on the left. The Oil Sand facility's names are listed in white labels.

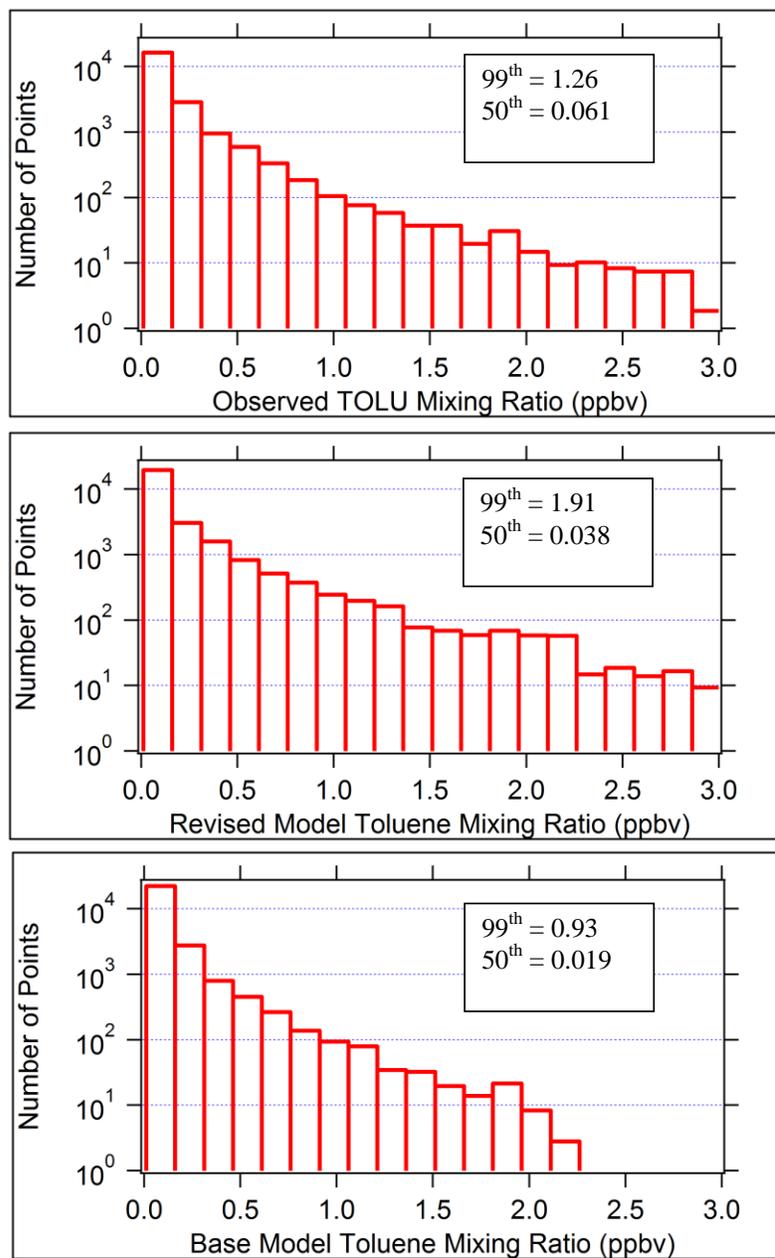


Figure 2. Histograms for (a) observed TOLU, (b) revised-emissions TOLU, and (c) base-case-emissions TOLU volume mixing ratios (ppbv). Points correspond to 10-sec averaged aircraft and model data, sorted into 20 bins by volume mixing ratio. The inset boxes show the 50th and 99th percentile values for each histogram.

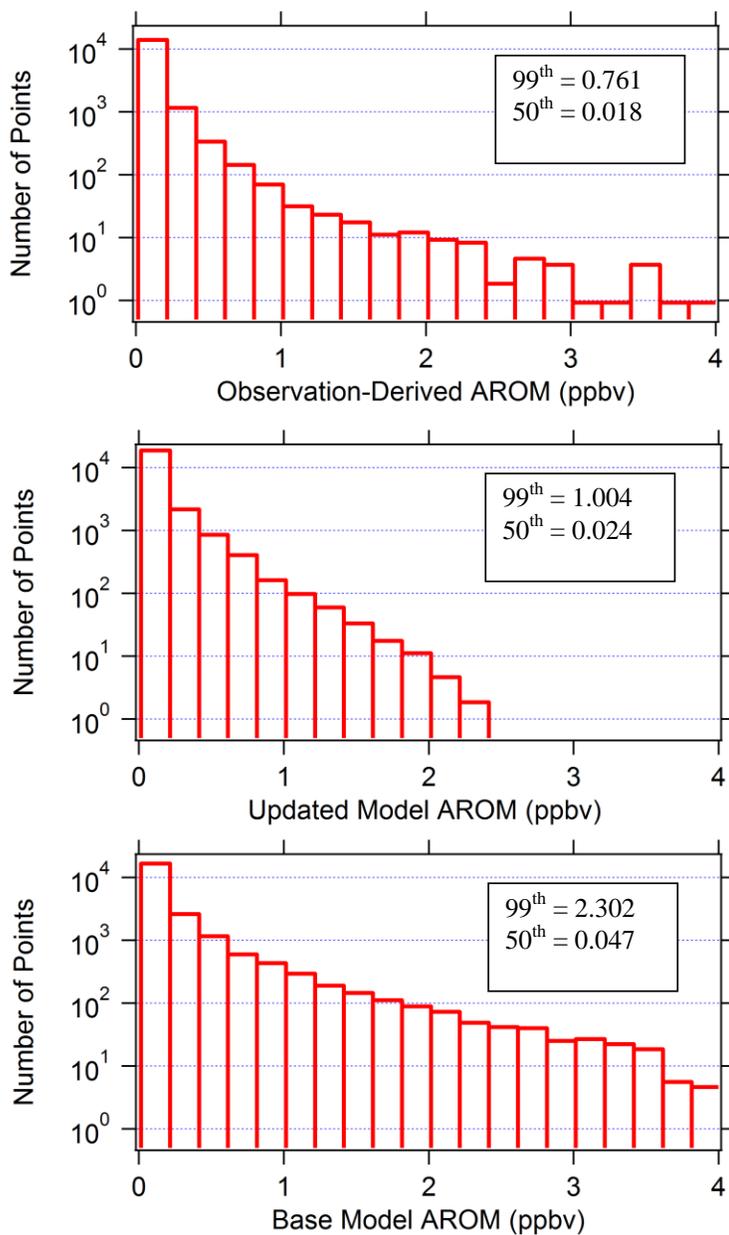


Figure 3. Histograms for (a) observed AROM, (b) revised-emissions AROM, and (c) base model AROM volume mixing ratios (ppbv). Points correspond to 10-sec averaged aircraft and model data, sorted into 20 bins by volume mixing ratio. The inset boxes show the 50th and 99th percentile values for each histogram

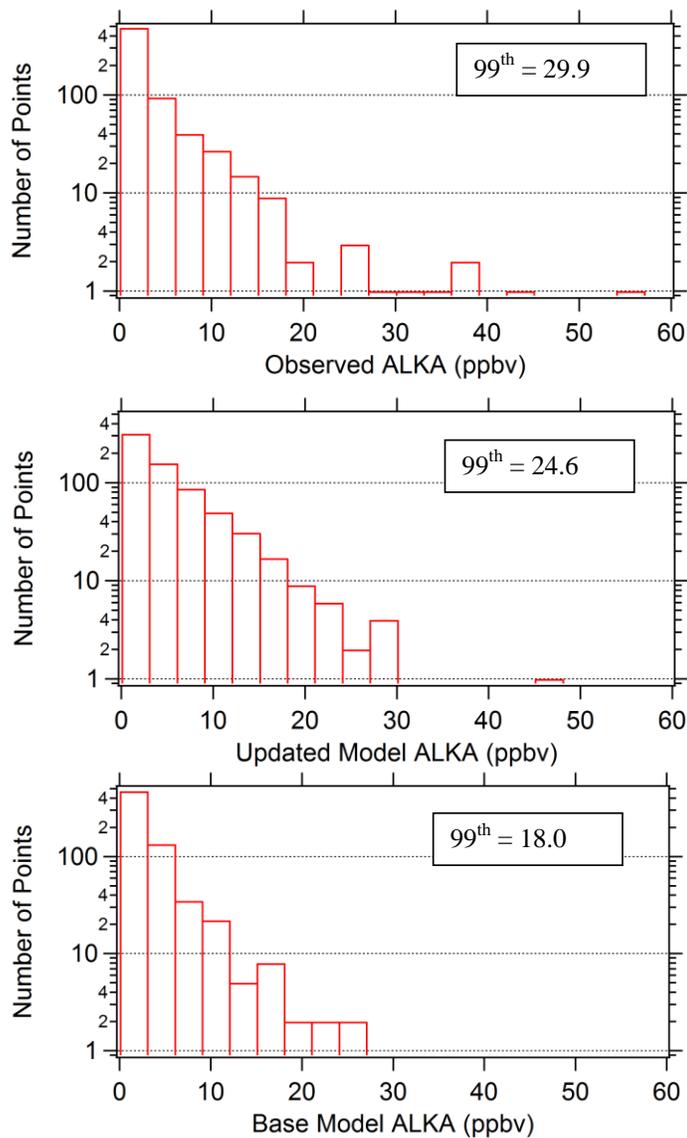


Figure 4. Histograms for (a) observed ALKA, (b) revised-emissions ALKA, and (c) base-case emissions ALKA volume mixing ratios (ppbv). Points correspond to canister grab samples and model data, sorted into 20 bins by mixing ratio. The inset boxes show the 99th percentile value for each histogram.

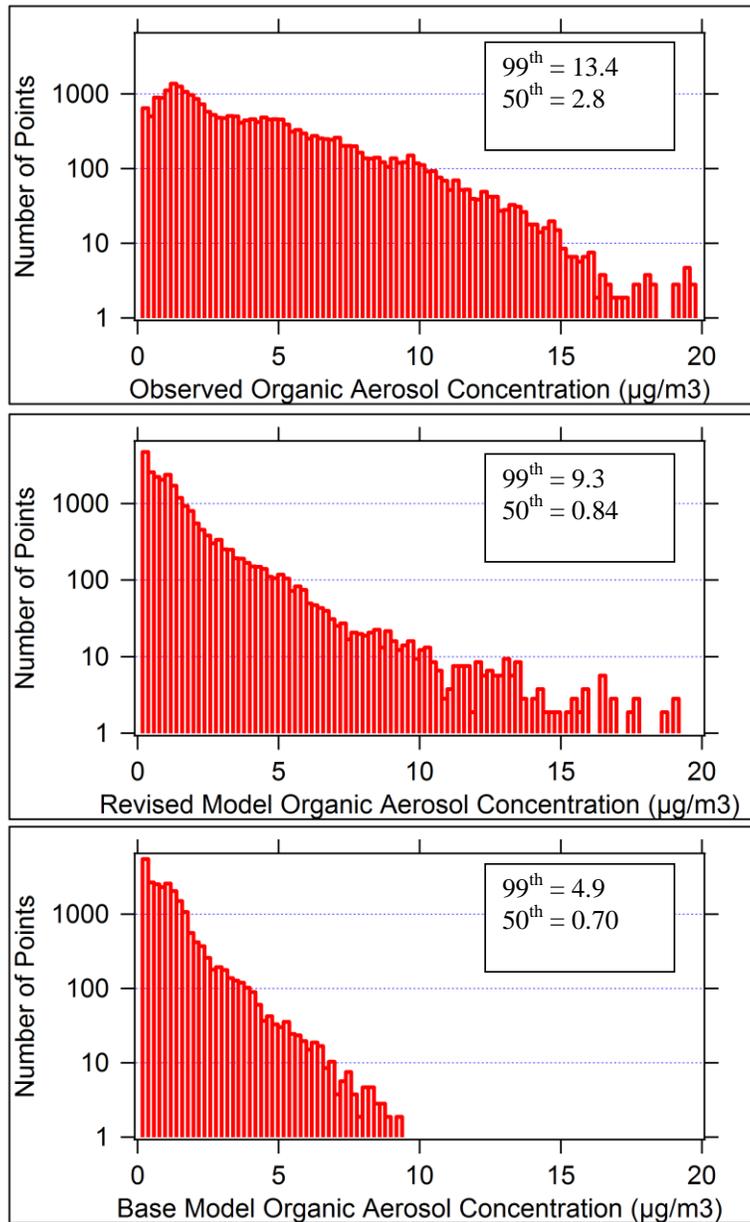


Figure 5. Histograms for (a) observed organic aerosol (OA), (b) revised-emissions OA, and (c) base-case emissions OA concentrations ($\mu\text{g}/\text{m}^3$). Points correspond to 10-sec averaged aircraft and model data. The inset boxes show the 50th and 99th percentile values for each histogram.

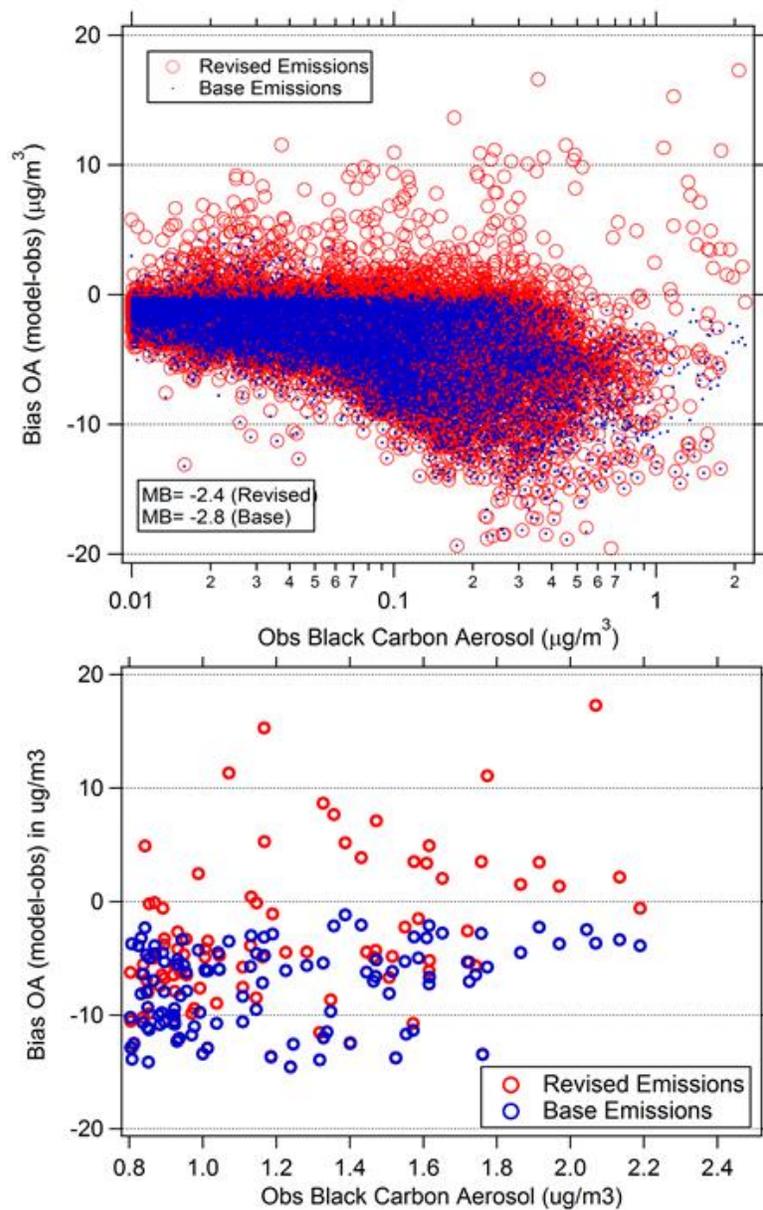


Figure 6ab. Organic aerosol model bias as a function of observed black carbon aerosol. The bottom panel is an enlargement of the upper panel showing only the data points for observed BC > 0.8 µg/m³. The model results for the base-case emissions run are plotted in blue and points in red correspond to the revised-emissions run. The data plotted is for all the aircraft flights.

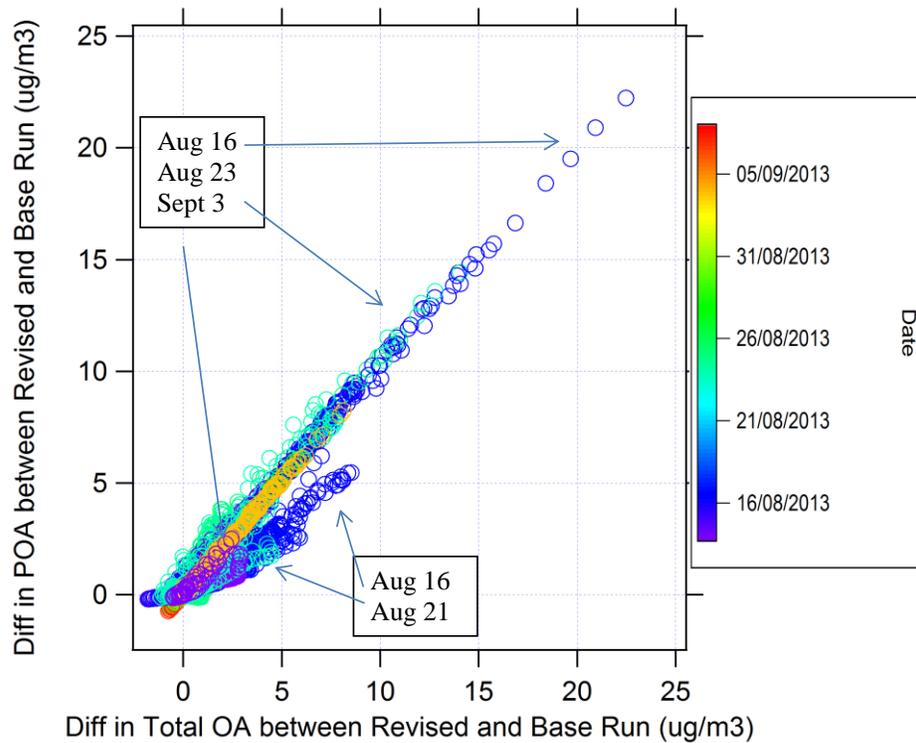


Figure 7. Difference in predicted POA concentrations between revised-emissions and base-case runs plotted as a function of the difference in predicted total OA concentration between the revised-emissions and base-case runs for all flights. Points along the 1:1 line show a difference solely from POA emission changes. Points below the 1:1 line show enhanced SOA formation.