

We thank all the reviewers for their constructive comments. We have modified the paper in response to their comments, questions, and suggestions. Please find below our response to the reviewers and the modified text in *italics*.

#### **Reviewer #1**

**In this study, the authors combined measurements and model to evaluate the role of oil and natural gas (O&G) emissions on the concentration of various gas species and SOA production in the Colorado Front Range. Firstly, the authors implemented top-down estimated O&G emissions in WRF-Chem model and revealed that including O&G emissions results in better agreements in ethane, toluene, OH, O<sub>3</sub> between model and measurements. Secondly, based on different simulation scenarios, the authors showed that the best agreement between measured and modeled OA is achieved by (1) assuming primary OA is non-volatile and (2) limiting the extent of biogenic VOCs aging and subsequent biogenic SOA formation. Thirdly, based on model results, the authors showed that O&G emissions contribute to <5% of total OA in this region. Overall, these findings are important to assess the roles of O&G emissions on air quality. The manuscript is clearly written. I recommend publication after minor revisions to address the main comments below.**

#### **Major Comment**

**In section 3.2, the authors showed that the mean OA concentration was 40-48% higher in O&G influenced plumes compared to urban plumes, which is hypothesized to be due to SOA formation from higher concentrations of aromatics and larger alkanes from O&G emissions. However, in section 3.3.2, including the O&G emissions in the model only increases the OA concentration by ~0.4 ug/m<sup>3</sup> compared to that without O&G emissions. This enhancement amount is not sufficient to explain the observed difference between O&G plume and urban plume (i.e., roughly 1.5 ug/m<sup>3</sup> according to Figure 4A). Similarly, in Figure 10(a) and (b), none of the model scenarios can reproduce the observed OA enhancement in O&G plumes compared to urban plumes. Thus, the authors' hypothesis is not well supported. Please comment on this.**

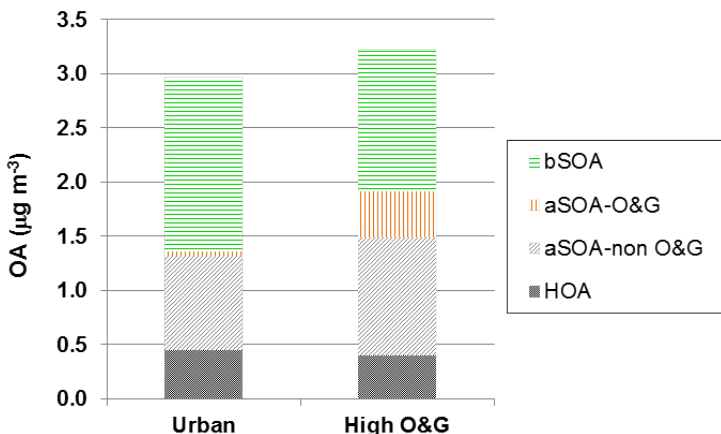
If we understood the comment correctly, the comparison the reviewer refers to in section 3.3.2 (~0.4 ug/m<sup>3</sup>) is not the same as the comparison in Fig. 4. We explored the effect of O&G emissions in plumes that have a strong influence from the O&G sector with and without these emissions in WRF-Chem whereas in Fig. 4 we compared OA values in urban and O&G-influenced plumes. The model comparison that is most similar to Fig. 4 is between urban and O&G plumes in Fig. 10, with top-down estimates of O&G emissions (e.g., gray or blue box and whiskers in Fig. 10). These figures show ~67% (~0.65  $\mu\text{g m}^{-3}$ ) increase in the median aSOA value in O&G influenced plumes compared to urban plumes. That said, the mass concentration difference in modeled OA in high O&G plumes and urban plumes (both with top-down estimates of O&G emissions) is not as high as the difference in the observed concentrations. However, one reason may be overestimation of OA in urban plumes, as discussed in the second paragraph in section 3.3.2. Additionally, since direct measurements of IVOCs are unavailable, their emissions ratios are uncertain. It's also unknown if representing the IVOC mixture in the model as C-16 alkane is realistic. Considering all these factors, we believe the hypothesis that O&G emissions led to increased OA formation in the Front Range is still valid and supported by WRF-Chem results although the magnitude of the influence can be refined in the future when more observation-based representation of IVOCs and their oxidation products are available.

#### **Minor Comments**

**1. In the manuscript, there are many fractional values. For example, O&G sector contributed to <5% of OA; O&G sector contributes up to 38% of anthropogenic SOA; biogenic SOA accounts for 40-54% of total SOA; etc. It is not straightforward for readers to get the whole picture about the OA sources in the studied region. I suggest to include a bar chart to summarize the contributions to**

total OA from different sources. For example, what is the contribution of anthropogenic SOA vs. biogenic SOA. In anthropogenic SOA, what is the contribution of O&G emissions vs other anthropogenic sources.

We thank the reviewer for this great suggestion. We have added the following figure to highlight contributions of different sources to total predicted OA and refer to it in Section 3.3.2: “It is worth highlighting that even with these reduced bSOA values, the predicted contribution of bSOA to total OA in the Front Range remained high, at ~54% and 40% in urban and O&G-influenced plumes, respectively (Fig. 11).”



**Figure 11.** Contributions from HOA, aSOA (non O&G and O&G sources), and bSOA to total OA as predicted by WRF-Chem in the case with non-volatile POA and limited bSOA formation assumptions.

**2. Page 7 Line 35-37.** It is stated that the OA concentration at background CO level was 0.8– 2.3  $\mu\text{g/m}^3$  based on the fitted lines in Figure 1. However, by eyeballing, the OA concentration is about 2  $\mu\text{g/m}^3$  for both lines at 100ppb CO. It is not clear how the reported range is obtained.

The indicated range of background OA represents the range of OA calculated from the ODR slopes at CO=105 ppbv, considering the 95% confidence intervals of the fit parameters. However, we understand that this might confuse the readers, so we have revised the text to only indicate one value corresponding to the calculated OA at CO=105 ppbv, using the best estimates of the slopes and intercepts of the ODR fits. This value, 1.82  $\mu\text{g/m}^3$ , is consistent with the mode of the OA frequency distribution in BL which is at 1.85  $\mu\text{g/m}^3$ . The text has been modified to reflect this change: “Additionally, using the best estimates of the ODR slope and intercept values of the regression lines to the data, the predicted OA at background levels of CO (~105 ppbv) was 1.82  $\mu\text{g m}^{-3}$ .”

**3. Page 11 Line 24-25.** It has been well established that POA is semi-volatile. Are there any reasons, rather than that the non-volatile assumption leads to better model and measurement agreement, to support the non-volatile POA conditions for the studied environment? Also, as mentioned in the manuscript, there are many other reasons why modeled POA is lower than measurement. Without ruling out other possible reasons, it is bold to draw the conclusion that POA is non-volatile in the studied environment.

We agree with the reviewer that uncertainties in POA emission ratios, especially in the O&G sector, or degree of volatility could both be contributing to the lower-than measured predictions of POA. Unlike other studies that use the VBS approach, as stated in the manuscript, we did not increase total POA emissions in the inventory to account for SVOCs. Therefore, total mass of the emitted POA is the same in all sensitivity studies presented in the paper. Note that with an increased POA emission ratio along with the assumption of semivolatile POA, additional SOA precursors would be introduced in the model, leading to additional overestimation of the ambient OA levels. Current emission inventories don’t provide

volatility distributions and/or emission rates for SVOCs. Therefore, it is hard to accurately represent both the volatility and total magnitude of POA emissions in the models. These uncertainties can have profound effects on simulated POA/SOA levels. However, in the absence of any better estimate of the emission ratios or volatility, we performed simulations with non-volatile POA to capture the most extreme effect of uncertainties in volatility. Our intent was not to give the impression that POA in this region is non-volatile, but rather that the predicted POA amounts with such an assumption provided better comparisons with the PMF-based estimates. We have rephrased the text to clarify this point: *“The non-volatile POA assumption may not be accurate, and improved volatility distributions of POA from different combustion sources would have to be considered to accurately account for semi-volatility of POA emissions in future air quality models. However, in the absence of better estimates of POA emission ratios or volatility, the predicted POA values in current simulations with non-volatile POA conditions are more comparable to the PMF-based estimates of HOA in this environment.”*

**4. Page 12 Line 8-9. Please elaborate on why assuming POA non-volatile would reduce anthropogenic SOA, but increase biogenic SOA.**

The reason for reduction in aSOA is that the semivolatile components of POA if assumed non-volatile are not available in the gas phase for oxidation, eliminating the possibility for condensation of the oxidized species on the aerosols. However, since POA concentration is higher when assumed non-volatile, available aerosol mass for absorptive partitioning is higher, resulting in increased partitioning of semivolatile bVOC oxidation products to the aerosol phase and an increase in bSOA concentration. This is now clarified in the text: *“The reason for the reduction in aSOA is that with the non-volatile assumption of POA, its semivolatile components are not available for gas phase oxidation, reducing concentrations of anthropogenic oxidized species that are condensable, thus leading to a decrease in aSOA. On the other hand, since POA concentration is higher when assumed non-volatile, available aerosol mass for absorptive partitioning is higher, resulting in increased partitioning of semivolatile bVOC oxidation products to the aerosol phase, thus an increase in bSOA concentration. Therefore, it appears that most of the increase in urban total OA in non-volatile POA scenarios is due to the contribution from POA.”*

**5. Figure 6. Are the data shown here from O&G plumes or urban plumes?**

Since no significant difference in the mean biogenic VOCs was observed in urban vs. O&G-influenced plumes, data in both plume types in the Front Range boundary layer were considered in Fig. 6. This is now reflected in the caption: *“Comparison of the measured and WRF-Chem predicted (top-down O&G emission scenario) mixing ratios of isoprene (a), methyl vinyl ketone (only available in measurements) and methacrolein (b), and monoterpenes (c) in the Front Range boundary layer”.*

**Reviewer #2**

Several particle and trace gas measurements made from the C-130 over the Colorado Front Range are used to estimate contributions to OA (SOA and POA) from the Oil and Gas (O&G) sector, relative to urban and biogenic contributions, for that region. Further, the authors contrast the results from the observations with simulations of OA (SOA and POA) from the WRF-Chem model. This is a challenging study because it means getting the relative contributions to OA about right from three main sources (biogenic, O&G and urban) in both the measurements and the model. Further, the OA is split between POA and SOA, and the terrain and source distributions are complex, resulting in the potential for many uncertainties. Still, the results of the comparisons are reasonable. With one major exception, I think the work is worthy of publication in ACP.

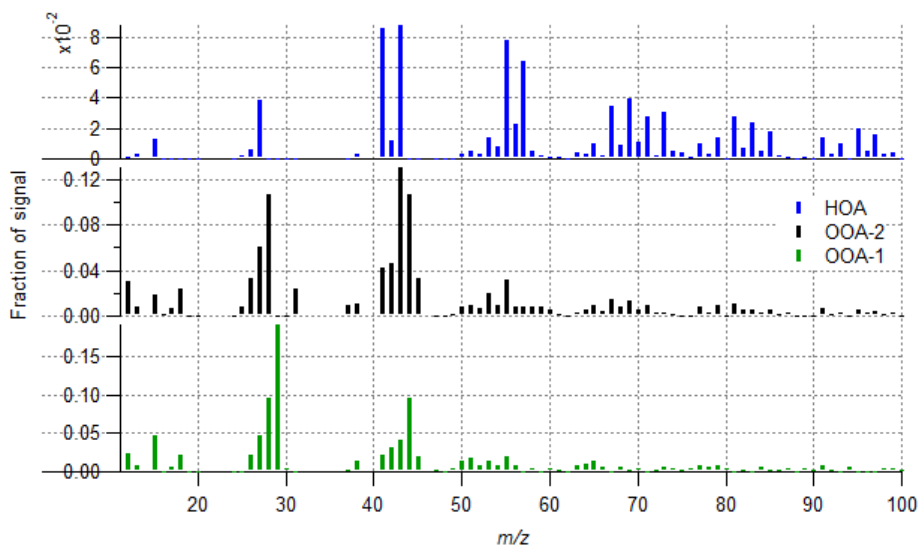
**Major comment:**

Slowik et al. (Figure 5, ACP, 2010, [www.atmos-chem-phys.net/10/2825/2010/](http://www.atmos-chem-phys.net/10/2825/2010/)) showed a large

slope for biogenic OA versus CO, at low NO<sub>x</sub>, that is very similar to many of the orange and yellow points representing the steepest slope of OA vs CO in your Figure 1. Also, their OOA-2 spectrum (possibly representative of semi-volatile OOA) is quite similar to your OOA spectrum (Fig. 3), which means that PMF may not identify a difference between O&G OA and biogenic OA.

I would like to see some improvement in the discussion of the biogenic contribution derived from the observations, including if or how well they can distinguish between biogenic OA and O&G OA. Further, it would be nice to see the authors improve their representation of the biogenic contribution to their observations in their analysis.

We agree with the reviewer that due to extensive fragmentation in the AMS, PMF factors are usually not strong indicators of different sources. In Slowik et al. (2010), air mass history was very distinct when OOA-I was dominating the profile vs. OOA-2. However, in the Front Range, biogenic sources are more mixed in with anthropogenic emissions. We had explored correlations of the OOA factors in a 3-factor solution with external tracers (shown below). Note that we named these factors in a way consistent with the terminology of Slowik et al. (2010), based on the relative intensity of m/z 43 and 44. However, correlations of the two OOA factors with MVK-MACR and sum of biogenic VOCs were very similar and not very strong (*r* values are tabulated below). Correlation of HOA and OOA with CO in this solution was also not as good as in the 2-factor solution. Therefore, we strongly believe that increasing the number of factors is splitting and combining the signals from the 2-factor solution and it will not provide an independent factor, similar to Slowik et al. (2010), in which they could separate out anthropogenic vs. biogenic SOA. We have added the following sentence in Section 3.1 to indicate the weakness of PMF in identifying sources of OOA: *“Increasing the number of factors resulted in split factors and a minimal decrease in  $Q/Q_{expected}$ . When examining correlation coefficients of two of the factors (in a 3-factor solution case) containing signal at m/z 44 with external tracers, only the correlations with CO were significantly different ( $r=0.03$  vs. 0.28) while correlations with other anthropogenic and biogenic tracers (e.g., acetylene, ethane, isoprene oxidation products (i.e., methyl vinyl ketone and methacrolein) and monoterpenes) or aerosol nitrate and sulfate were not significantly different. We therefore believe that the 3-factor solution is unable to determine a meaningful and independent 3<sup>rd</sup> factor, and thus PMF is unable to clearly isolate the contribution of biogenic vs. anthropogenic sources to OOA in this environment.”*



**Figure R1.** Mass spectral profile of factors in a 3-factor PMF solution.

	CO	Acetylene	C2H6	MVK-MACR	Monoterpenes	NO3	SO4	HOA	OOA
HOA	0.35	0.21	0.37	0.50	0.28	0.36	0.45	0.94	0.28
OOA-1	0.28	0.30	0.33	0.48	0.26	0.50	0.57	0.31	0.75
OOA-2	0.03	0.25	0.35	0.44	0.26	0.60	0.60	0.55	0.90

**Table R1.** Correlation coefficients (r) of factors in a 3-factor solution with external tracers. HOA\* and OOA\* factors are as identified in Ng et al. (2011).

**The assumption of low CO underestimates the background OA contribution, and a couple of statements in the conclusions (“with the best match obtained in runs when consecutive aging of bVOCs and bSOA formation was turned off”; “A large fraction (~40-54%) of OA in the Front Range was predicted to be from bSOA”) suggest the use of a constant “background” OA may be a substantial weakness in the observational analysis. The authors obviously recognize this weakness, as demonstrated by their statement on page 13: “It is worth noting that not considering variable background levels of OOA and CO and the uncertainties associated with PMF analysis might have also impacted the comparisons discussed here.”**

We agree with the reviewer that most likely one background value for OA and CO was not representative for all the flights. However, we could not determine appropriate upwind (i.e., background) values of OA or CO in each flight with our flight tracks; thus we decided to not subtract any value from the measurements and let the linear regression analysis determine an average enhancement ratio of OA with respect to CO. The indicated background for CO (105 ppbv) was determined from the mode of the frequency distribution of CO in the BL of Front Range while the indicated range of background OA represented the range of OA calculated from the ODR slopes at CO=105 ppbv, considering the 95% confidence intervals of the fit parameters. However, we understand that this might confuse the readers, so we have revised the text to only indicate one background OA value corresponding to the calculated OA at CO=105 ppbv, using the best estimates of the slopes and intercepts of the ODR fits. This value, 1.82  $\mu\text{g}/\text{m}^3$ , is consistent with the mode of the OA frequency distribution in BL at 1.85  $\mu\text{g}/\text{m}^3$  (which could represent the average background OA). The text has been modified to reflect this: *“Since daily flight patterns did not include regular upwind tracks, it was not possible to determine daily background values to subtract from the measured OA and CO. Therefore, the enhancement ratios were determined by weighted, linear orthogonal distance regression (ODR) fits...”* and *“Additionally, using the best estimates of the ODR slope and intercept values of the regression lines to the data, the predicted OA at background levels of CO (~105 ppbv) was 1.82  $\mu\text{g}/\text{m}^3$ . This value, which was very similar to the mode of the OA frequency distribution in the BL at 1.85  $\mu\text{g}/\text{m}^3$ , is a substantial portion of total OA, suggesting presence of relatively high concentrations of non-combustion related OA, likely of biogenic origin, in the region.”*

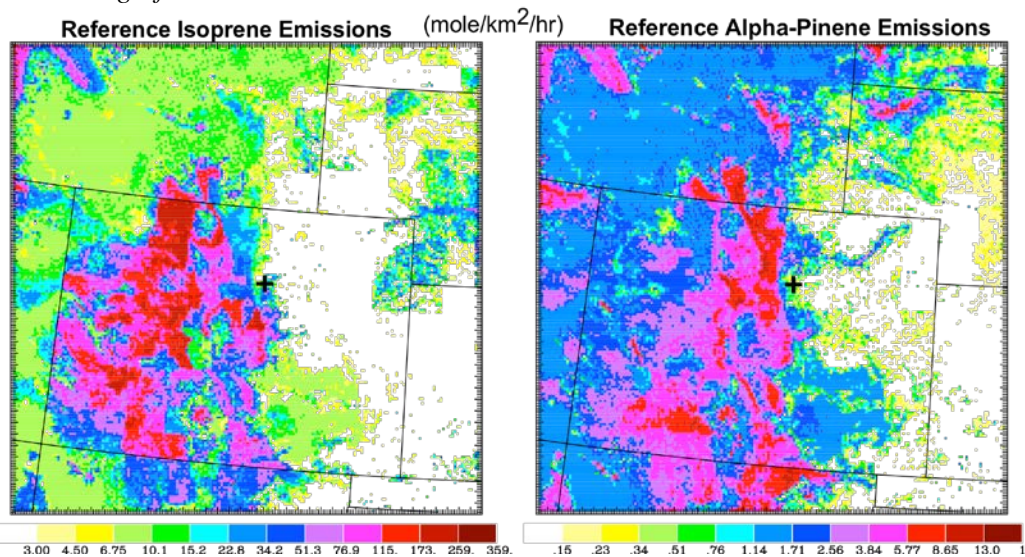
Note that slope values presented in this revision are slightly different than in the submitted draft. In addressing reviewers’ comments, it was realized that some of the data from July flights were not included in the fits by mistake. This affected only the data in Figure 1 and Figure S3 and their references, all of which are now corrected and updated.

Related, I would like to see an improved discussion of the synoptic situation, including temperatures and wind directions in the region. Towards the bottom of page 3, you mention that easterly wind cases were sampled up to 5500 m, but it's unclear what the general flow was for the cases below 2500 m.

The first paragraph in section 2.1 is modified to include a description of the general flow patterns during the project: “The mountainous terrain of the Front Range leads to terrain-induced air mass flow patterns in the region. Typically, during the day, thermally-driven easterly flow transports pollutants towards and up the foothills while at night the flow reverses. During July 27-28, the region was also under the influence of a mesoscale cyclonic flow, leading to counterclockwise movement of air masses and transfer of pollutants from the northern latitudes towards Denver Metro (Vu et al., 2016).” And “Average temperature in the plumes presented in this work was  $20.7 \pm 5.8$  °C.”

**What are the main sources of BVOCs to the region: local vegetation, mountain valleys to the west, etc.?**

Based on the BEIS 3.14 inventory used in WRF-Chem (now also added to Table 1), isoprene and monoterpenes are emitted mostly to the south and west of Denver, and over the mountains in western Colorado. Since typical daytime flow of air masses was from east to west, it's apparent that transport of BVOCs into the Front Range compared to local sources was not significant. These emission maps are now added to SI (Fig. S2) and the following sentences are added to section 2.4: “Based on BEIS 3.14 inventory, biogenic emission sources are mostly in the south and west of Denver, and over the mountains in western Colorado (Fig. S2). Since typical daytime flow of air masses during FRAPPÉ was from east to west, it is apparent that transport of BVOCs into Front Range compared to local sources was not significant.”



**Figure R2.** Isoprene and alpha-pinene emissions at reference temperature (30° C) and photosynthetic photon flux density (PPFD = 1000  $\mu\text{mole}/\text{m}^2/\text{s}$ ) from the BEIS inventory over the 4-km model domain. Dark crosses show the location of Denver, CO.

**Minor comments:**

1) Page 3, line 6 – Is “Summer 2015,” an acronym or should it be summer, 2015?

Changed

2) Page 4, line 32 – A total. . .

Changed

**3) Page 5, lines 4-6 – Did the regional BB show up as a separate factor in the PMF?**

No, PMF even with additional number of factors was unable to resolve a factor with a significant contribution at  $m/z$  60 and 73.

**4) Page 9, line 23 – 4e rather than 4d, and 4f instead of 4e.**

changed- thanks for catching these.

**5) Page 9, line 32 – “...Emissions: Modeling”?**

Changed

**6) Page 9 and Figure 9 – I don’t see the advantage of the cumulative plot vs a frequency plot that is simpler to digest.**

We decided to show cumulative distributions as they are more informative than frequency distributions since they not only show the distribution of the values, but also readily show the median values.

**7) Page 9, lines 29-32 - Is the 4 km resolution over the sampled region for the specific time of year sufficient to compare with the airborne observations without contributing to differences in extremes?**

We’re unclear on exactly what the reviewer means, but we’d like to clarify that with the 100 m/s speed of the C-130 in the boundary layer with a full payload, there are 2-3 values from the AMS in a 4 km × 4 km grid cell that are averaged to compare the model to. This means there might be some smearing of the extremes when averaging, but trends in the averaged values should still stand out. Please also see our response to comment #2 of Reviewer #3 and the clarification we’ve added to the text (section 2.3: “*To determine model predictions along the flight track, aircraft’s flight track is traced in the model domain and measured parameters along this track are averaged over model grid-cells. The speed of the C-130 in the boundary layer with a full payload is ~100 m/s; thus with the nominal AMS averaging time of 15 s, 2-3 values from the AMS measurements are available to average in a 4 km × 4 km grid cell to compare the model to. There is no interpolation of the data in space or within the hourly temporal resolution of the model. Note also that there was no drastic variability within the hourly time scale of the modeled parameters.*”)

**8) Page 13 – The reduction of bSOA implies that many of the BVOC sources are mixed with the urban sources. Is transported bSOA unimportant?**

Please see our response above regarding regional distribution and transport of BVOCs.

**Reviewer #3**

**This study characterizes the impact of oil and gas (O&G) emissions on urban OA levels during the FRAPPE field campaign. A combination of measurements and modeling is used to better constrain O&G emissions and to estimate their contributions to primary and secondary OA. The study concludes that O&G emissions have a relatively minor (~5%) effect on OA concentrations during summer in the sampled domain (Colorado Front Range). The study also highlights the need to update O&G emissions inventories. These are both novel and important results. The topic is highly relevant for ACP - the manuscript is nicely organized and clearly written. I strongly recommend its publication after the below issues are addressed.**

**Specific Comments:**

**1. Overall, my biggest concern is with the predictions of biogenic SOA. There are several problems with the methodology and/or the interpretation of results. These are:**

**i) There is clearly a problem with the biogenic emissions inventory: Fig. 6b shows a large systematic difference in the measured and modeled monoterpene concentrations. The manuscript dismisses this as unimportant (Pg. 10, line 23-34), but I completely disagree. First, monoterpene emissions often peak at night and their lifetime against oxidation by nitrate radical and ozone is short. From my understanding, the aircraft measurements were mostly carried out during the daytime, so nighttime conditions are not represented here. Therefore, the difference in Fig. 6 does not actually show how large the bias in emissions (and hence biogenic SOA) may be.**

We disagree with the reviewer that monoterpene emissions peak at night; actually, because of the positive temperature dependence of monoterpene emissions, their emissions are highest during the afternoon (Guenther et al., 1993). Their concentration might peak at night depending on the oxidant levels and also for typically lower boundary layer heights at night. The reviewer is correct that the measurements presented here were obtained during 7 am- 7 pm (local time) and not representative of nighttime emissions/processing. Because of this, we also focused on the daytime model-measurement comparisons when the atmosphere is well-mixed and the measurements are more representative of the daytime conditions. Note however that all the chemical species in the model are recycled from one day of simulation to the next. Therefore, the model carries all the chemicals emitted at night to daytime unless they are removed by deposition or chemical loss processes. We agree with the reviewer that emission rates from the BEIS 3.14 model may need to be improved in order to better compare with the observed monoterpene concentrations; however, this is beyond the scope of this paper.

**ii) Overall, the predicted amount of biogenic SOA (54% and 40% in urban and O&G plumes, respectively) seems quite low. The present simulations do not seem at all consistent with the results of Schichtel et al. (2008) and Ridley et al. (2018), who found measured and predicted non-fossil OC fractions in Colorado during summer to be ~85%.**

We agree with the reviewer that the contribution of biogenic SOA in certain parts of Colorado might be higher than what was predicted in the Front Range. For example, Bench et al. (2007) reported that >90% of carbonaceous aerosol in the Rocky Mountain was contemporary while the summertime fraction of contemporary carbon was only 47% in Denver (Kleindienst and Currie, 1999). The analysis of Schichtel et al. (2008) and Ridley et al. (2018) are both also based on IMPROVE samples measured in non-urban environments and National Parks, i.e., the Rocky Mountains NP, where biogenic emissions are significantly higher than in the Front Range. Additionally, the non-fossil fraction of OC vs. OA are not necessarily the same value since OA mass includes the mass of non-carbon atoms, mostly oxygen, as well. We therefore don't believe our results are inconsistent with the above-mentioned studies. In order to translate modeled OC fractions to non-fossil/fossil SOA, one needs to accurately account for O/C ratios in the emissions and the model; however, such an analysis is beyond the scope of this paper (please see our response below).

**iii) Limiting biogenic VOC oxidation seems to provide an unrealistic constraint on SOA formation. This may improve predictions of OA mass concentrations, but my suspicion is that the predictions of carbon oxidation state or O:C will suffer in these model scenarios. Recent studies have shown that this is a critically important dimension to evaluate (Murphy et al., 2011; Chen et al., 2015). Otherwise, it is possible that the improvements in OA mass prediction are achieved for the wrong reasons. I strongly encourage adding this dimension to the analysis.**

Smog chamber experiments have indeed indicated additional contribution of multi-generation oxidation products to SOA from biogenics (e.g., Ng et al., 2006; Zhao et al., 2015); however, rates of oxidation of the 1<sup>st</sup> generation products have not been reported for a variety of terpenes and therefore remain uncertain (Jenkin et al., 2012). We are aware of the modeling studies which simulate O:C ratios in addition to the



OA mass. There are however some uncertainties associated with modeling of O:C ratios. First, all of the gas chemistry mechanisms including the ones cited by the reviewer use lumped mechanisms. Therefore, different VOCs with different carbon content are lumped as a single chemical species with specific composition. Moreover, the number of carbon and oxygen atoms aren't conserved in the gas chemistry mechanisms. Lastly, there are other SOA precursors such as SVOCs and IVOCs, for which O:C ratios are very uncertain, and again due to lumping it's impossible to track accurately molecular composition of all these compounds in the model. Adding another metric (O:C) to atmospheric SOA models makes them computationally very expensive. For example, Murphy et al. (2011) simulated a 2D VBS approach in a Lagrangian model, not in a full 3D Eulerian framework. In our study, it's crucial to simulate the complex 3D meteorological transport phenomena and influence of multiple sources of air pollutants across the region within a 3D model. We believe simulation of O:C ratios is computationally outside the scope of this study. Note also that the mAMS used in this project doesn't provide a direct measure of O:C. Although the  $\text{CO}_2^+$  signal in the mass spectra can be converted to an estimate of O:C using recently updated parameterizations (Canagaratna et al., 2015), there's still a ~30% uncertainty in the estimated O:C.

**iv) The authors hypothesize that higher urban VOCs contribute to the overprediction of OA (Pg. 11, line 35-36), but the response is to limit aging of biogenics?**

As apparent in Fig. 10a, even with limited aging of biogenic VOCs, modeled urban OA was overpredicted by ~20%, which is a ~15% improvement in predicting OA compared to the other cases, but still not a perfect comparison. This suggests that additional factors must have contributed to the overprediction of urban OA. We have changed the text to indicate this: *“This overprediction may partly stem from higher than measured mixing ratios of urban VOCs in the model (Fig. 5c).”*

**2. Perhaps related to the above point, but clarification is needed for how the model-measurement comparison has been carried out. The resolution of measurements is not always consistent with the 4 km x 4 km model resolution. For example, 15-s AMS measurements at a likely aircraft speed of ~200 – 300 m/s would provide AMS measurement resolution of 3 – 4.5 km. Many of the (single) AMS measurements no-doubt cross grid lines. Other measurements will have the same issues. Pg. 10, lines 1-2 makes reference to the problem, but it is unclear how the actual averaging and comparison was carried out.**

The discussion in Section 3.3.1 is not suggestive of an artifact in the averaging or comparison scheme, but it rather suggests that there are differences in the modeled transport patterns of plumes vs. measurements. The following sentences have been added to Section 2.3 to illustrate the framework of model-measurement averaging and comparisons: *“To determine model predictions along the flight track, aircraft's flight track was traced in the model domain and measured parameters along this track were averaged over the model grid-cells. The speed of the C-130 in the boundary layer with a full payload is ~100 m/s; thus with the AMS averaging time of 15 s, 2-3 values from the AMS measurements were available to average in a 4 km × 4 km grid cell to compare the model to. There was no interpolation of the data in space or within the hourly temporal resolution of the model. Note also that there was no drastic variability within the hourly time scale of the modeled parameters.”*

**3. For the  $\Delta\text{OA}/\Delta\text{CO}$  analysis (Section 3.1), the CO background is given (105 ppb), but the corresponding OA background is given as a range (Pg. 7, line 35)? The choice of the OA background value has a direct (and profound) effect on the absolute  $\Delta\text{OA}/\Delta\text{CO}$  values: additional discussion is definitely needed.**

The indicated background for CO (105 ppbv) was determined from the mode of the frequency distribution of CO in the BL of Front Range while the indicated range of background OA represented the range of OA calculated from the ODR slopes at CO=105 ppbv, considering the 95% confidence intervals of the fit

parameters. However, we understand that this might confuse the readers, so we have revised the text to only indicate one value corresponding to the calculated OA at CO=105 ppbv, using the best estimates of the slopes and intercepts of the ODR fits. This value,  $1.82 \mu\text{g}/\text{m}^3$ , is consistent with the mode of the OA frequency distribution in the BL, which is at  $1.85 \mu\text{g}/\text{m}^3$ .

Given that most likely one background value for OA and CO is not representative for all the flights and the fact we could not determine appropriate upwind (i.e., background) values of OA or CO in each flight given our flight tracks, we decided to not subtract any value from the measurements and let the linear regression analysis determine an average enhancement ratio of OA with respect to CO. The text has been modified to reflect this: *“Since daily flight patterns did not include regular upwind tracks, it was not possible to determine daily background values to subtract from the measured OA and CO. Therefore, the enhancement ratios were determined by weighted, linear orthogonal distance regression (ODR) fits...”* and *“Additionally, using the best estimates of the ODR slope and intercept values of the regression lines to the data, the predicated OA at background levels of CO (~105 ppbv) was  $1.82 \mu\text{g m}^{-3}$ . This value, which was very similar to the mode of the OA frequency distribution in the BL at  $1.85 \mu\text{g m}^{-3}$ , is a substantial portion of total OA, suggesting presence of relatively high concentrations of non-combustion related OA, likely of biogenic origin, in the region.”*

Note that slope values presented in this revision are slightly different than in the submitted draft. In addressing reviewers’ comments, it was realized that some of the data from July flights were not included in the fits by mistake. This affected only data in Figure 1 and Figure S3 which are now corrected and updated.

**4. Pg. 2 line 33-34: can the authors provide a brief explanation of what is meant by “liquid- rich” and “wet gas” (e.g., which liquid).**

Liquid-rich or wet-gas terms are used to differentiate natural gas that has a higher content of hydrocarbons heavier than methane compared to dry-gas. These hydrocarbons are either present in the condensed phase when brought up to the surface, are liquefied and sold as liquefied petroleum gas, or are processed to produce gasoline. This is now briefly described in the text: *“Gas composition in this field is liquid-rich (containing more than  $3.8e-4 \text{ m}^3$  of condensable hydrocarbons per  $28 \text{ m}^3$  of extracted gas) (Britannica 1998), making Colorado among the top 5 U.S. states with high yields of wet-gas production (USED 2015).”*

**5. Pg. 3 line 30-34: can the authors clarify what are these altitudes in m AGL? It is also unclear which criteria were used to expand the altitude limit on plumes? How were the “recirculated air masses” identified, and how many were there relative to the total?**

Recirculated air masses were identified based on personal communications with LIDAR PIs who were measuring atmospheric structure and aerosols at the Boulder Atmospheric Observatory tower during the project. They had determined days when aerosol layers aloft were identified to be from recirculated air masses. However, these events were very rare, with their data being <4% of the total boundary layer data. The altitudes reported in the text were “above sea level” (ASL) since AGL altitudes were not available when the manuscript was first prepared, but the archived data now include AGL altitudes, and so we have updated the text to include all altitudes as “above ground level (AGL)”: *“To limit the current analysis to air masses influenced by emissions in the boundary layer (BL) of the Front Range, analysis from samples collected over the Denver Metropolitan area and the eastern plains were limited to those at altitudes below 1000 m above ground level (AGL); over the foothills and the Continental Divide, air masses under the influence of easterly winds sampled at altitudes up to 2500 m AGL were also considered. Additionally, recirculated air masses, occasionally observed at altitudes up to 1800 m AGL over the metropolitan area were also included in this analysis. Overall, 91% of the data presented here are from*

*altitudes lower than 1000 m AGL and the contribution of the recirculated air masses to the data was minor (<4%).”*

**6. Pg. 11 line 14-16: this seems like it could easily be tested by comparing modeled and measured aerosol black carbon (or equivalent) concentrations.**

Unfortunately there was no measure of BC or EC available on the aircraft.

**7. While the “best” predictions are achieved using the non-volatile POA assumption, it is important to acknowledge that this assumption is inconsistent with many direct observations (see extensive body of work from A. L. Robinson). This may highlight other uncertainties (perhaps unspiciated emissions, IVOCs, etc.), but non-volatile POA is not consistent with actual emissions measurements. Therefore, I strongly suggest adding a brief disclaimer on this point, and rewording some of the current discussion (e.g., Pg. 11 line 25: non-volatile POA is not “more realistic” even if we can’t model it well).**

We agree with the reviewer that uncertainties in POA emission ratios, especially in the O&G sector, or degree of volatility could both be contributing to the lower-than measured predictions of POA. Unlike other studies that use the VBS approach, as stated in the manuscript, we did not increase total POA emissions in the inventory to account for SVOCs. Therefore, total mass of the emitted POA is the same in all sensitivity studies presented in the paper. Note that with an increased POA emission ratio along with the assumption of semivolatile POA, additional SOA precursors would be introduced in the model, leading to additional overestimation of the ambient OA levels. Current emission inventories don’t provide volatility distributions and/or emissions for SVOCs. Therefore, it is hard to accurately represent both the volatility and total magnitude of POA emissions in the models. These uncertainties can have profound effects on simulated POA/SOA levels. However, in the absence of any better estimate of the emission ratios or volatility, we performed simulations with non-volatile POA to capture the most extreme effect of uncertainties in volatility. Our intent was not to give the impression that POA in this region is non-volatile, but rather that the predicted POA amounts with such an assumption provided better comparisons with the PMF-based estimates. We have rephrased the text to clarify this point: *“The non-volatile POA assumption may not be accurate, and improved volatility distributions of POA from different combustion sources would have to be considered to accurately account for semi-volatility of POA emissions in future air quality models. However, in the absence of better estimates of POA emission ratios or volatility, the predicted POA values in current simulations with non-volatile POA conditions are more comparable to the PMF-based estimates of HOA in this environment.”*

**8. Pg. 12 lines 36-37: what do the authors mean by  $\Delta$ SOA/ $\Delta$ CO and  $\Delta$ SOA/ $\Delta$ Ox? Have the authors subtracted background values? If so, these should be stated clearly. If it is just the slope of OOA vs. CO, then I suggest stating this clearly and dropping the “ $\Delta$ ”.**

The indicated values are the values based on ODR slopes of modeled SOA vs. modeled CO and Ox, and backgrounds have not been subtracted (please see our response to Reviewer #2 regarding background subtraction for OA and CO). By not fixing the intercept of the ODR fits, the intercepts are free to be fitted to represent the most probable background; the slope values in practice indicate the expected enhancement in SOA for a given enhancement in CO or Ox. This is different than enhancements in SOA relative to its background or that of CO relative to its background. The text has been modified to clarify this: *“With the standard treatment of bVOC oxidation and bSOA formation, urban plumes with  $NO_x/NO_y < 0.3$  displayed a 50% greater enhancement in SOA with respect to CO ( $\Delta$ SOA/ $\Delta$ CO) compared to plumes with a high O&G influence (Fig. 11a). On the other hand, SOA enhancement with respect to  $O_x$  ( $\Delta$ SOA/ $\Delta$ O<sub>x</sub>) was 30% higher in high O&G-influenced plumes (Fig. 11c).”*

#### **Technical Corrections:**

**1. Pg. 3 line 9: clarify that this 80% is not aerosol organic carbon?**

The reviewer is correct in understanding this estimate to be referring to gaseous OC only. The text is change to "...estimated ~80% of gaseous organic carbon...".

**2. Can the authors also clarify all of the various dates? Why is there not consistency between the field campaign time period (20 July – 18 Aug) and either the modeling period (24 July – 14 Aug and 27 July – 13 Aug) or the AMS PMF dates (26 July – 11 Aug)?**

The first research flight for the project was on July 26<sup>th</sup> while the flight on July 20<sup>th</sup> was a test flight. We have changed the start date in the beginning of the section 2.1 to reflect the start of research flights. The PMF runs concentrated on a period of flights where majority of the flight legs were in the Front Range, with a goal of characterizing local emissions and processing. The modeling period for the larger domain started on a date earlier than the first research flight to establish initial boundary conditions. The end date of the modeling work was later than the PMF-focus period in case there were other scientific questions we'd want to explore for the flight on Aug. 12<sup>th</sup>.

**3. Pg. 3 line 36: delete “ ’s ”**

Changed

**4. Pg. 4 line 4: define HAIPER**

HAIPER refers to the NSF Gulfstream GV aircraft; the text is now changed to reflect this: "...NCAR High-performance Instrumented Airborne Platform for Environmental Research (HAIPER) modular Inlet (HIMIL)...".

**5. Pg. 10 line 19: clarify what is meant by “these species”**

We have modified the text to clarify that the referenced species were biogenic VOCs: "*Since emissions of biogenic VOCs were not modified....*".

**References:**

- Bench, G., S. Fallon, B. A. Schichtel, W. C. Malm, and C. McDade (2007), Relative contributions of fossil and contemporary carbon sources to PM<sub>2.5</sub> aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network, *J. Geophys. Res.*, 112, doi: 10.1029/2006JD007708
- Britannica (1998). 2018, from <https://www.britannica.com/science/wet-gas>.
- Canagaratna, M. R., J. L. Jimenez, J. H. Kroll, Q. Chen, S. H. Kessler, P. Massoli, L. H. Ruiz, E. Fortner, L. R. Williams, K. R. Wilson, J. D. Surratt, N. M. Donahue, J. T. Jayne and D. R. Worsnop (2015). "Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications." *Atmos. Chem. Phys.* 15, doi:0.5194/acp-15-253-2015.
- Guenther, A. B., P. R. Zimmerman, P. C. Harley, R. K. Monson and R. Fall (1993). "Isoprene and monoterpene emissions rate variability: Model evaluations and sensitivity analysis." *J. Geophys. Res.-Atmos.* 98, doi:10.1029/93JD00527.
- Jenkin, M. E., K. P. Wyche, C. J. Evans, T. Carr, P. S. Monks, M. R. Alfarra, M. H. Barley, G. B. McFiggans, J. C. Young and A. R. Rickard (2012). "Development and chamber evaluation of the MCM v3.2 degradation scheme for beta-caryophyllene." *Atmospheric Chemistry and Physics* 12(11): 5275-5308, doi:10.5194/acp-12-5275-2012.
- Klinedinst, D. B., and L. A. Currie (1999), Direct quantification of PM<sub>2.5</sub> fossil and biomass carbon within the Northern Front Range Air Quality Study's domain, *Environ. Sci. Technol.*, 33(23), 4146– 4154.
- Ng, N. L., M. R. Canagaratna, J. L. Jimenez, Q. Zhang, I. M. Ulbrich and D. R. Worsnop (2011). "Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data." *Environ. Sci. Technol.* 45, doi:10.1021/es102951k.

- Ng, N. L., J. H. Kroll, M. D. Keywood, R. Bahreini, V. Varutbangkul, R. C. Flagan and J. H. Seinfeld (2006). "Contribution of First- versus Second Generation Products to Secondary Organic Aerosols Formed in the Oxidation of Biogenic Hydrocarbons." *Environ. Sci. Technol.*, doi:doi:10.1021/es052269u.
- Ridley, D. A., et al. (2018), Causes and consequences of decreasing atmospheric organic aerosol in the United States, *PNAS*, 115 (2) 290-295.
- Schichtel, B. A., et al. (2008), Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States, *J. Geophys. Res.*, 113, D02311.
- Slowik, J. G., C. Stroud, J. W. Bottenheim, P. C. Brickell, R. Y. W. Chang, J. Liggio, P. A. Makar, R. V. Martin, M. D. Moran, N. C. Shantz, S. J. Sjostedt, A. van Donkelaar, A. Vlasenko, H. A. Wiebe, A. G. Xia, J. Zhang, W. R. Leitch and J. P. D. Abbatt (2010). "Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests." *Atmospheric Chemistry and Physics* 10(6): 2825-2845, doi:10.5194/acp-10-2825-2010.
- U.S. Energy Development Corporation (2015). "Natural gas: dry vs. wet." 2015, from [http://www.usenergydevcorp.com/media\\_downloads/Natural%20Gas%20Dry%20Vs%20Wet\\_050913.pdf](http://www.usenergydevcorp.com/media_downloads/Natural%20Gas%20Dry%20Vs%20Wet_050913.pdf).
- Vu, K. T., J. H. Dingle, R. Bahreini, P. J. Reddy, T. L. Campos, G. S. Diskin, A. Fried, S. C. Herndon, R. S. Hornbrook, G. Huey, L. Kaser, D. D. Montzka, J. B. Nowak, D. Richter, J. R. Roscioli, S. Shertz, M. Stell, D. Tanner, G. Tyndall, J. Walega, P. Weibring, A. J. Weinheimer, G. Pfister and F. Flocke (2016). "Impacts of the Denver Cyclone on Regional Air Quality and Aerosol Formation in the Colorado Front Range during FRAPPÉ 2014." *Atmos. Chem. Phys.* 2016: 1-40, doi:10.5194/acp-16-12039-2016.
- Zhao, D. F., M. Kaminski, P. Schlag, H. Fuchs, I. H. Acir, B. Bohn, R. Haseler, A. Kiendler-Scharr, F. Rohrer, R. Tillmann, M. J. Wang, R. Wegener, J. Wildt, A. Wahner and T. F. Mentel (2015). "Secondary organic aerosol formation from hydroxyl radical oxidation and ozonolysis of monoterpenes." *Atmospheric Chemistry and Physics* 15(2): 991-1012, doi:10.5194/acp-15-991-2015.

# Sources and Characteristics of Summertime Organic Aerosol in the Colorado Front Range: Perspective from Measurements and WRF-Chem Modeling

Roya Bahreini<sup>1,2</sup>, Ravan Ahmadov<sup>3,4</sup>, Stu A. McKeen<sup>3,4</sup>, Kennedy T. Vu<sup>2</sup>, Justin H. Dingle<sup>2</sup>,  
Eric C. Apel<sup>5</sup>, Donald R. Blake<sup>6</sup>, Nicola Blake<sup>6</sup>, Teresa L. Campos<sup>5</sup>, Chris Cantrell<sup>7</sup>, Frank  
Flocke<sup>5</sup>, Alan Fried<sup>8</sup>, Jessica B. Gilman<sup>3</sup>, Alan J. Hills<sup>5</sup>, Rebecca S. Hornbrook<sup>5</sup>, Greg Huey<sup>9</sup>,  
Lisa Kaser<sup>5</sup>, Brian M. Lerner<sup>3,4,10</sup>, Roy L. Mauldin<sup>7</sup>, Simone Meinardi<sup>6</sup>, Denise D.  
Montzka<sup>5</sup>, Dirk Richter<sup>8</sup>, Jason R. Schroeder<sup>6,11</sup>, Meghan Stell<sup>5</sup>, David Tanner<sup>9</sup>, James  
Walega<sup>8</sup>, Peter Weibring<sup>8</sup>, Andrew Weinheimer<sup>5</sup>

<sup>1</sup> Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

<sup>2</sup> Environmental Toxicology Graduate Program, University of California, Riverside, CA 92521, USA

<sup>3</sup> Earth Systems Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA

<sup>4</sup> Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80301, USA

<sup>5</sup> Atmospheric Chemistry Observations & Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO 80301, USA

<sup>6</sup> Department of Chemistry, University of California, Irvine, CA 92697, USA

<sup>7</sup> Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO 80303, USA

<sup>8</sup> Institute for Arctic and Alpine Research, University of Colorado, Boulder, CO 80303, USA

<sup>9</sup> Department of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30033, USA

<sup>10</sup> Now at Aerodyne Research, Inc., Billerica, MA, 01821

<sup>11</sup> Now at NASA Langley Research Center, Newport News, VA, 23666

Correspondence to: Roya Bahreini ([Roya.Bahreini@ucr.edu](mailto:Roya.Bahreini@ucr.edu))

**Abstract.** Evolution of organic aerosol (OA) and their precursors in the boundary layer of Colorado Front Range during the Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ, July-August 2014) was analyzed by in-situ measurements and chemical transport modeling. Measurements indicated significant production of secondary OA (SOA), with enhancement ratio of OA with respect to carbon monoxide (CO) reaching  $0.085 \pm 0.003$   $0.068 \pm 0.004$   $\mu\text{g m}^{-3}$  ppbv<sup>-1</sup>. At background mixing ratios of CO, up to  $\sim 2-1.8$   $\mu\text{g m}^{-3}$  background OA was observed, suggesting significant non-combustion contribution to OA in the Front Range. The mean concentration of OA in plumes with a high influence of oil and natural gas (O&G) emissions was  $\sim 40\%$  higher than in urban-influenced plumes. Positive matrix factorization confirmed a dominant contribution of secondary, oxygenated OA (OOA) in the boundary layer instead of fresh, hydrocarbon-like OA (HOA). Combinations of primary OA (POA) volatility assumptions, aging of semi-volatile species, and different emission estimates from the O&G sector were used in the Weather Research and Forecasting model, coupled with Chemistry (WRF-Chem) simulation scenarios. The assumption of semi-volatile POA resulted in greater than a factor of 10 lower POA concentrations compared to PMF-resolved HOA. Including a top-down modified O&G emissions resulted in substantially better agreements in modeled ethane, toluene, hydroxyl radical, and ozone compared to measurements in the high O&G-influenced

plumes. By including emissions from the O&G sector using the top-down approach, it was estimated that the O&G sector contributed to <5% of total OA, but up to 38% of anthropogenic SOA in the region. The best agreement between the measured and simulated median OA was achieved by limiting the extent of biogenic hydrocarbon aging and consequently biogenic SOA (bSOA) production. Despite a lower production of bSOA in this scenario, contribution of bSOA to total SOA remained high at 40-54%. Future studies aiming at a better emissions characterization of POA and intermediate volatility organic compounds (IVOCs) from the O&G sector are valuable.

## 1 Introduction

Secondary organic aerosol (SOA) particles are formed from condensation of relatively low vapor pressure species in the atmosphere, generated through oxidation of volatile, semi-volatile, or intermediate-volatility organic compounds (VOCs, SVOCs, or IVOCs, respectively). Since both biogenic and anthropogenic sources contribute to SOA precursors (Hallquist et al., 2009), SOA particles are ubiquitous in the atmosphere and contribute to a large fraction of the submicron non-refractory aerosol mass globally (Zhang et al., 2007). Similar to other aerosol particles, SOA particles deteriorate air quality and visibility and impact the climate directly through absorption and scattering of radiation and indirectly through interactions with clouds (Monks et al., 2009). Despite recent advances in the measurement and modeling aspects of SOA and their precursors (e.g., Donahue et al., 2006; Ervens and Volkamer 2010; Hodzic et al., 2010a; de Gouw et al., 2011; Hodzic and Jimenez 2011; Shrivastava et al., 2011; Ahmadov et al., 2012; Isaacman et al., 2012; Yatavelli et al., 2012; Ehn et al., 2014; Ensberg et al., 2014; Fast et al., 2014; Lopez-Hilfiker et al., 2014; Williams et al., 2014), the full extent of SOA sources, formation processes, and therefore their impact on air quality, human health, and climate are not fully understood.

In recent decades, stricter regulations by the U.S. Environmental Protection Agency and state agencies have resulted in lower emissions of black carbon, hydrocarbons (including air toxics), and nitrogen oxides in many urban environments (e.g., Parrish et al., 2002; Peischl et al., 2010; Sather and Cavender 2012; Warneke et al., 2012; Zhou et al., 2014; Kirchstetter et al., 2017) while in other areas, both populated and remote, expansion or emergence of new oil and natural gas (O&G) exploration and production activities has led to higher emissions of air toxics, methane, and non-methane hydrocarbons, e.g., C<sub>2</sub>-C<sub>8</sub> and larger alkanes, benzene and larger aromatic species (e.g., Petron et al., 2012; Gilman et al., 2013; Adgate et al., 2014; Helmig et al., 2014; Pekney et al., 2014; Warneke et al., 2014; Field et al., 2015; Koss et al., 2015; Rutter et al., 2015; Swarthout et al., 2015; Helmig et al., 2016; Prenni et al., 2016; Abeleira et al., 2017; Koss et al., 2017). The impact of higher emissions of such hydrocarbons from oil and gas fields of Utah and Wyoming on wintertime ozone has been assessed through recent measurement and modeling studies (Carter and Seinfeld 2012; Edwards et al., 2014; Rappenglück et al., 2014; Ahmadov et al., 2015).

The Wattenberg Field, located in the Denver-Julesburg basin (DJB) in the Colorado Front Range and NE of Denver, is the largest oil and natural gas producing field in the state of Colorado and is one of the 20 largest O&G fields in the U.S. (RockyMountainEnergyForum 2015). Gas composition in this field is liquid-rich (containing more than 3.8e-4 m<sup>3</sup> of condensable hydrocarbons per 28 m<sup>3</sup> of extracted gas) (Britannica 1998), making Colorado among the top 5 U.S. states with high yields of wet-gas production (USED C 2015). Since 2007, several studies in the Front Range have been carried out in an effort to characterize emissions of methane and light alkanes (up to C<sub>8</sub>) and

aromatic species, including benzene, toluene, C<sub>8</sub>- and C<sub>9</sub>- aromatics from the O&G activities in the Front Range and their atmospheric impacts in the region (Petron et al., 2012; Gilman et al., 2013; Swarthout et al., 2013; Petron et al., 2014; Abeleira et al., 2017). In the measurement study by Gilman *et al.* (2013), conducted during February-March 2011 at a site SW of the Wattenberg Field, O&G emissions contributed to 70% and 20-30% of emissions of light alkanes and aromatic species, respectively. Additionally, a high fraction of OH reactivity ( $55 \pm 18\%$ ) was attributed to the light alkanes emitted from the O&G activities in Wattenberg Field, highlighting the significance of these emissions as ozone precursors. In ~~Summer-summer~~ 2015, morning OH reactivity was dominated by O&G VOC emissions while in the afternoon, isoprene contributed to a higher OH reactivity (Abeleira et al., 2017). Box model simulations corresponding to observations made at Erie, CO (southwest corner of Wattenberg Field) in summer 2012 and 2014 estimated ~80% of gaseous organic carbon had originated from O&G alkane emissions while contribution of these species to local ozone production was estimated to be < 20% (McDuffie et al., 2016). On the high ozone days, O&G emissions have been estimated to contribute to 30-40% of ozone in the northern Colorado Front Range- Denver Metro area, based on data synthesized from airborne measurements in the Front Range during summer 2014 (Pfister et al., 2017). Despite these recent studies, contribution of O&G emissions to summertime organic aerosol in the region has not been explored before.

During July-August 2014, the Colorado Department of Public Health and Environment (CDPHE), National Science Foundation (NSF), and National Aeronautics and Space Administration (NASA) co-sponsored multiplatform field projects in the Colorado Front Range to characterize emissions, processing, and transport of various pollutants in the region. Here, analyses of the airborne data obtained from the NSF/CDPHE-sponsored Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) project, investigating emissions of hydrocarbons, their impact on SOA formation, and OA chemical characterization through positive matrix factorization are presented. A regional chemical transport model, Weather Research and Forecasting coupled with Chemistry (WRF-Chem), is used with volatility-basis set parameterization and sensitivity runs to examine effects of primary OA (POA) volatility, biogenic SOA aging schemes, and updated emissions of hydrocarbons from the O&G sector on SOA formation in the Front Range.

## 2. Methods

### 2.1 Measurements

In-situ measurements were made aboard the NSF/NCAR C-130 aircraft during July ~~2026~~-August 18, 2014. The mountainous terrain of the Front Range leads to terrain-induced air mass flow patterns in the region. Typically, during the day, thermally-driven easterly flow transports pollutants towards and up the foothills while at night the flow reverses. During July 27-28, the region was also under the influence of a mesoscale cyclonic flow, leading to counterclockwise movement of air masses and transfer of pollutants from the northern latitudes towards Denver Metro. (Vu et al., 2016). To limit the current analysis to air masses influenced by emissions in the boundary layer (BL) of the Front Range, analysis from samples collected over the Denver Metropolitan area and the eastern plains were limited to those at altitudes typically below 1000 m above ground level (AGL) 2500 m (ASL); over the foothills and the Continental Divide, air masses under the influence of easterly winds sampled at altitudes up to 2500



~~m AGL 5500 m (ASL)~~ were also considered. Additionally, recirculated air masses, occasionally observed at altitudes up to ~~1800 m AGL 4000 m~~ over the metropolitan area were also included in this analysis. Overall, 91% of the data presented here are from altitudes lower than 1000 m AGL, and the contribution of recirculated air masses to the data was minor (<4%). Average temperature in the plumes presented in this work was  $20.7 \pm 5.8$  °C. Influence of different emission sources on sampled air masses was determined based on the measured trace gases as further explained in Section 2.2.

Non-refractory submicron aerosol composition, including organic aerosol (OA), was measured with 15-s frequency using a compact version (mAMS) of the Aerodyne's Aerosol Mass Spectrometer equipped with a compact time-of-flight detector. Except for the shorter particle time-of-flight chamber and a different pumping system, principles of operation of the mAMS are similar to the full-size AMS instruments, described previously (Jayne et al., 2000; Drewnick et al., 2005; Canagaratna et al., 2007). The mAMS sampled ambient air through a forward facing, diffusion-type NCAR High-performance Instrumented Airborne Platform for Environmental Research (HIAPER) modular inlet (HIMIL), mounted under the aircraft, and a pressure-controlled inlet (Bahreini et al., 2008; Dingle et al., 2016; Vu et al., 2016). Residence time in the inlet was estimated to be ~0.5 s. Sensitivity calibrations of the instrument were carried out routinely during the project. Variability in the individual calibrations was observed to be less than 10% and thus an average calibration value was applied to the data obtained from all flights (Vu et al., 2016). Composition-dependent collection efficiency was applied to all the data (Middlebrook et al., 2012a). The estimated uncertainty in the mass concentration of OA was ~30% (Bahreini et al., 2009) and the detection limit was  $\sim 0.4 \mu\text{g m}^{-3}$  (15-s interval measurements).

Auxiliary gas-phase data used in this analysis are carbon monoxide (CO) by vacuum UV resonance fluorescence (Gerbig et al., 1999), nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) by chemiluminescence (Ridley et al., 2004), ethane (C<sub>2</sub>H<sub>6</sub>) by infrared spectrometry (Richter et al., 2015), aromatic and biogenic species by on-line proton-transfer reaction mass spectrometry (Lindinger et al., 1998; de Gouw and Warneke 2007), hydrogen cyanide (HCN), *i*-pentane and *n*-pentane by on-line cryogenic gas chromatography-mass spectrometry (GC-MS) (Apel et al., 2015), methylcyclohexane and *n*-octane by offline analysis of whole air canister samples (WAS) by GC-MS (Colman et al., 2001), nitric acid (HNO<sub>3</sub>) by chemical ionization mass spectrometry (CIMS) using SF<sub>6</sub><sup>-</sup> as the reagent ion (Huey et al., 1998), peroxy acyl nitrates (PAN and PPN) by I<sup>-</sup> CIMS (Zheng et al., 2011), alkyl nitrates by thermal dissociation-laser induced fluorescence (Day et al., 2002), and hydroxyl (OH), hydroperoxy (HO<sub>2</sub>), and alkyl peroxy (RO<sub>2</sub>) radicals by CIMS (Mauldin et al., 1998; Hornbrook et al., 2011; Ren et al., 2012). NO<sub>y</sub> was calculated by summing up the individually measured nitrogen oxide species, namely NO, NO<sub>2</sub>, HNO<sub>3</sub>, particulate nitrate, PAN, PPN, and alkyl nitrates.

## 2.2 Source Characterization

To quantify the contribution of different types of OA factors to total OA, positive matrix factorization (PMF) was applied to the measured OA spectra, during July 26-Aug. 11. PMF is a multivariate factor analysis method by which input data are categorized into constant profile factors (i.e., factor mass spectra) with varying, positive contributions across time (i.e., factor time series) while minimizing the residual matrix considering the errors associated with each

sample (Paatero and Tapper 1994; Paatero 1997). The input mass spectra and error matrix of OA were generated by ToF Analysis Toolkit (v. 159) and used in PMF Evaluation Toolkit (v. 2.08D). Down-weighting of uncertain and weak fragments with signal to noise ratio of 0.2-2 and fragments related to  $\text{CO}_2^+$  (i.e.,  $m/z$  16, 17, 18, 28, and 44) was carried out following the procedures outlined in previous studies (Ulbrich et al., 2009; Ng et al., 2010; Zhang et al., 2011). ~~Total~~ A total of 100 bootstrap iterations with the ideal number of factors (2 as discussed further in Section 3.1) were also carried out to determine robustness of the resolved factors.

To compare OA production in plumes with an influence of pure urban vs. high O&G-related emissions, two air mass categories were defined using the auxiliary gas phase data of CO and  $\text{C}_2\text{H}_6$  as tracers for urban and O&G emissions, respectively. Urban-influenced air masses were defined as air masses where CO enhancement over the background (105 ppbv, defined by the mode in the frequency distribution of CO in the Front Range boundary layer) was observed while  $\text{C}_2\text{H}_6/\text{CO} < 20$  pptv ppbv<sup>-1</sup> (Warneke et al., 2007; Borbon et al., 2013). Plumes with a high influence of O&G emissions were defined by  $\text{C}_2\text{H}_6/\text{CO} > 80$  pptv ppbv<sup>-1</sup> and  $\text{C}_2\text{H}_6$  mixing ratios greater than 10 ppbv (Warneke et al., 2007; Borbon et al., 2013). Data from 11-12 Aug, when influence from regional biomass burning emissions resulted in a higher HCN background values (540 pptv vs. 300 pptv), were eliminated from analysis of the ambient measurements, although the PMF input matrix included data from 11 Aug.

### 2.3 WRF-Chem Modeling

The Weather Research and Forecasting model coupled with chemistry (WRF-Chem) [<https://ruc.noaa.gov/wrf/wrf-chem/>] is an online meteorology-chemistry model, which is widely used in air quality and atmospheric chemistry applications (Grell et al., 2005; Powers et al., 2017). Table 1 lists the main configurations and parameterizations used to run WRF-Chem. The model includes multiple gas and aerosol chemistry parameterizations with varying levels of complexity, photolysis and removal (dry and wet) mechanisms. The model also contains the state of the art SOA schemes based on a volatility basis set approach. In this study, we used an SOA scheme mostly based on the RACM\_SOA\_VBS mechanism described in Ahmadov (2012). In the model, five volatility bins ( $10^{-1}$ ,  $10^0$ ,  $10^1$ ,  $10^2$ ,  $10^3$   $\mu\text{g}/\text{m}^3$ ) are assumed for organic aerosols. For the computational efficiency of the model simulations, it is assumed that all the OA species in the first bin ( $10^{-1}$   $\mu\text{g}/\text{m}^3$ ) are in particle phase. The major modification to the SOA scheme here is the treatment of semi-volatile POA emissions. The WRF-Chem model with the updated SOA code allows assigning different volatility distributions for the POA emissions. Here, two scenarios for POA volatility are presented. In the base case scenario, POA is emitted with a volatility distribution similar to that of Tsimpidi et al. (2010), except that the distribution used to partition the POA emissions in this study conserves total POA mass. Specifically, we used the following coefficients to partition the POA emissions across the five saturation bins: 0.09, 0.09, 0.14, 0.18, and 0.5. In the other scenario, the POA is assumed to be non-volatile. Thus, in this scenario all the emitted POA remains in particle phase in the atmosphere until it is removed by dry or wet deposition processes. Since there are large uncertainties related to the missing SVOC emissions in inventories, we did not scale up the POA emissions in this study. Therefore, total mass of the emitted POA is the same in both modeling scenarios.

Another major update to the model is the addition of intermediate VOCs (IVOCs). Unlike many other SOA modeling studies, we did not scale up the IVOC emissions according to the POA emissions. Here, the unidentified

VOC emissions from the U.S. EPA NEI-2011v1 inventory were used as IVOCs. In WRF-Chem the IVOCs are emitted and transported as other gaseous species. They are oxidized by hydroxyl radical with the rate of  $2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , as hexadecane. A similar approach was first applied in another WRF-Chem study in order to simulate SOA formation from the Deepwater Horizon oil spill in the Gulf of Mexico (Middlebrook et al., 2012b). As further discussed in Section 2.4, in the top-down emission simulation scenarios, IVOC emissions from the O&G sector were scaled using the top-down estimates of the alkane species (namely the HC8 species in the RACM mechanism). Lack of direct measurements of ambient IVOC species makes it impossible to directly constrain their emissions using the top-down approach. Table 2 highlights differences in emission estimates and POA volatility assumptions used in the different simulation scenarios. In the simulation case with limited biogenic SOA formation, the first generation semi-volatile organic condensable vapors are not oxidized further, and therefore, only first-generation BVOC oxidation products contributed to biogenic SOA production.

The WRF-Chem model, which includes the new SOA formation mechanisms, was simulated on two domains, covering the contiguous US (CONUS) and entire Colorado, at 12-km and 4-km resolutions, respectively. In addition to the full gas and aerosol chemistry, a photolysis scheme, dry and wet removal parameterizations for both gaseous and aerosol species were incorporated in WRF-Chem. The anthropogenic and biogenic emissions were also included in the simulations. First, all the model simulations were conducted on the CONUS domain for 24 July – 14 August 2014 time period. Then, using a one-way nesting approach, initial and boundary conditions for the inner domain (Figure S1) were created to conduct various sensitivity simulations for 27 July – 13 August. Simulations on the 4-km domain were conducted in 24-hour intervals. The model was initialized by using meteorological input from the 12-km domain, which in turn used North American Mesoscale analysis fields ([www.emc.ncep.noaa.gov](http://www.emc.ncep.noaa.gov)) as boundary and initial conditions. Simulated chemical species were cycled between the 4-km domain runs to preserve the fine-scale features captured by the inner domain. All the WRF-Chem modeling results presented here are based on the 4-km domain simulations. To determine model predictions along the flight track, aircraft's flight track was traced in the model domain and measured parameters along this track were averaged over the model grid-cells. The speed of the C-130 in the boundary layer with a full payload is ~100 m/s; thus with the AMS averaging time of 15 s, 2-3 values from the AMS measurements were available to average in a 4 km × 4 km grid cell to compare the model to. There was no interpolation of the data in space or within the hourly temporal resolution of the model. Note also that there was no drastic variability within the hourly time scale of the modeled parameters.

## 2.4 Emissions

Since the focus of this paper is on quantification of SOA formation in the Front Range, two emission scenarios are explored. Both emissions scenarios are based on the U.S. EPA NEI-2011 emission inventory with the exception that O&G activity emissions in the DJB are modified to allow direct quantification of SOA formation from this sector. The NEI-2011 emissions rely on the version 6.0 platform (<https://www.epa.gov/air-emissions-modeling/2011-version-60-platform>), and are basically the same emissions used and documented in Ahmadov et al. (2015) except for the chemical speciation profiles of the O&G sectors. In some of the scenarios, all O&G-related activity emissions are removed from the simulations. For other scenarios, VOC emissions from O&G activity in the DJB are

specified according to a top-down approach from observations collected at the Boulder Atmospheric Observatory (BAO) tower, on the western edge of the DJB. As previously mentioned, the “unknown” VOC species within the NEI-2011 inventory is also included, representing direct emissions of IVOCs. Summertime (July) conditions are assumed within the NEI temporal allocation specifications, as are the diurnal profiles and spatial allocations at 4-km horizontal resolution.

The top-down emissions from the DJB are derived using the same strategy as in Ahmadov et al. (2015) whereby CH<sub>4</sub> flux observations over a basin are combined with basin-wide VOC to CH<sub>4</sub> emission ratios. In this case, the O&G activity sector CH<sub>4</sub> flux estimate for May 2012 within the DJB of Petron et al. (2014) (19.3±6.9 tonne/hr) is adopted. VOC to CH<sub>4</sub> from O&G activity in the DJB for individual compounds are derived from VOC measurements at the BAO tower during July/August 2012 SONNE (Summer Ozone Near Natural Gas Emissions) field study (<https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2012sonne/>). Identical to the VOC analysis for the NACHTT-2011 field campaign, linear regressions using two variables (propane and acetylene) are used to distinguish O&G activity versus transportation-related sources (Gilman et al., 2013). Table S1 (supplement) summarizes the correlation statistics of NO<sub>x</sub> and 43 VOCs with CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> during SONNE. Derived emission ratios relative to propane are nearly identical between the two field studies for the 18 VOCs measured during NACHTT 2011, and are within 20% of the emission ratios of five of the VOCs from aircraft samples reported in Petron et al. (2014). All three DJB studies imply strong correlations between propane, CH<sub>4</sub>, and other VOCs from O&G activity, allowing high confidence in the regression slopes that define the emission ratios used here. Spatial allocation and the area/point sector ratios of the top-down inventory are taken from the O&G sector totals within NEI-2011, and no diurnal variation is assumed. As discussed in Gilman et al. (2013), NO<sub>x</sub> and CO emissions from the oil/gas sector are indeterminable due to their overwhelming correlation with acetylene, so no NO<sub>x</sub> or CO adjustments are possible in the top-down case. Likewise, no changes to NEI-2011 aerosol emissions are considered.

Tables 3a-3b provide emission totals from the NEI-2011 and the top-down VOC inventories for areas covering the DJB and Denver-metro region, respectively. The DJB latitude/longitude limits in Table 3a are chosen to capture sources contributing to the CH<sub>4</sub> emission totals within Petron et al. (2014), which also includes some northern suburbs of Denver. O&G activity emissions are only included within “area” and “point” emission sector categories, and are indeterminable within the mobile categories. The area category in particular dominates the ethane and “unknown” VOC emissions. We note that the NEI-2011 does not specifically contain any POA emissions associated with O&G activity. The largest area sources of POA in Table 3a are from agricultural tilling, construction, and fugitives emissions from paved and unpaved roads, though commercial cooking sources account for ~43%. Emissions in the Denver-metro region are dominated by mobile sources while the main source of POA (66%) is commercial cooking.

Based on BEIS 3.14 inventory, biogenic emission sources are mostly in the south and west of Denver, and over the mountains in western Colorado (Fig. S2). Since typical daytime flow of air masses during FRAPPÉ was from east to west, it is apparent that transport of BVOCs into the Front Range compared to local sources was not significant.

### 3. Results and Discussion

#### 3.1 Ambient OA Observations

Figure 1 highlights the general trends observed for OA vs. CO in the Front Range BL. Data points appear to be bound by enhancement ratios of  $\Delta\text{OA}/\Delta\text{CO} = \text{0.016-0.085-0.018-0.068} \mu\text{g m}^{-3} \text{ppbv}^{-1}$ , with higher values observed in air masses with  $\text{NO}_x/\text{NO}_y < 0.3$ , i.e., air masses with a higher degree of photochemical processing, compared to fresher air masses with  $\text{NO}_x/\text{NO}_y > 0.7$ . Note that these age categories best represent processing of plumes with  $\text{NO}_x$  emissions while true aging of emissions in the absence of  $\text{NO}_x$  is not captured. Since daily flight patterns did not include regular upwind tracks, it was not possible to determine daily background values to subtract from the measured OA and CO. Therefore, these the enhancement ratios were determined by weighted, linear orthogonal distance regression (ODR) fits, with weights representing the uncertainty in OA (30%) and CO (3%). Uncertainties in the slopes represent 95% confidence intervals. Almost a factor of 4-5.5 increase in  $\Delta\text{OA}/\Delta\text{CO}$  indicates a significant production of SOA with photochemical aging in the Front Range. Another notable feature in Fig. 1 is the higher  $\Delta\text{OA}/\Delta\text{CO}$  enhancement ratios observed in the fresher plumes sampled in the Front Range compared to the typical enhancement ratio of primary OA to CO ( $\Delta\text{POA}/\Delta\text{CO} \sim 0.010 \pm 0.005 \mu\text{g m}^{-3} \text{ppbv}^{-1}$ ) observed in fresh air masses over other urban environments (de Gouw et al., 2008). This difference may arise from contributions of sources other than urban vehicular exhaust to POA in this region, as is further discussed below. Additionally, using the best estimates of the ODR slope and intercept values of the regression the fit lines to the data, the predicated OA at background levels of CO ( $\sim 105 \text{ppbv}$ ) was -0.8-2.31.82  $\mu\text{g m}^{-3}$ . This value, which was very similar to the mode of the OA frequency distribution in the BL at 1.85  $\mu\text{g m}^{-3}$ , is, a substantial portion of total OA, which suggestsuggesting- the presence of relatively high concentrations of non-combustion related OA, likely of biogenic origin, in the region.

For a more detailed investigation of OA formation in different plumes, correlations of OA vs. CO in  $\sim 94$  individual plumes in the boundary layer on 26 July- 11 August were investigated to determine the corresponding  $\Delta\text{OA}/\Delta\text{CO}$  values by the slope of weighted ODR fits. The spatial distribution of  $\Delta\text{OA}/\Delta\text{CO}$  values, color-coded with the observed ratio of *i*-pentane/*n*-pentane is summarized in Fig. 2 for cases where the correlation coefficient (*r*) of OA vs. CO was greater than 0.5 and where the standard deviation of the ODR slopes was less than 50% of the slope itself. Urban emissions of the pentane isomers typically result in *i*-pentane/*n*-pentane values  $> 2$  (Warneke et al., 2007; Warneke et al., 2013) while O&G emissions in DJB have shown characteristic ratios  $\sim 1$  (Petron et al., 2012; Gilman et al., 2013). Considering the location of the active O&G wells in the Front Range (Fig. 2), the lower *i*-pentane/*n*-pentane values observed to the North of Denver Metro are a strong indicator for the influence of O&G emissions in these plumes. There are several plumes with a high O&G emission influence in this area that also display a large enhancement in OA with respect to CO. The apparent difference in the enhancement ratios may be due to the lower CO mixing ratios in the non-urban plumes or higher OA concentration in plumes sampled to the north of Denver Metro, either because of longer photochemical age or higher concentrations of OA precursors in such plumes. We further investigate these differences in the next sections.

PMF analysis of the OA spectra resolved two distinct profiles with spectra shown in Figure 3a. ~~Increasing the number of factors resulted in split factors and a minimal decrease in  $Q/Q_{\text{expected}}$ .~~ In the 2-factor solution, the first factor had a higher contribution of  $m/z$  44 and is identified as the secondary and oxygenated factor (OOA) as it correlated best with the OOA factor previously identified in several field studies (Ng et al., 2011) as well as secondary species such as sulfate and nitrate (Table 4). ~~Increasing the number of factors resulted in split factors and a minimal decrease in  $Q/Q_{\text{expected}}$ .~~ When examining correlation coefficients of two of the factors (in a 3-factor solution case) containing signal at  $m/z$  44 with external tracers, only the correlations with CO were significantly different ( $r=0.03$  vs.  $0.28$ ) while correlations with other anthropogenic and biogenic tracers (e.g., acetylene, ethane, isoprene oxidation products (i.e., methyl vinyl ketone and methacrolein) and monoterpenes) or aerosol nitrate and sulfate were not. We therefore believe that the 3-factor solution is unable to determine a meaningful and independent 3<sup>rd</sup> factor, and thus PMF is unable to clearly isolate the contribution of biogenic vs. anthropogenic sources to OOA in this environment. Statistically similar enhancement ratios of OOA relative to CO or odd oxygen ( $O_x$ ) in aged (i.e.,  $NO_x/NO_y < 0.3$ ) urban and high O&G-influenced plumes were obtained (Fig. S2S3); however, median and mean OOA concentrations in plumes with a large influence of O&G emissions were ~25% higher than the values in urban-only plumes, under similar non-cyclonic atmospheric conditions (Fig. 3c) (Sullivan et al., 2016; Vu et al., 2016). The uncorrelated relationship between OOA and  $O_x$  under cyclonic conditions in plumes with a high O&G influence is similar to an observed large scatter in CO versus  $O_3$  (not shown). Influence of upwind sources of CO and OOA that were not correlated with  $O_3$  formation (e.g. biomass burning) cannot be ruled out under the cyclonic episodes sampled here, resulting in mean and median OOA values in O&G-influenced plumes during cyclonic flow that were outside the variability range of the values observed during the non-cyclonic flow. More discussion on the role of different emissions source on OA is presented in Sections 3.2-3.3. Overall, the OOA factor dominated the OA composition, contributing to 85% of OA mass. The second factor, referred to as HOA, had a pronounced fragmentation pattern at delta patterns 0 and 2 (e.g.,  $m/z$  41, 43, 55, 57, 69, 71, etc.) that are common for hydrocarbons (McLafferty and Turecek 1993), correlated best with the HOA factor in previous field studies (Ng et al., 2011) as well as primary combustion tracers such as acetylene and CO; it therefore represents the fresh, hydrocarbon-like components of OA. Mean HOA concentrations were ~35% higher (Fig. 3d) in high O&G-influenced plumes compared to urban plumes, under similar non-cyclonic conditions, suggesting contribution of primary aerosol (in this case, POA) emissions from equipment associated with O&G-related activities (Field et al., 2014; Prenni et al., 2016). Averaged over all plume types, contribution of HOA to total OA mass was 15%. Although airborne measurements of aerosol optical extinction and HCN provided evidence for long-range transport of biomass burning plumes during 11-12 August (Dingle et al., 2016) to the Front Range, a factor with a significant contribution at fragments associated with levoglucosan combustion (i.e.,  $m/z$  60 and 73) was not identified. Therefore, either the contribution of wildfires to non-refractory OA composition during the days of PMF analysis was negligible or that photochemistry of the fire plumes during transport resulted in chemical transformation of the BB markers (Hennigan et al., 2010; Hennigan et al., 2011).

### 3.2 Influence of Urban and O&G Emissions: Measurements

To better understand the impact of urban vs. O&G emissions on SOA formation in the Front Range, data on measured OA, known precursors of SOA, and photochemical markers were examined in urban air masses and those with a high influence of O&G emissions (Fig. 4). Mean and median values of OA were ~40-48% higher in high O&G- influenced plumes compared to urban plumes. As discussed in Section 3.1 and Fig. 3, most of the OA in the Front Range is oxygenated and secondary in nature. More efficient SOA production in an air mass could be due to differences in oxidation time scales, amounts of SOA precursors or oxidants, or oxidation conditions, and thus SOA production yields. Statistical data in Fig. 4b-d indicate that while the mixing ratio of biogenic species (sum of the measured isoprene, monoterpene, and 2× (methyl vinyl ketone and methacrolein)) in the two air mass types were similar within 20%, the median mixing ratio of the sum of aromatic species (i.e., benzene, toluene, C<sub>8</sub>-, and C<sub>9</sub>-aromatics) and sum of methylcyclohexane and *n*-octane, which are known SOA precursors (Odum et al., 1997a; Odum et al., 1997b; Lim and Ziemann 2005), were higher by factors of 2.4 and 4.7, respectively, in high O&G-influenced plumes relative to urban plumes. Therefore, it is not surprising that higher OA and OOA concentrations were measured in high O&G-influenced plumes. Next, we examine photochemical conditions that affect SOA production yields. Radical chemistry in different NO<sub>x</sub> regimes leads to different SOA formation potentials, depending on the branching ratio of RO<sub>2</sub> radicals reacting with HO<sub>2</sub> vs. NO (Kroll et al., 2005; Ng et al., 2007a; Ng et al., 2007b; Henze et al., 2008). Median NO mixing ratios in urban and high O&G plumes were at least 350 pptv (Fig. 4d), which is about a factor of 10 higher than the median HO<sub>2</sub> mixing ratios in these plumes (Fig. 4e), suggesting that the oxidation conditions encountered in both urban- and high O&G- influenced air masses were NO-rich, and hence provide the conditions where RO<sub>2</sub> radicals predominantly react with NO rather than HO<sub>2</sub> radicals. Furthermore, mean and median OH concentrations in both urban and high O&G-influenced plumes were similar to within ~15%. The dominance of NO over HO<sub>2</sub> and lack of a significant difference in OH concentrations in urban- and high O&G- influenced air masses indicate presence of similar oxidation conditions in the two air mass types. Thus, the higher OA values in high O&G- influenced plumes compared to pure urban plumes is hypothesized to be due to SOA formation from higher concentrations of aromatics and larger alkanes. We further investigate the contribution of O&G sources to SOA formation in simulation scenarios with WRF-Chem modeling.

### 3.3 Influence of Urban and O&G Emissions: Modeling

#### 3.3.1 WRF-Chem Simulations of Gaseous Species

We begin examining the results of WRF-Chem simulation runs by first comparing predicted mixing ratios of various primary and secondary gases in urban and high O&G-influenced air masses. This exercise was not performed as a point and point comparison along the flight track since locations of the simulated pollution plumes were sometimes shifted compared to the measurements. An example of differences between the measured and modeled distribution of plumes is shown for ethane in Fig. S4. Because of this, flags similar to those used for characterizing plumes measured with urban and high O&G emissions were defined, based on the modeled values of CO and C<sub>2</sub>H<sub>6</sub>, and statistical analysis of data under each flag type were carried out. To assess the impact of the emission scenarios, we first compare measured and modeled values of C<sub>2</sub>H<sub>6</sub>, toluene, and CO in urban and high O&G-influenced air

masses. Figures 5a-b demonstrate that there is a large influence of  $C_2H_6$  from the O&G sector in the Front Range and that neglecting those emissions significantly underestimates  $C_2H_6$  mixing ratios in both urban and high O&G-influenced plumes. In urban plumes (Fig. 5c, 5e), the mean toluene and CO mixing ratios were very similar under both emission scenarios and overestimated compared to the measurements by a factor of 2 and 20%, respectively. In the high O&G-influenced plumes (Fig. 5b, 5d, 5f), neglecting the O&G emissions of VOCs resulted in underestimation of  $C_2H_6$  (by a factor >10) and toluene (by 35%) and ~10% overestimation of CO compared to the measurements. When modifying the O&G emissions with the top-down approach, a reasonable comparison for  $C_2H_6$  was achieved in the high O&G-influenced plumes; additionally, mean toluene mixing ratio was now within 12% of the measurements while the mean values for CO did not change. These comparisons demonstrate that adjusting the O&G sector emissions by the top-down approach was necessary to realistically capture the influence of such emissions in the Front Range.

We next compare the mixing ratios of biogenic SOA precursors with the modified NEI emissions. Since emissions of ~~these species~~ biogenic VOCs were not modified in the top-down approach and because one goal of the current study is to investigate the contribution of O&G emissions to OA formation, we focus on the comparison between the measured values and only the modified, top-down O&G emission scenario (Fig. 6). These comparisons suggest that isoprene and its oxidation products are well represented in the model whereas the monoterpene mixing ratios are underestimated by as much as 50%. The effect of this underestimation on total SOA formation however may not be significant given the very low measured monoterpene mixing ratios (average and median values of ~40 pptv).

Overall, measured and predicted OH concentrations in urban and high O&G-influenced plumes compared very well with the top-down estimates of O&G emissions (Fig. 7a-b). Mean and median OH concentrations without O&G emissions were overestimated in O&G-influenced plumes by ~40%. Mean and median values of  $HO_2$  were predicted very well in the high O&G-influenced plumes regardless of the emission scenario, but with a lower degree of variability compared to the measurements. Median and mean values of the measured urban  $HO_2$  were about twice as much as the predicted values. However, given the measurement uncertainty levels (up to 35%), the comparison is still very good (Fig. 7c-d). Predicted mean and median NO mixing ratios in urban plumes compared well with the measurements, while the high NO values in plumes with a high influence from O&G emissions were not predicted well, resulting in 60% lower mean NO values in these plumes (Fig. 7e-f). Since NO emissions from the O&G sector remained the same in the different scenarios, comparisons with only one scenario are shown here.

Measured and predicted values of  $O_3$  are compared in Fig. 8. Without emissions from the O&G sector, mean predicted  $O_3$  in urban and high O&G-influenced plumes were ~8.5 ppbv and ~2 ppbv lower than measurements. The higher discrepancy observed in urban plumes might be due to overestimation of primary urban emissions (e.g., toluene, CO, and NO), and subsequently higher  $O_3$  titration by NO, or due to lower extent of mixing in the model. In simulations including the O&G emissions, a minor (<1 ppbv) increase in the mean urban  $O_3$  was predicted while the increase in high O&G-influenced plumes was more significant, at ~4.5 ppbv. It should be noted that the uncertainties in meteorological simulations (e.g. wind speed and direction) also contribute to the overall model-measurement discrepancies of the chemical species discussed here.



### 3.3.2 WRF-Chem Simulations of Organic Aerosol

In this section we examine simulated values of different OA types in the different simulation runs and compare them with the factors resolved by PMF. The cumulative distributions of PMF-derived HOA and simulated POA concentrations in the Front Range boundary layer are shown in Fig. 9a. It is apparent that the median value of POA in the base case and all the runs using a similar volatility assumption of POA is significantly lower than the HOA estimate derived from PMF. It is worth noting that cooking POA contributions in NEI might be underestimated for the Front Range area, while there could be some contribution of POA from cooking or sources other than vehicular exhaust to the PMF-resolved HOA factor. For example, as shown in Fig. 3d and discussed previously, there appears to be some contribution to HOA from O&G-related activities. A higher POA emission factor from O&G-related activities is not unexpected given typically high emissions from diesel engines without after-treatment technology that might be working at these sites (Ban-Weiss et al., 2008; Jathar et al., 2017); however, as mentioned before, there were no adjustments to POA emissions for the O&G sector in WRF-Chem when modifying the top-down estimates of gaseous emissions. Despite this, it is unlikely that NEI emission factors of POA from the urban areas are underestimated by factors up to 8 (mean HOA  $\sim 0.45 \mu\text{g m}^{-3}$  vs. mean POA  $\sim 0.05 \mu\text{g m}^{-3}$ ). One possible explanation for this discrepancy is the assumed volatility distribution of the POA. Given the large uncertainties in volatility estimates of POA from different sources (Hodzic et al., 2010b; May et al., 2013), to explore the effect of POA volatility, simulations were repeated assuming non-volatile POA. In these runs and regardless of O&G emission treatments, the mean and median POA values increased by a factor of 5, bringing the predicted POA values within a factor of 2 of the PMF-based HOA concentrations. The non-volatile POA assumption may not be accurate, and improved volatility distributions of POA from different combustion sources would have to be considered to accurately account for semi-volatility of POA emissions in future air quality models. However, in the absence of better estimates of POA emission ratios or volatility, it is therefore believed that the predicted POA values in current simulations with non-volatile POA conditions are more realistic-comparable to the PMF-based estimates of HOA for-in this environment.

Modeled total OA values in the Front Range BL are compared with the observed values in Fig. 9b. The median values of most model scenarios, except when biogenic aging was turned off, were  $\sim 35\%$  higher than measurements, which is an excellent agreement considering the uncertainties in measurements, emissions (magnitude and speciation), meteorological simulations, and other input parameters of the model. The extremely low and high values of measured OA, however, were not predicted well with any of the model runs, likely due to uncertainties in emissions of IVOCs from urban and O&G sector as well as uncertainties in the aging mechanisms of hydrocarbons (e.g., extent of fragmentation vs. functionalization reactions or aging of biogenic SVOC products). Measured and modeled total OA values in urban and O&G-influenced plumes are compared in Fig. 10a-b. Regardless of model assumptions, predicted median values of OA were  $0.6$  to  $1.8 \mu\text{g m}^{-3}$  (25 to 58%) higher than the measured median values in urban plumes. This overprediction may partly stem from higher than measured mixing ratios of urban VOCs in the model (Fig. 5c). Comparisons in the high O&G-influenced plumes were better, with differences of only  $-0.2$  to  $0.8 \mu\text{g m}^{-3}$  (-6 to 25%) between measured and predicted values. Consistent with the observations in Fig. 9b,

there was a bias towards higher values in the modeled urban OA while the measured high values in O&G-influenced plumes were underpredicted.

The effect of POA volatility was most apparent in predicted OA values in the urban plumes. Considering results of pairs of runs with similar consideration of O&G emissions, non-volatile POA runs resulted in ~13% (~0.4  $\mu\text{g m}^{-3}$ ) increase in total OA compared to scenarios where POA was assumed to be semi-volatile (Fig. 10a). To determine how different components of OA were affected by changes in POA volatility, anthropogenic and biogenic SOA values (aSOA and bSOA, respectively) were considered separately. Assuming POA was non-volatile actually reduced aSOA by < 5% (~0.05  $\mu\text{g m}^{-3}$ ) in urban plumes (Fig. 10c) while it increased bSOA by 2-4% (0.04-0.08  $\mu\text{g m}^{-3}$ ) (Fig. 10e). ~~When POA is treated as semi-volatile, a fraction of POA emissions remain in the gas phase in the atmosphere, thereby not contributing to total OA. The reason for the reduction in aSOA is that with the non-volatile assumption of POA, its semivolatile components are not available for gas phase oxidation, reducing concentrations of anthropogenic oxidized species that are condensable, thus leading to a decrease in aSOA. On the other hand, since POA concentration is higher when assumed non-volatile, available aerosol mass for absorptive partitioning is higher, resulting in increased partitioning of semivolatile bVOC oxidation products to the aerosol phase, thus an increase in bSOA concentration.~~ Therefore, it appears that most of the increase in urban total OA in non-volatile POA scenarios is due to the contribution from POA ~~itself~~.

The effect of including top-down estimates of O&G emissions on predicted OA was quantified from changes in predicted OA, under the same POA volatility assumption, in the high O&G-influenced plumes. Results indicate at most a 4.7% increase in OA from O&G emissions. Although the net increase in OA due to O&G emissions was relatively small, there was a ~30-38% (~0.4  $\mu\text{g m}^{-3}$ ) increase in aSOA due to these emissions, depending on POA volatility. On the other hand, median bSOA values decreased by 8-10% (<0.2  $\mu\text{g m}^{-3}$ ) after including the top-down estimates of O&G emissions, likely due to reductions in OH with the additional VOC emissions in the high O&G-influenced plumes (Fig. 7b).

As apparent in the cumulative distribution of OA (Fig. 9b), the model cases discussed so far do not capture ~10% of the data where measured OA values are lower than 1  $\mu\text{g m}^{-3}$ , suggesting that the background OA in these runs might be overpredicted. A final model run was designed to investigate the role of successive biogenic VOC aging on the predicted OA and its background values. Although the low-concentration OA data points were still overpredicted in this model run (Fig. 10), the overall comparisons with the observed OA values (Fig. 10a-b) were best when consecutive formation of bSOA was turned off. Specifically, total predicted OA values in these run were 0.8-1  $\mu\text{g m}^{-3}$  lower than the scenarios with similar POA volatility and O&G emissions while consecutive formation of bSOA was active. This decrease was predominantly due to the decrease in bSOA portion of OA (Fig. 10 e-f). It is worth highlighting that even with these reduced bSOA values, the predicted contribution of bSOA to total OA in the Front Range remained high, at ~54% and 40% in urban and O&G-influenced plumes, respectively (Fig. 11). This is qualitatively consistent with the relatively high values of OA at background CO mixing ratios as was shown in Fig. 1.

We further examine simulations of SOA formation in two scenarios with non-volatile POA. With the standard treatment of bVOC oxidation and bSOA formation, urban plumes with  $\text{NO}_x/\text{NO}_y < 0.3$  displayed a 50% greater

enhancement in SOA with respect to CO ( $\Delta\text{SOA}/\Delta\text{CO}$ ) compared to plumes with a high O&G influence (Fig. ~~4a12a~~). On the other hand, SOA enhancement with respect to  $\text{O}_x$  ( $\Delta\text{SOA}/\Delta\text{O}_x$ ) was 30% higher in high O&G-influenced plumes (Fig. ~~4e12c~~). By turning off consecutive formation of bSOA, similar  $\Delta\text{SOA}/\Delta\text{CO}$  enhancement ratios were obtained in urban and high O&G-influenced plumes (Fig. ~~4b12b~~) while the difference in  $\Delta\text{SOA}/\Delta\text{O}_x$  increased, with the ratio in high O&G-influenced plumes being ~66% higher than in urban plumes (Fig. ~~4d12d~~). Both of these trends are consistent with reductions in bSOA in urban plumes. Neither of the simulation scenarios resulted in  $\Delta\text{SOA}/\Delta\text{CO}$  values similar to the observed  $\Delta\text{OOA}/\Delta\text{CO}$  in urban plumes although the predicted values in high O&G-influenced plumes were consistent with the lower values of the ODR fits to the observations considering the 95% confidence intervals (Fig. ~~S2S3~~). It is worth noting that not considering variable background levels of OOA and CO and the uncertainties associated with PMF analysis might have also impacted the comparisons discussed here. Simulated  $\Delta\text{SOA}/\Delta\text{O}_x$  were also significantly lower than observed  $\Delta\text{OOA}/\Delta\text{O}_x$  in urban plumes indicating that neither runs predicted an accurate relationship for SOA and  $\text{O}_x$  formation in these plumes, despite predicting OA well. Contrary to the measurements, predicted CO (Fig. 5e-f), NO (Fig. 7e-f), and  $\text{O}_3$  (Fig. 8a-b) mixing ratios were different in urban and high O&G-influenced plumes, therefore contributing to some of the differences in predicted  $\Delta\text{SOA}/\Delta\text{CO}$  and  $\Delta\text{OOA}/\Delta\text{O}_x$  in urban vs. O&G-influenced plumes.

#### 4 Conclusions and Implications

Summertime OA in the Front Range displayed significant enhancement with respect to CO in photochemically aged plumes. Substantial contributions of OOA in plumes impacted by urban and O&G emissions were confirmed with PMF analysis. In the absence of cyclonic flow and under similar atmospheric conditions, differences in OOA and HOA concentrations in urban vs. high O&G-influenced plumes were within the observed variabilities while mean and median concentrations of OOA were significantly higher during the Denver cyclone. Mixing ratios of aromatics, methyl cyclohexane, octane, and  $\text{RO}_2$  radicals were significantly higher in high O&G-influenced plumes compared to urban plumes. Despite this, OH and  $\text{HO}_2$  mixing ratios were highly similar.

To assess the role of O&G emissions on SOA production, WRF-Chem model runs were carried out, with different considerations for POA volatility and emission strengths from the O&G sector. Assuming a semi-volatile nature for POA resulted in greater than factor of 10 lower mean and median POA concentrations compared to the PMF-based HOA while simulations with the assumption of non-volatile POA resulted in only a factor of 2 lower POA compared to HOA. Assuming non-volatile POA increased the predicted total OA by ~13%, mainly through additional contribution of POA to OA. Much improved comparisons between predicted mixing ratios of VOCs and the measurements were achieved when using a top-down modified emission factors from the O&G sector in DJB. Overall, comparisons of the median measured and predicted OA were satisfactory, with the best match obtained in runs when consecutive aging of bVOCs and bSOA formation was turned off. The extent of SOA formation due to emissions from the O&G sector was estimated to be less than 5% of total OA; however, the contribution of O&G emissions to aSOA was more significant at ~30-38%. Given the uncertainties in emissions of IVOCs from the O&G sector, more simulations need to be carried out to better quantify the contribution of O&G IVOC emissions to total OA. In addition, it is important to characterize POA emissions associated with the O&G sector in future emission

inventories. A large fraction (~40-54%) of OA in the Front Range was predicted to be from bSOA. Uncertainties in photochemical processing and aging of bVOCs also warrant additional studies to constrain the production of bSOA. It is worth noting that in wintertime with lower boundary layer heights and lower temperatures, subsequently higher aerosol mass and more favorable conditions for partitioning of semivolatile species to the aerosol phase, as well as significantly lower emissions of bVOCs, contributions of O&G emissions to SOA in the Front Range could be more significant than what was observed during this study.

## 5 Data Availability

Data used in this analysis are available at <http://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq.co-2014?C130=1>.

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Category	Selected Options and Parameters
Land Surface	Noah Land Surface Model
PBL Scheme	Mellor-Yamada Nakanishi and Niino
Microphysics	WRF Single-moment, 5 class scheme
Cumulus	Grell-Freitas scheme (12 km domain only)
Short- and Longwave Radiation	RRTMG short and longwave
Gas Chemistry	RACM ESRL 5
Aerosol	MADE, VBS-based SOA parameterization
Photolysis	Madronich
Anthropogenic Emissions	NEI 2011v1
<b>Biogenic Emissions</b>	<b>BEIS 3.14</b>

**Table 1.** Settings and parameterizations used for the WRF-Chem simulations.

Case Identifier	Emissions	POA volatility	BVOC oxidation rate and subsequent SOA formation
BC-nOG	NEI, no O&G	Semi-volatile	$k_{OH} = 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
BC-tdOG	NEI, top-down O&G	Semi-volatile	$k_{OH} = 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
nvPOA-nOG	NEI, no O&G	Non-volatile	$k_{OH} = 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
nvPOA-tdOG	NEI, top-down O&G	Non-volatile	$k_{OH} = 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
nvPOA-tdOG- bVOCox	NEI, top-down O&G	Non-volatile	Limited formation of bSOA

10 **Table 2.** Details on input parameters and assumptions used in the different WRF-Chem simulation scenarios.

Species	Total	Mobile		Area	Point
		On-road	Non-road		
NO <sub>x</sub>	144.36	53.50	20.56	14.28	56.00
CO	874.37	366.07	426.84	11.76	69.70
C <sub>2</sub> H <sub>6</sub>	232.34	0.56	0.57	221.93	9.28
Toluene	4.52	1.08	0.97	1.82	0.65
Unknown	1.87	0.15	0.00	1.35	0.36
POC	3.66	0.47	0.72	1.78	0.69
PNCOM	1.28	0.13	0.18	0.71	0.26

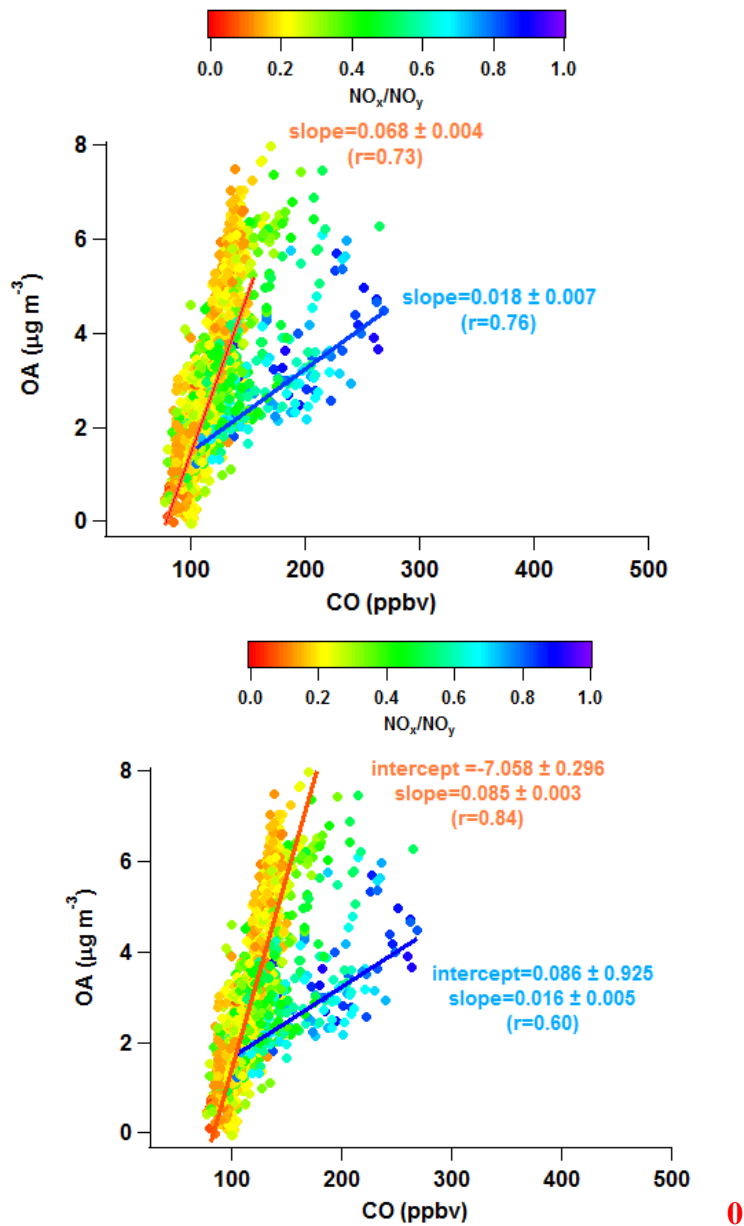
**Table 3a.** NEI-2011 Emissions (July, weekday) for Denver Julesburg Basin box, 39.8-40.7°N, 104.25-105.4°W (9764 km<sup>2</sup>). Top-down estimates for C<sub>2</sub>H<sub>6</sub> and Toluene Point and Area sources are indicated. Units are kilo mole/hr for gas-phase species, short-ton/day for POC (primary organic carbon) and PNCOM (primary non-carbon organic matter).

Species	Total	Mobile		Area	Point
		On-road	Non-road		
NO <sub>x</sub>	153.70	90.27	27.86	0.76	34.81
CO	1351.82	646.56	684.47	2.24	18.56
C <sub>2</sub> H <sub>6</sub>	3.76	0.94	0.81	1.50	0.52
Toluene	4.61	1.86	1.47	0.75	0.53
Unknown	0.68	0.26	0.01	0.06	0.36
POC	4.53	0.79	1.04	2.37	0.33
PNCOM	1.55	0.21	0.26	0.95	0.13

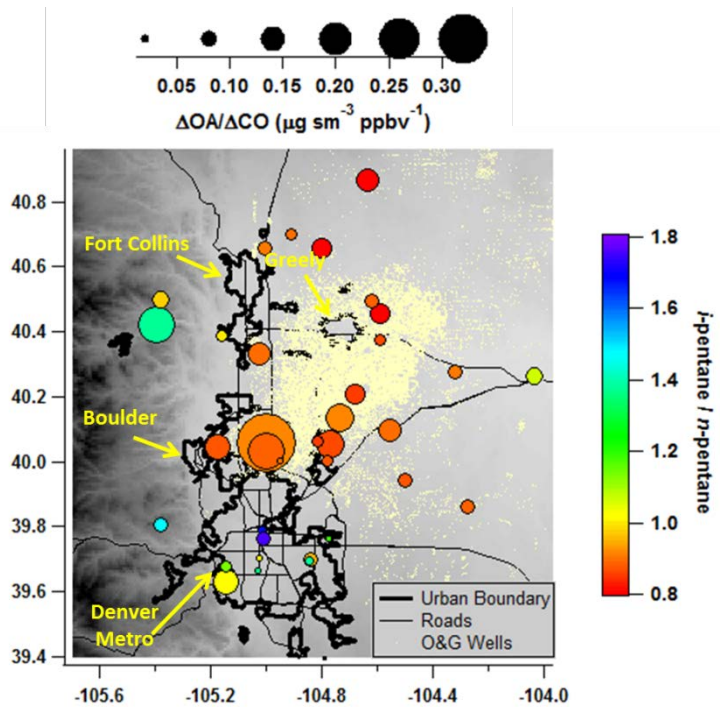
15 **Table 3b.** NEI-2011 Emissions (July, weekday) for Denver Metropolitan box, 39.5-40.0°N, 104.7-105.2°W (2376 km<sup>2</sup>). Units are kilo mole/hr for gas-phase species, short-ton/day for POC and PNCOM.

	CO	Acetylene	C <sub>2</sub> H <sub>6</sub>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HOA <sup>a</sup>	OOA <sup>a</sup>
<b>Factor 1- OOA</b>	0.68	0.71	0.46	0.64	0.69	0.50	0.95
<b>Factor 2- HOA</b>	0.68	0.76	0.44	0.47	0.40	0.92	0.50

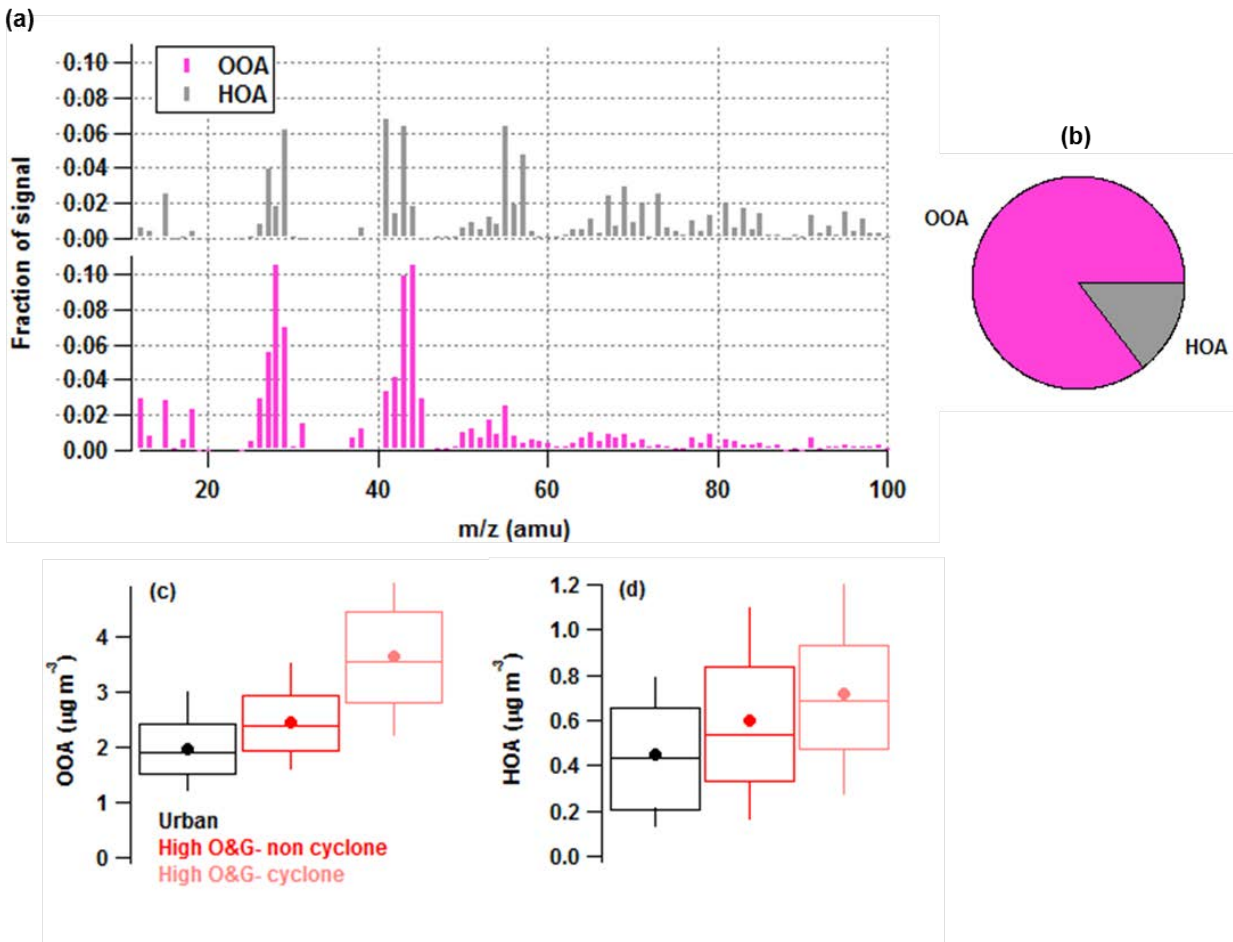
**Table 4.** Correlation coefficient of PMF factors with different species. <sup>a</sup>HOA and OOA factors as identified in Ng *et al.* (2011)



5 **Figure 1.** Scatter plot of OA against CO. The slopes are from weighted (by 30% uncertainty in OA and 3% uncertainty in CO) ODR fits to the data in relative fresh ( $\text{NO}_x/\text{NO}_y > 0.7$ ) and aged ( $\text{NO}_x/\text{NO}_y < 0.3$ ) plumes. The estimated uncertainties in the slope values represent 95% confidence intervals.

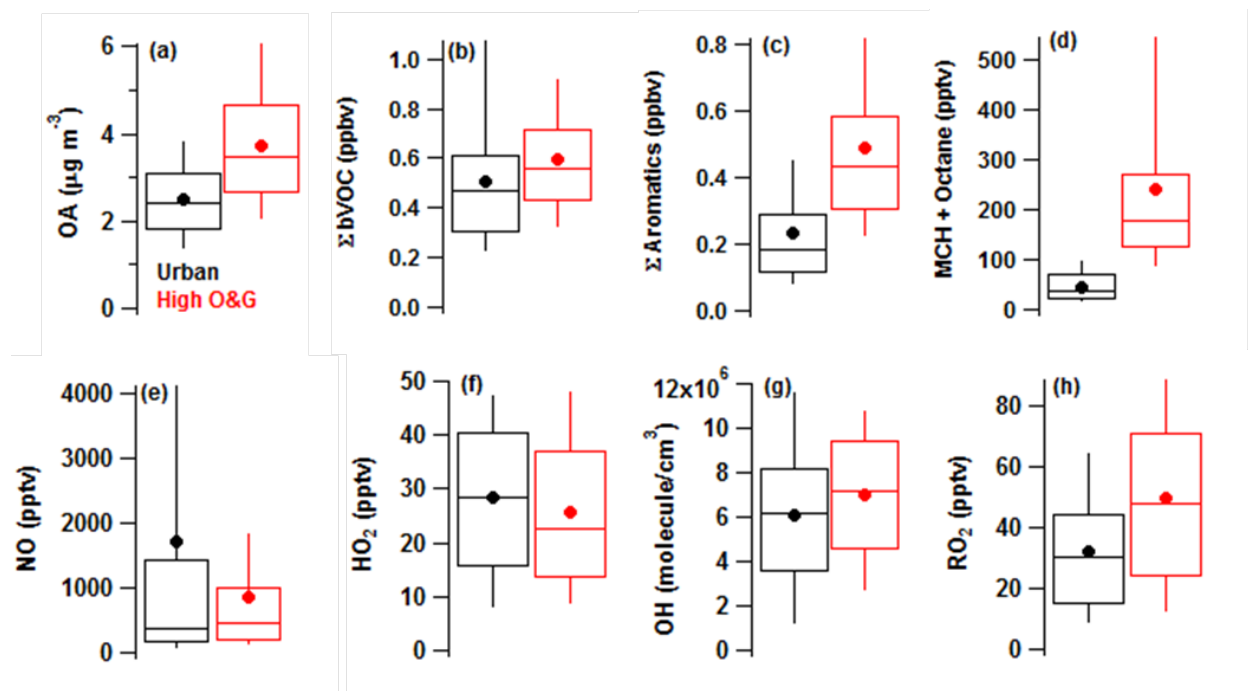


**Figure 2.** Enhancement ratios of OA with respect to CO in individual plumes sampled in the Front Range BL. Points are sized with  $\Delta OA/\Delta CO$  and color coded by the *i*-pentane/*n*-pentane ratio. Only cases where the correlation coefficient (*r*) of OA vs. CO was greater than 0.5 and the standard deviation of the ODR slopes was less than 50% of the slope itself are highlighted. Locations of O&G wells are shown with yellow dots.



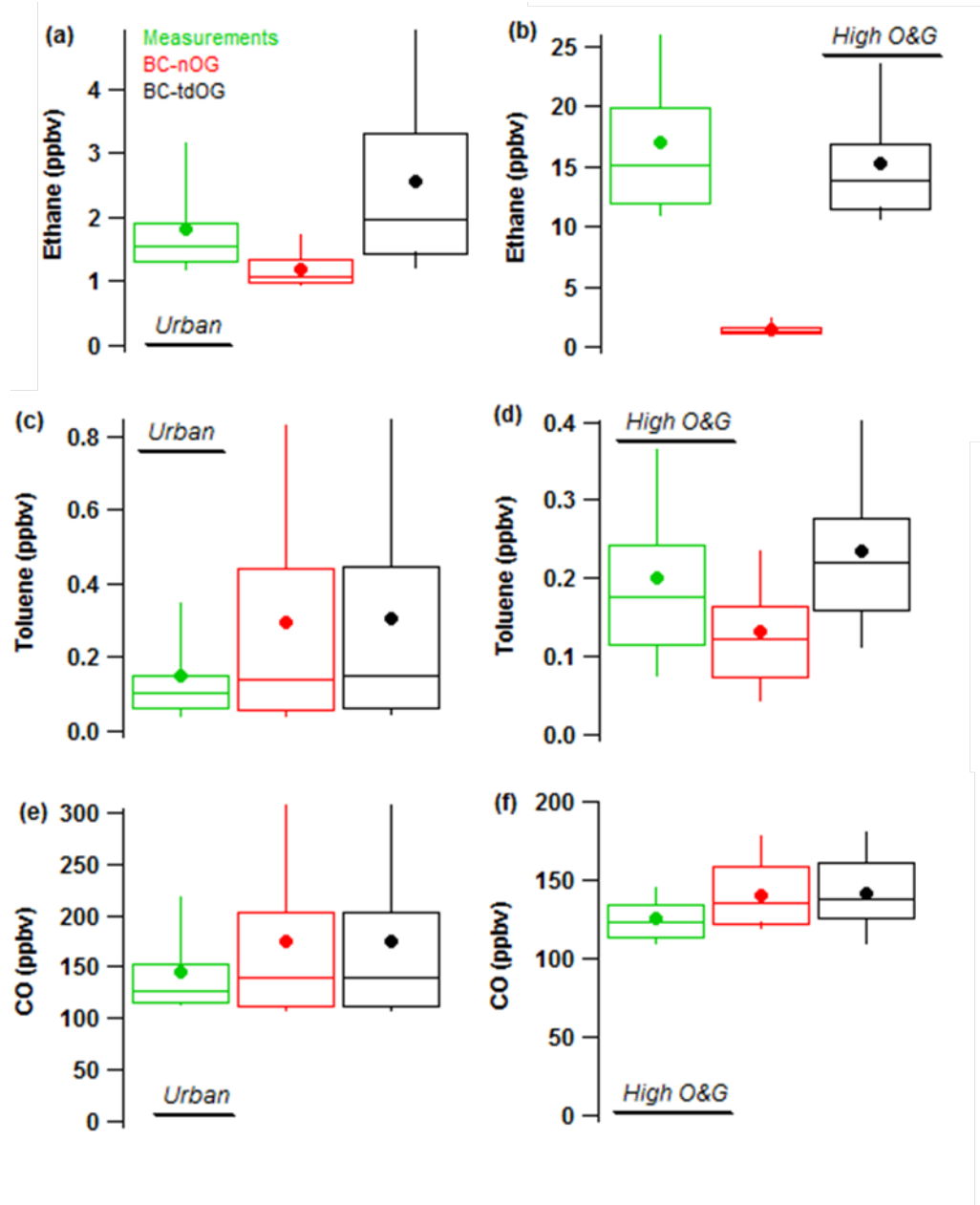
**Figure 3.** Mass spectra (a), fractional contribution (b), and mass concentrations of OOA (c) and HOA (d) factors. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Mean values of OOA and HOA in each plume type are shown in circles.



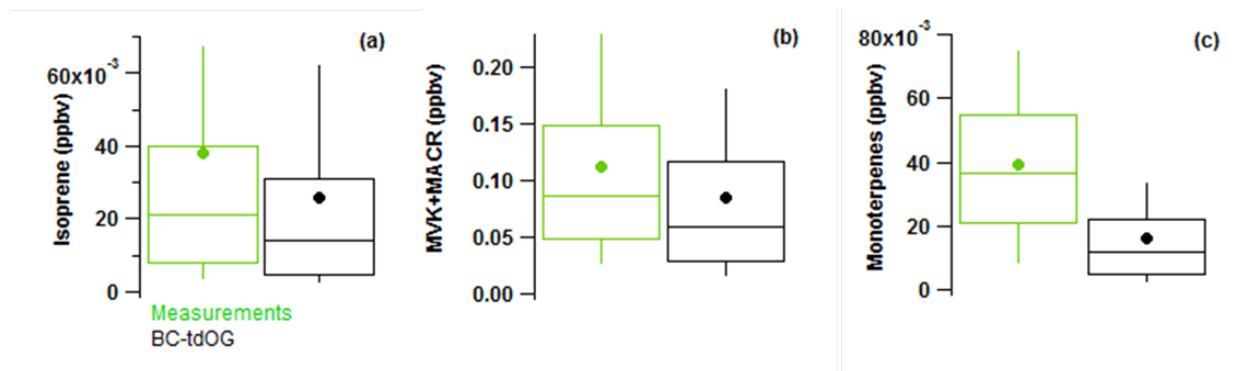


**Figure 4.** Statistical analysis of measured OA (a), various hydrocarbons (sum of biogenic VOCs, bVOC, defined as isoprene+2×(methyl vinyl ketone + methacrolein) + monoterpenes (b), sum of aromatic VOCs defined as benzene+toluene+C<sub>8</sub>-aromatics+C<sub>9</sub>-aromatics (c), sum of methylcyclohexane and octane (d), NO (e), and radicals (HO<sub>2</sub>(f), OH (g), and RO<sub>2</sub> (h)) in urban and high O&G-influenced plumes. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Mean values in each plume type are shown in circles.

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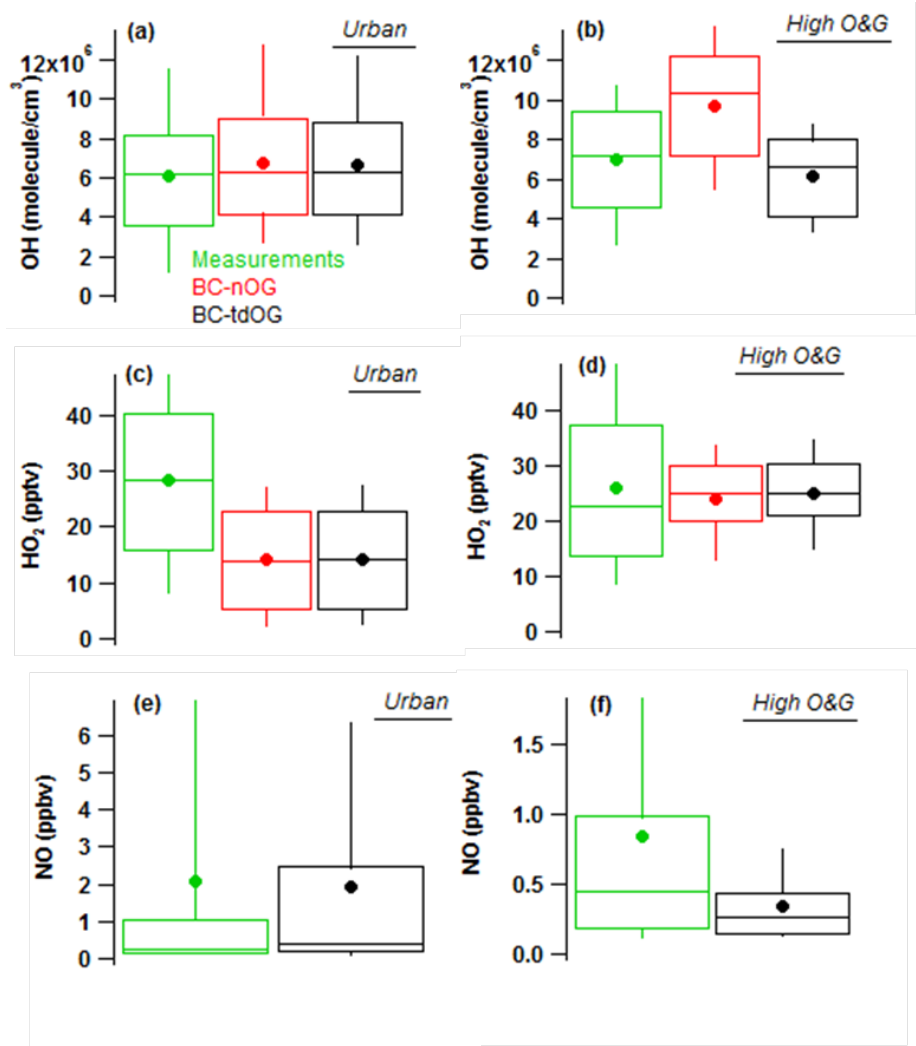


**Figure 5.** Comparison of the measured and WRF-Chem predicted (no O&G and top-down O&G emission scenarios) mixing ratios of ethane (a and b), toluene (c and d), and CO (e and f) in urban and high O&G-influenced plumes. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Mean values are shown in circles.



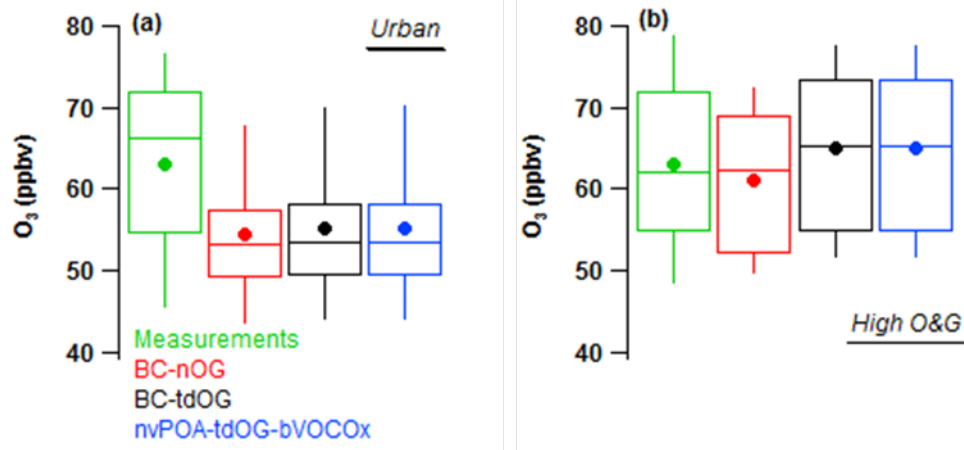
**Figure 6.** Comparison of the measured and WRF-Chem predicted (top-down O&G emission scenario) mixing ratios of isoprene (a), methyl vinyl ketone (only available in measurements) and methacrolein (b), and monoterpenes (c) in the Front Range boundary layer. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Mean values are shown in circles.

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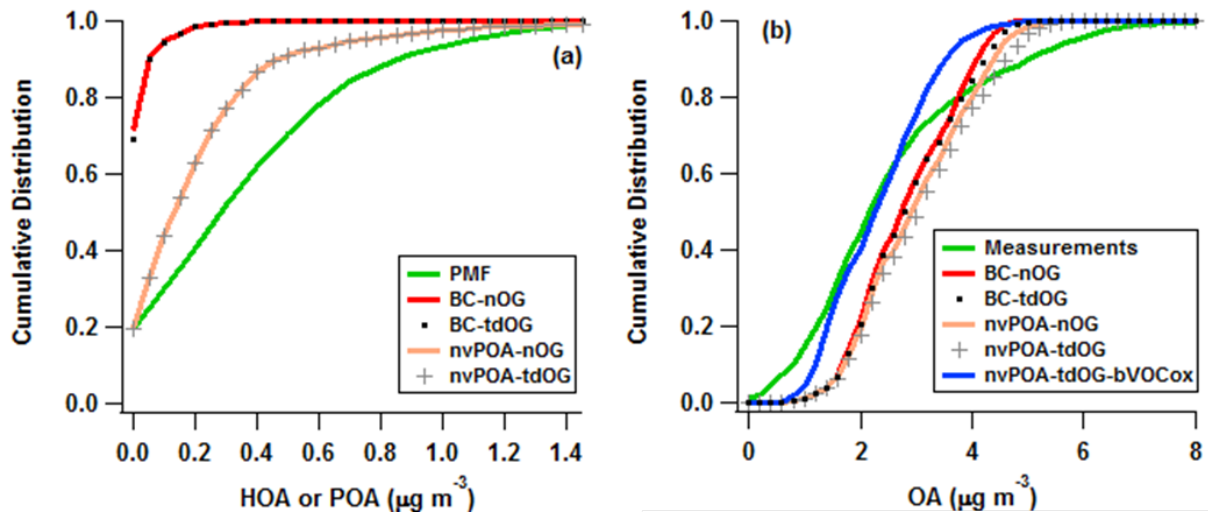


**Figure 7.** Comparison of the measured and WRF-Chem predicted (no O&G and top-down O&G emission scenarios) amounts of OH (a and b), HO<sub>2</sub> (c and d) and NO in urban and high O&G-influenced plumes. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Mean values are shown in circles.

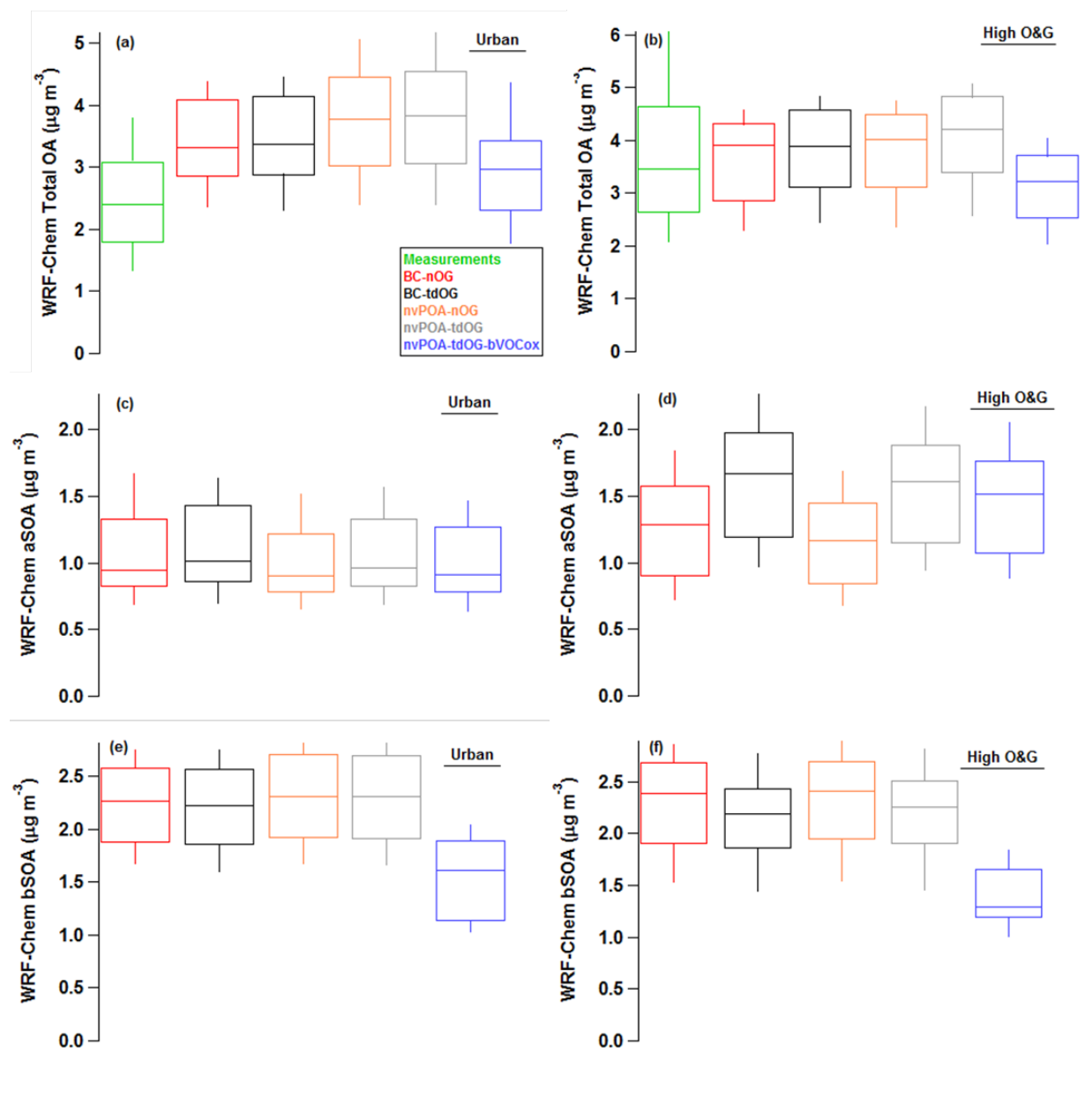
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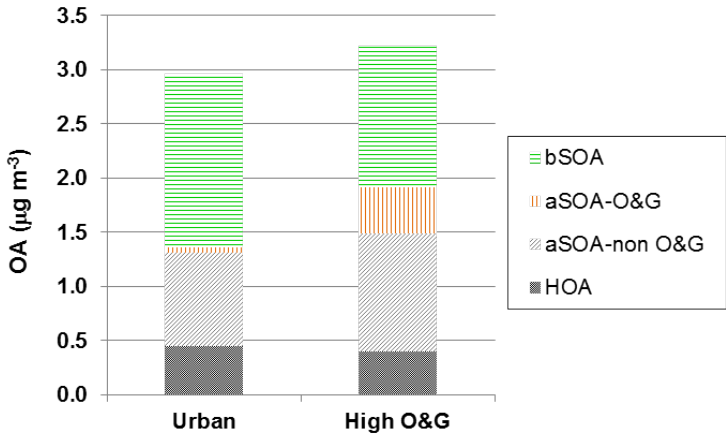
**Figure 8.** Comparison of the measured and WRF-Chem predicted mixing ratios of ozone in urban (a) and high O&G-influenced (b) plumes. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Mean values are shown in circles.



**Figure 9.** Cumulative distribution of HOA or POA (a) and OA (b) based on measurements and various simulation scenarios.

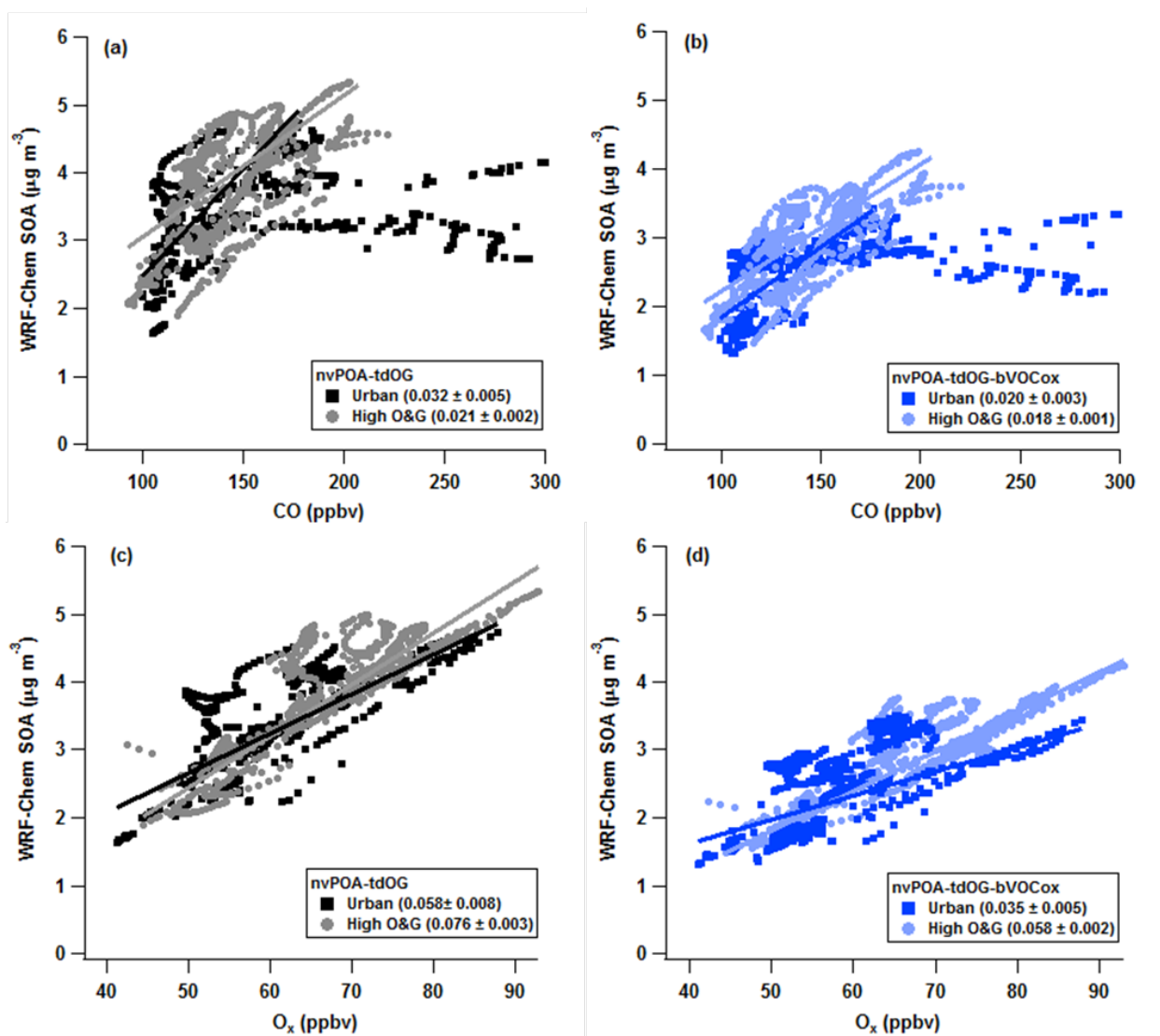


**Figure 10.** Statistical comparisons of predicted OA, anthropogenic SOA (aSOA) and biogenic SOA (bSOA) in urban (a, c, e) and high O&G-influenced (b, d, e) plumes in different model scenarios. Data from measured OA are also included in a-b. Box and whiskers depict 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles.



**Figure 11.** Contributions from HOA, aSOA (non O&G and O&G sources), and bSOA to total OA as predicted by WRF-Chem in the case with non-volatile POA and limited bSOA formation assumptions.





5 | **Figure 1412.** Correlation plots of predicted SOA against CO (a-b) and odd oxygen,  $O_x$  defined as  $O_3 + NO_2$  (c-d) for model runs with non-volatile POA and top-down estimates of O&G emissions when biogenic SOA aging was turned on (a and c) and off (b and d). ODR slope values indicated in parenthesis are obtained considering data when simulated  $NO_x/NO_y < 0.3$ .

## References

- 5 Abeleira, A., I. B. Pollack, B. Sive, Y. Zhou, E. V. Fischer and D. K. Farmer (2017). "Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015." *Journal of Geophysical Research-Atmospheres* 122(6): 3595-3613, doi:10.1002/2016jd026227.
- Adgate, J. L., B. D. Goldstein and L. M. McKenzie (2014). "Potential Public Health Hazards, Exposures and Health Effects from Unconventional Natural Gas Development." *Environmental Science & Technology* 48(15): 8307-8320, doi:10.1021/es404621d.
- 10 Ahmadov, R., S. McKeen, M. Trainer, R. Banta, A. Brewer, S. Brown, P. M. Edwards, J. A. de Gouw, G. J. Frost, J. Gilman, D. Helmig, B. Johnson, A. Karion, A. Koss, A. Langford, B. Lerner, J. Olson, S. Oltmans, J. Peischl, G. Petron, Y. Pichugina, J. M. Roberts, T. Ryerson, R. Schnell, C. Senff, C. Sweeney, C. Thompson, P. R. Veres, C. Warneke, R. Wild, E. J. Williams, B. Yuan and R. Zamora (2015). "Understanding high wintertime ozone pollution events in an oil- and natural gas-producing region of the western US." *Atmospheric Chemistry and Physics* 15(1): 411-429, doi:10.5194/acp-15-411-2015.
- 15 Ahmadov, R., S. A. McKeen, A. L. Robinson, R. Bahreini, A. M. Middlebrook, J. A. d. Gouw, J. Meagher, E.-Y. Hsie, E. Edgerton, S. Shaw and M. Trainer (2012). "A volatility basis set model for summertime secondary organic aerosols over the eastern United States in 2006." *J. Geophys. Res.- Atmos.* 117, doi:10.1029/2011JD016831.
- 20 Apel, E. C., R. S. Hornbrook, A. J. Hills, N. J. Blake, M. C. Barth, A. Weinheimer, C. Cantrell, S. A. Rutledge, B. Basarab, J. Crawford, G. Diskin, C. R. Homeyer, T. Campos, F. Flocke, A. Fried, D. R. Blake, W. Brune, I. Pollack, J. Peischl, T. Ryerson, P. O. Wennberg, J. D. Crouse, A. Wisthaler, T. Mikoviny, G. Huey, B. Heikes, D. O'Sullivan and D. D. Riemer (2015). "Upper tropospheric ozone production from lightning NO<sub>x</sub>-impacted convection: Smoke ingestion case study from the DC3 campaign." *J. Geophys. Res.- Atmos.* 120, doi:10.1002/2014JD022121.
- 25 Bahreini, R., E. J. Dunlea, B. M. Matthew, C. Simons, K. S. Docherty, P. F. DeCarlo, J. L. Jimenez, C. A. Brock and A. M. Middlebrook (2008). "Design and Operation of a Pressure-Controlled Inlet for Airborne Sampling with an Aerodynamic Aerosol Lens." *Aerosol Sci. Technol.* 42(6): 465-471, doi:10.1080/02786820802178514.
- 30 Bahreini, R., B. Ervens, A. M. Middlebrook, C. Warneke, J. A. d. Gouw, P. F. DeCarlo, J. L. Jimenez, E. Atlas, J. Brioude, C. A. Brock, A. Fried, J. S. Holloway, J. Peischl, D. Richter, T. B. Ryerson, H. Stark, J. Walega, P. Weibring, A. G. Wollny and F. C. Fehsenfeld (2009). "Organic aerosol formation in urban and industrial plumes near Houston and Dallas, TX." *J. Geophys. Res.* 114(D00F16), doi:10.1029/2008JD011493.
- 35 Ban-Weiss, G. A., J. P. McLaughlin, R. A. Harley, M. M. Lunden, T. W. Kirchstetter, A. J. Kean, A. W. Strawa, E. D. Stevenson and G. R. Kendall (2008). "Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles." *Atmos. Environ.* 42, doi:10.1016/j.atmosenv.2007.09.049.
- 40 Borbon, A., J. B. Gilman, W. C. Kuster, N. Grand, S. Chevaillier, A. Colomb, C. Dolgorouky, V. Gros, M. Lopez, R. Sarda-Esteve, J. Holloway, J. Stutz, H. Petetin, S. McKeen, M. Beekmann, C. Warneke, D. D. Parrish and J. A. de Gouw (2013). "Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris." *Journal of Geophysical Research-Atmospheres* 118(4): 2041-2057, doi:10.1002/jgrd.50059.
- 45 (1998). 2018, from <https://www.britannica.com/science/wet-gas>.
- Canagaratna, M. R., J. T. Jayne, J. L. Jimenez, J. D. Allan, M. R. Alfarra, Q. Zhang, T. B. Onasch, F. Drewnick, H. Coe, A. M. Middlebrook, A. Delia, L. R. Williams, A. M. Trimborn, M. J. Northway, P. F. DeCarlo, C. E. Kolb, P. Davidovits and D. R. Worsnop (2007). "Chemical and Microphysical

Characterization of Ambient Aerosols with the Aerodyne Aerosol Mass Spectrometer." *Mass Spectrometry Reviews* 26: 185-222.

- 5 Carter, W. P. L. and J. H. Seinfeld (2012). "Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming." *Atmospheric Environment* 50: 255-266, doi:10.1016/j.atmosenv.2011.12.025.
- Colman, J. J., A.L. Swanson, S. Meinardi, B. C. Sive, D. R. Blake and F. S. Rowland (2001). "Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B." *Anal. Chem.* 73: 3723–3731, doi:10.1021/ac010027g.
- 10 Day, D. A., P. J. Wooldridge, M. B. Dillon, J. A. Thornton and R. C. Cohen (2002). "A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO<sub>2</sub>, peroxy nitrates, alkyl nitrates, and HNO<sub>3</sub>." *J. Geophys. Res.- Atmos.* 107: 4046.
- de Gouw, J. A., C. A. Brock, E. L. Atlas, T. S. Bates, F. C. Fehsenfeld, P. D. Goldan, J. S. Holloway, W. C. Kuster, B. M. Lerner, B. M. Matthew, A. M. Middlebrook, T. B. Onasch, R. E. Peltier, P. K. Quinn, C. J. Senff, A. Stohl, A. P. Sullivan, M. Trainer, C. Warneke, R. J. Weber and E. J. Williams (2008)
- 15 "Sources of Particulate Matter in the Northeastern United States in Summer: 1. Direct Emissions and Secondary Formation of Organic Matter in Urban Plumes " *J. Geophys. Res.- Atmos.* 113, doi:10.1029/2007JD009243.
- de Gouw, J. A., A. M. Middlebrook, C. warneke, R. Ahmadov, E. L. Atlas, R. Bahreini, D. R. Blake, C. A. Brock, J. Brioude, D. W. Fahey, F. C. Fehsenfeld, J. S. Holloway, M. L. Henaff, R. A. Lueb, S. A. McKeen, J. F. Meagher, D. M. Murphy, C. Paris, D. D. Parrish, A. E. Perring, I. B. Pollack, A. R. Ravishankara, A. L. Robinson, T. B. Ryerson, J. P. Schwarz, J. R. Spackman, A. Srinivisan and L. A. Watts (2011). "Organic Aerosol Formation Downwind from the Deepwater Horizon Oil Spill." *Science* 331, doi:10.1126/science.1200320.
- 20 de Gouw, J. A. and C. Warneke (2007) "Measurements of Volatile Organic Compounds in the Earth's Atmosphere Using Proton-Transfer-Reaction Mass Spectrometry." *Mass Spectrom. Rev.* 26, 223-257, doi:10.1002/mas.20119.
- 25 Dingle, J. H., K. Vu, R. Bahreini, E. C. Apel, T. L. Campos, F. Flocke, A. Fried, S. Herndon, A. J. Hills, R. S. Hornbrook, G. Huey, L. Kaser, D. D. Montzka, J. B. Nowak, M. Reeves, D. Richter, J. R. Roscioli, S. Shertz, M. Stell, D. Tanner, G. Tyndall, J. Walega, P. Weibring and A. Weinheimer (2016).
- 30 "Aerosol Optical Extinction during the Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) 2014 Summertime Field Campaign, Colorado U.S.A." *Atmos. Chem. Phys.* 2016: 1-21, doi:10.5194/acp-16-11207-2016.
- Donahue, N. M., A.L. Robinson, C. O. Stanier and S. N. Pandis (2006). "Coupled partitioning, dilution, and chemical aging of semivolatile organics." *Environ. Sci. Technol.* 40: 2635-2643.
- 35 Drewnick, F., S. S. Hings, P. DeCarlo, J. T. Jayne, M. Gonin, K. Fuhrer, S. Weimer, J. L. Jimenez, K. L. D. S. Borrmann and D. R. Worsnop (2005). "A new time-of-flight aerosol mass spectrometer (TOF-AMS)- Instrument description and first field deployment." *Aerosol Sci. Technol.* 39(7): 637-658, doi:10.1080/02786820500182040.
- Edwards, P. M., S. S. Brown, J. M. Roberts, R. Ahmadov, R. M. Banta, J. A. deGouw, W. P. Dube, R. A. Field, J. H. Flynn, J. B. Gilman, M. Graus, D. Helmig, A. Koss, A. O. Langford, B. L. Lefer, B. M. Lerner, R. Li, S. M. Li, S. A. McKeen, S. M. Murphy, D. D. Parrish, C. J. Senff, J. Soltis, J. Stutz, C. Sweeney, C. R. Thompson, M. K. Trainer, C. Tsai, P. R. Veres, R. A. Washenfelder, C. Warneke, R. J. Wild, C. J. Young, B. Yuan and R. Zamora (2014). "High winter ozone pollution from carbonyl photolysis in an oil and gas basin." *Nature* 514(7522): 351-+, doi:10.1038/nature13767.
- 40 Ehn, M., J. A. Thornton, E. Kleist, M. Sipila, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, S. Andres, I.-H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurten, L. B. Nielsen, S. Jorgensen, H. G. Kjaergaard, M. Canagaratna, M. D. Maso, T. Berndt, T. Petaja, A. Wahner, V.-M. Kerminen, M. Kulmala, D. R.

- Worsnop, J. Wildt and T. F. Mentel (2014). "A large source of low-volatility secondary organic aerosol." *Nature* 506(7489): 476-479, doi:10.1038/nature13032.
- 5     Ensborg, J. J., P. L. Hayes, J. L. Jimenez, J. B. Gilman, W. C. Kuster, J. A. de Gouw, J. S. Holloway, T. D. Gordon, S. Jathar, A. L. Robinson and J. H. Seinfeld (2014). "Emission factor ratios, SOA mass yields, and the impact of vehicular emissions on SOA formation." *Atmospheric Chemistry and Physics* 14(5): 2383-2397, doi:10.5194/acp-14-2383-2014.
- 10    Ervens, B. and R. Volkamer (2010). "Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles." *Atmos. Chem. Phys.* 10: 8219-8244, doi:10.5195/acp-1-8219-2010.
- 15    Fast, J. D., J. Allan, R. Bahreini, J. Craven, L. Emmons, R. Ferrare, P. L. Hayes, A. Hodzic, J. Holloway, C. Hostetler, J. L. Jimenez, H. Jonsson, S. Liu, Y. Liu, A. Metcalf, A. Middlebrook, J. Nowak, M. Pekour, A. Perring, L. Russell, A. Sedlacek, J. Seinfeld, A. Setyan, J. Shilling, M. Shrivastava, S. Springston, C. Song, R. Subramanian, J. W. Taylor, V. Vinoj, Q. Yang, R. A. Zaveri and Q. Zhang (2014). "Modeling regional aerosol and aerosol precursor variability over California and its sensitivity to emissions and long-range transport during the 2010 CalNex and CARES campaigns." *Atmospheric Chemistry and Physics* 14(18): 10013-10060, doi:10.5194/acp-14-10013-2014.
- 20    Field, R. A., J. Soltis, M. C. McCarthy, S. Murphy and D. C. Montague (2015). "Influence of oil and gas field operations on spatial and temporal distributions of atmospheric non-methane hydrocarbons and their effect on ozone formation in winter." *Atmospheric Chemistry and Physics* 15(6): 3527-3542, doi:10.5194/acp-15-3527-2015.
- 25    Field, R. A., J. Soltis and S. Murphy (2014). "Air quality concerns of unconventional oil and natural gas production." *Environmental Science-Processes & Impacts* 16(5): 954-969, doi:10.1039/c4em00081a.
- 30    Gerbig, C., S. Schmitgen, D. Kley, A. Volz-Thomas, K. Dewey and D. Haaks (1999). "An improved fast-response vacuum-UV resonance fluorescence CO instrument,." *J. Geophys. Res.-Atmos.* 104: 1699–1704.
- 35    Gilman, J. B., B. M. Lerner, W. C. Kuster and J. A. de Gouw (2013). "Source Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado." *Environmental Science & Technology* 47(3): 1297-1305, doi:10.1021/es304119a.
- 40    Grell, G. A., S. E. Peckham, R. Schmitz, S. A. McKeen, G. Frost, W. C. Skamarock and B. Eder (2005). "Fully coupled "online" chemistry within the WRF model." *Atmos. Environ.* 39(37), doi:10.1016/j.atmosenv.2005.04.027.
- 45    Hallquist, M., J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M. E. Jenkin, J. L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, T. F. Mentel, A. Monod, A. S. H. Prevot, J. H. Seinfeld, J. D. Surratt, R. Szmigielski and J. Wildt (2009). "The formation, properties and impact of secondary organic aerosol: current and emerging issues." *Atmospheric Chemistry and Physics* 9(14): 5155-5236.
- 50    Helmig, D., S. Rossabi, J. Hueber, P. Tans, S. A. Montzka, K. Masarie, K. Thoning, C. Plass-Duelmer, A. Claude, L. J. Carpenter, A. C. Lewis, S. Punjabi, S. Reimann, M. K. Vollmer, R. Steinbrecher, J. Hannigan, L. K. Emmons, E. Mahieu, B. Franco, D. Smale and A. Pozzer (2016). "Reversal of global atmospheric ethane and propane trends largely due to US oil and natural gas production." *Nature Geoscience* 9(7): 490-495, doi:10.1038/ngeo2721.
- 55    Helmig, D., C. R. Thompson, J. Evans, P. Boylan, J. Hueber and J. H. Park (2014). "Highly Elevated Atmospheric Levels of Volatile Organic Compounds in the Uintah Basin, Utah." *Environmental Science & Technology* 48(9): 4707-4715, doi:10.1021/es405046r.

- Hennigan, C. J., M. A. Miracolo, G. J. Engelhart, A. A. May, A. A. Presto, T. Lee, A. P. Sullivan, G. R. McMeeking, H. Coe, C. E. Wold, W.-M. Hao, J. B. Gilman, W. C. Kuster, J. d. Gouw, B. A. Schichtel, J. L. C. Jr., S. M. Kreidenweis and A. L. Robinson (2011). "Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber." *Atmos. Chem. Phys.* 11, doi:10.5194/acp-11-7669-2011.
- 5 Hennigan, C. J., A. P. Sullivan, J. L. Collett and A. L. Robinson (2010). "Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals." *Geophysical Research Letters* 37, doi:10.1029/2010gl043088.
- Henze, D. K., J. H. Seinfeld, N. L. Ng, J. H. Kroll, T.-M. Fu, D. J. Jacob and C. L. Heald (2008). "Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs. low-yield pathways." *Atmos. Chem. Phys.* 8: 2405-2420.
- 10 Hodzic, A. and J. L. Jimenez (2011). "Modeling anthropogenically controlled secondary organic aerosols in a megacity: a simplified framework for global and climate models." *Geosci. Model. Dev.* 4: 901-917, doi:10.5194/gmd-4-901-2011.
- 15 Hodzic, A., J. L. Jimenez, S. Madronich, M. R. Canagaratna, P. F. DeCarlo, L. Kleinman and J. Fast (2010a). "Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary aerosol formation." *Atmos. Chem. Phys.* 10(12): 5491-5514.
- Hodzic, A., J. L. Jimenez, S. Madronich, M. R. Canagaratna, P. F. DeCarlo, L. Kleinman and J. Fast (2010b). "Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation." *Atmospheric Chemistry and Physics* 10(12): 5491-5514, doi:10.5194/acp-10-5491-2010.
- 20 Hornbrook, R. S., J.H. Crawford, G. D. Edwards, O. O. Goyea, R.L. Mauldin III, J. S. J.S. Olson and C. A. Cantrell (2011). "Measurements of tropospheric HO<sub>2</sub> and RO<sub>2</sub> by oxygen dilution modulation and chemical ionization mass spectrometry." *Atmos. Meas. Tech.* 4, doi:10.5194/amt-4-735-2011.
- 25 Huey, L. G., E. J. Dunlea, E. R. Lovejoy, D. R. Hanson, R. B. Norton, F. C. Fehsenfeld and C. J. Howard (1998). "A chemical ionization mass spectrometer for fast time response measurements of HNO<sub>3</sub> in air." *Journal of Geophysical Research-Atmospheres* 103: 3355-3360.
- 30 Isaacman, G., K. R. Wilson, A. W. H. Chan, D. R. Worton, J. R. Kimmel, T. Nah, T. Hohaus, M. Gonin, J. H. Kroll, D. R. Worsnop and A. H. Goldstein (2012). "Improved Resolution of Hydrocarbon Structures and Constitutional Isomers in Complex Mixtures Using Gas Chromatography-Vacuum Ultraviolet-Mass Spectrometry." *Analytical Chemistry* 84(5): 2335-2342, doi:10.1021/ac2030464.
- Jathar, S. H., B. Friedman, A. A. Galang, M. F. Link, P. Brophy, J. Volckens, S. Eluri and D. K. Farmer (2017). "Linking Load, Fuel, and Emission Controls to Photochemical Production of Secondary Organic Aerosol from a Diesel Engine." *Environ. Sci. Technol.* 51, doi:10.1021/acs.est.6b04602.
- 35 Jayne, J. T., D. C. Leard, X. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb and D. W. Worsnop (2000). "Development of an Aerosol Mass Spectrometer for size and composition analysis of submicron particles." *Aerosol Sci. Technol.* 33: 49-70.
- 40 Kirchstetter, T. W., C. V. Preble, O. L. Hadley, T. C. Bond and J. S. Apte (2017). "Large reductions in urban black carbon concentrations in the United States between 1965 and 2000." *Atmospheric Environment* 151: 17-23, doi:10.1016/j.atmosenv.2016.11.001.
- Koss, A., B. Yuan, C. Warneke, J. B. Gilman, B. M. Lerner, P. R. Veres, J. Peischl, S. Eilerman, R. Wild, S. S. Brown, C. R. Thompson, T. Ryerson, T. Hanisco, G. M. Wolfe, J. M. S. Clair, M. Thayer, F. N. Keutsch, S. Murphy and J. de Gouw (2017). "Observations of VOC emissions and photochemical products over US oil- and gas-producing regions using high-resolution H<sub>3</sub>O<sup>+</sup> CIMS (PTR-ToF-MS)." *Atmospheric Measurement Techniques* 10(8): 2941-2968, doi:10.5194/amt-10-2941-2017.
- 45

- 5 Koss, A. R., J. de Gouw, C. Warneke, J. B. Gilman, B. M. Lerner, M. Graus, B. Yuan, P. Edwards, S. S. Brown, R. Wild, J. M. Roberts, T. S. Bates and P. K. Quinn (2015). "Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event." *Atmospheric Chemistry and Physics* 15(10): 5727-5741, doi:10.5194/acp-15-5727-2015.
- Kroll, J. H., N. L. Ng, S. M. Murphy, R. C. Flagan and J. H. Seinfeld (2005). "Secondary organic aerosol formation from isoprene photooxidation under high-NO<sub>x</sub> conditions." *Geophys. Res. Lett.* 32: L18808, doi:10.1029/2005GL023637.
- 10 Lim, Y. B. and P. J. Ziemann (2005). "Products and mechanism of secondary organic aerosol formation from reactions of n-alkanes with OH radicals in the presence of NO<sub>x</sub>." *Environ. Sci. Technol.* 39: 9229-9236, doi: 9210.1021/es051447g.
- Lindinger, W., A. Hansel and A. Jordan (1998). "On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research " *Int. J. Mass Spectrom.* 173: 191-241, doi:10.1016/S0168-1176(97)00281-4.
- 15 Lopez-Hilfiker, F. D., C. Mohr, M. Ehn, F. Rubach, E. Kleist, J. Wildt, T. F. Mentel, A. Lutz, M. Hallquist, D. Worsnop and J. A. Thornton (2014). "A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO)." *Atmospheric Measurement Techniques* 7(4): 983-1001, doi:10.5194/amt-7-983-2014.
- 20 Mauldin, R. L. I., G. J. Frost, G. Chen, D. J. Tanner, A. S. H. Prevot, D. D. Davis and F. L. Eisele (1998). "OH measurements during ACE-1: Observations and model comparisons." *J. Geophys. Res.* 103, doi:10.1029/98JD00882.
- May, A. A., A. A. Presto, C. J. Hennigan, N. T. Nguyen, T. D. Gordon and A. L. Robinson (2013). "Gas-Particle Partitioning of Primary Organic Aerosol Emissions: (2) Diesel Vehicles." *Environmental Science & Technology* 47(15): 8288-8296, doi:10.1021/es400782j.
- 25 McDuffie, E. E., P. M. Edwards, J. B. Gilman, B. M. Lerner, W. P. Dube, M. Trainer, D. E. Wolfe, W. M. Angevine, J. deGouw, E. J. Williams, A. G. Tevlin, J. G. Murphy, E. V. Fischer, S. McKeen, T. B. Ryerson, J. Peischl, J. S. Holloway, K. Aikin, A. O. Langford, C. J. Senff, R. J. Alvarez, S. R. Hall, K. Ullmann, K. O. Lantz and S. S. Brown (2016). "Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range." *Journal of Geophysical Research-Atmospheres* 121(14): 8712-8729, doi:10.1002/2016jd025265.
- 30 McLafferty, F. W. and F. Turecek (1993). *Interpretation of Mass Spectra*. Sausalito, CA, University Science Books.
- Middlebrook, A. M., R. Bahreini, J. L. Jimenez and M. R. Canagaratna (2012a). "Evaluation of composition-dependent collection efficiencies for the aerodyne aerosol mass spectrometer using field data." *Aerosol Science and Technology* 46(3): 258-271.
- 35 Middlebrook, A. M., D. M. Murphy, R. Ahmadov, E. L. Atlas, R. Bahreini, D. R. Blake, J. Brioude, J. A. de Gouw, F. C. Fehsenfeld, G. J. Frost, J. S. Holloway, D. A. Lack, J. M. Langridge, R. A. Lueb, S. A. McKeen, J. F. Meagher, S. Meinardi, J. A. Neuman, J. B. Nowak, D. D. Parrish, J. Peischl, A. E. Perring, I. B. Pollack, J. M. Roberts, T. B. Ryerson, J. P. Schwarz, J. R. Spackman, C. Warneke and A. R. Ravishankara (2012b). "Air quality implications of the Deepwater Horizon oil spill." *Proceedings of the National Academy of Sciences of the United States of America* 109(50): 20280-20285, doi:10.1073/pnas.1110052108.
- 40 Monks, P. S., C. Granier, S. Fuzzi, A. Stohl, M. L. Williams, H. Akimoto, M. Amann, A. Baklanov, U. Baltensperger, I. Bey, N. Blake, R. S. Blake, K. Carslaw, O. R. Cooper, F. Dentener, D. Fowler, E. Fragkou, G. J. Frost, S. Generoso, P. Ginoux, V. Grewe, A. Guenther, H. C. Hansson, S. Henne, J. Hjorth, A. Hofzumahaus, H. Huntrieser, I. S. A. Isaksen, M. E. Jenkin, J. Kaiser, M. Kanakidou, Z. Klimont, M. Kulmala, P. Laj, M. G. Lawrence, J. D. Lee, C. Liousse, M. Maione, G. McFiggans, A.
- 45

- Metzger, A. Mieville, N. Moussiopoulos, J. J. Orlando, C. D. O'Dowd, P. I. Palmer, D. D. Parrish, A. Petzold, U. Platt, U. Poschl, A. S. H. Prevot, C. E. Reeves, S. Reimann, Y. Rudich, K. Sellegri, R. Steinbrecher, D. Simpson, H. ten Brink, J. Theloke, G. R. van der Werf, R. Vautard, V. Vestreng, C. Vlachokostas and R. von Glasow (2009). "Atmospheric composition change - global and regional air quality." *Atmos. Environ.* 43(33): 5268-5350, doi:10.1016/j.atmosenv.2009.08.021.
- 5 Ng, N. L., M. R. Canagaratna, J. L. Jimenez, Q. Zhang, I. M. Ulbrich and D. R. Worsnop (2011). "Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data." *Environ. Sci. Technol.* 45, doi:10.1021/es102951k.
- Ng, N. L., M. R. Canagaratna, Q. Zhang, J. L. Jimenez, J. Tian, I. M. Ulbrich, J. H. Kroll, K. S. Docherty, P. S. Chhabra, R. Bahreini, S. M. Murphy, J. H. Seinfeld, L. Hildebrandt, N. M. Donahue, P. F. DeCarlo, 10 V. A. Lanz, A. S. H. Prévôt, E. Dinar, Y. Rudich and D. R. Worsnop (2010) "Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry." *Atmos. Chem. Phys.* 10, 4625–4641 doi:10.5194/acp-10-4625-2010.
- Ng, N. L., P. S. Chhabra, A. W. H. Chan, J. D. Surratt, J. H. Kroll, A. J. Kwan, D. C. McCabe, P. O. Wennberg, 15 A. Sorooshian, S. M. Murphy, N. F. Dalleska, R. C. Flagan and J. H. Seinfeld (2007a). "Effect of NO<sub>x</sub> level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes." *Atmos. Chem. Phys.* 7: 5159-5174.
- Ng, N. L., J. H. Kroll, A. W. H. Chan, P. S. Chhabra, R. C. Flagan and J. H. Seinfeld (2007b). "Secondary 20 organic aerosol formation from m-xylene, toluene, and benzene." *Atmos. Chem. Phys.* 7: 3909-3922.
- Odum, J. R., T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan and J. H. Seinfeld (1997a). "The atmospheric aerosol-forming potential of whole gasoline vapor." *Science* 276: 96-99, doi:10.1126/science.276.5309.96.
- Odum, J. R., T. P. W. Jungkamp, R. J. Griffin, H. J. L. Forstner, R. C. Flagan and J. H. Seinfeld (1997b). 25 "Aromatics, reformulated gasoline, and atmospheric organic aerosol formation." *Environ. Sci. Technol.* 31(7): 1890-1897.
- Paatero, P. (1997). "A weighted non-negative least squares algorithm for three-way 'PARAFAC' factor analysis." *Chemometr Intell Lab* 38: 223-242.
- Paatero, P. and U. Tapper (1994). "Positive Matrix Factorization - a Nonnegative Factor Model with 30 Optimal Utilization of Error-Estimates of Data Values." *Environmetrics* 5: 111-112.
- Parrish, D. D., M. Trainer, D. Hereid, E. J. Williams, K. J. Olszyna, R. A. Harley, J. F. Meagher and F. C. Fehsenfeld (2002). "Decadal change in carbon monoxide to nitrogen oxide ratio in US vehicular emissions." *Journal of Geophysical Research-Atmospheres* 107(D12), doi:10.1029/2001jc000720.
- Peischl, J., T. B. Ryerson, J. S. Holloway, D. D. Parrish, M. Trainer, G. J. Frost, K. C. Aikin, S. S. Brown, W. P. 35 Dube, H. Stark and F. C. Fehsenfeld (2010). "A top-down analysis of emissions from selected Texas power plants during TexAQs 2000 and 2006." *Journal of Geophysical Research-Atmospheres* 115, doi:10.1029/2009jd013527.
- Pekney, N. J., G. Veloski, M. Reeder, J. Tamilia, E. Rupp and A. Wetzel (2014). "Measurement of 40 atmospheric pollutants associated with oil and natural gas exploration and production activity in Pennsylvania's Allegheny National Forest." *Journal of the Air & Waste Management Association* 64(9): 1062-1072, doi:10.1080/10962247.2014.897270.
- Petron, G., G. Frost, B. R. Miller, A. I. Hirsch, S. A. Montzka, A. Karion, M. Trainer, C. Sweeney, A. E. Andrews, L. Miller, J. Kofler, A. Bar-Ilan, E. J. Dlugokencky, L. Patrick, C. T. Moore, T. B. Ryerson, C. Siso, W. Kolodzey, P. M. Lang, T. Conway, P. Novelli, K. Masarie, B. Hall, D. Guenther, D. Kitzi, 45 J. Miller, D. Welsh, D. Wolfe, W. Neff and P. Tans (2012). "Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study." *J. Geophys. Res.* 117, doi:D0430410.1029/2011jd016360.

- Petron, G., A. Karion, C. Sweeney, B. R. Miller, S. A. Montzka, G. J. Frost, M. Trainer, P. Tans, A. Andrews, J. Kofler, D. Helmig, D. Guenther, E. Dlugokencky, P. Lang, T. Newberger, S. Wolter, B. Hall, P. Novelli, A. Brewer, S. Conley, M. Hardesty, R. Banta, A. White, D. Noone, D. Wolfe and R. Schnell (2014). "A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin." *Journal of Geophysical Research-Atmospheres* 119(11): 6836-6852, doi:10.1002/2013jd021272.
- 5
- Pfister, G., F. Flocke, R. Hornbrook, J. Orlando, S. Lee and J. Schroeder (2017). "Process-Based and Regional Source Impact Analysis for FRAPPÉ and DISCOVER -AQ 2014." from [https://www.colorado.gov/airquality/tech\\_doc\\_repository.aspx?action=open&file=FRAPPE-NCAR\\_Final\\_Report\\_July2017.pdf](https://www.colorado.gov/airquality/tech_doc_repository.aspx?action=open&file=FRAPPE-NCAR_Final_Report_July2017.pdf).
- 10
- Powers, J. G., J. B. Klemp, W. C. Skamarock, C. A. Davis, J. Dudhia, D. O. Gill, J. L. Coen, D. J. Gochis, R. Ahmadov, S. E. Peckham, G. A. Grell, J. Michalakes, S. Trahan, S. G. Benjamin, C. R. Alexander, G. J. Dimego, W. Wang, C. S. Schwartz, G. S. Romine, Z. Q. Liu, C. Snyder, F. Chen, M. J. Barlage, W. Yu and M. G. Duda (2017). "THE WEATHER RESEARCH AND FORECASTING MODEL Overview, System Efforts, and Future Directions." *Bulletin of the American Meteorological Society* 98(8): 1717-1737, doi:10.1175/bams-d-15-00308.1.
- 15
- Prenni, A. J., D. E. Day, A. R. Evanoski-Cole, B. C. Sive, A. Hecobian, Y. Zhou, K. A. Gebhart, J. L. Hand, A. P. Sullivan, Y. Li, M. I. Schurman, Y. Desyaterik, W. C. Malm, J. L. Collett and B. A. Schichtel (2016). "Oil and gas impact on air quality in federal lands in the Bakken region: an overview of the Bakken Air Quality Study and first results." *Atmospheric Chemistry and Physics* 16(3): 1401-1416, doi:10.5194/acp-16-1401-2016.
- 20
- Rappenglück, B., L. Ackermann, S. Alvarez, J. Golovko, M. Buhr, R. A. Field, J. Soltis, D. C. Montague, B. Hauze, S. Adamson, D. Risch, G. Wilkerson, D. Bush, T. Stoeckenius and C. Keslar (2014). "Strong wintertime ozone events in the Upper Green River basin, Wyoming." *Atmospheric Chemistry and Physics* 14(10): 4909-4934, doi:10.5194/acp-14-4909-2014.
- 25
- Ren, X., J. Mao, W. H. Brune, C. A. Cantrell, R. L. Mauldin, R. S. Hornbrook, E. Kosciuch, J. R. Olson, J. H. Crawford, G. Chen and H. B. Singh (2012). "Airborne intercomparison of HO<sub>x</sub> measurements using laser-induced fluorescence and chemical ionization mass spectrometry during ARCTAS." *Atmospheric Measurement Techniques* 5(8): 2025-2037, doi:10.5194/amt-5-2025-2012.
- 30
- Richter, D., P. Weibring, J. Walega, A. Fried, S. M. Spuler and M. S. Taubmans (2015). "Compact highly sensitive multi-species airborne mid-IR spectrometer." *Applied Physics B: Lasers and Optic* 119, doi:10.1007/s00340-015-6038-8.
- Ridley, B., L. Ott, K. Pickering, L. Emmons, D. Montzka, A. Weinheimer, D. Knapp, F. Grahek, L. Li, G. Heymsfield, M. McGill, P. Kucera, M. J. Mahoney, D. Baumgardner, M. Schultz and G. Brasseur (2004). "Florida thunderstorms: A faucet of reactive nitrogen to the upper troposphere." *J. Geophys. Res.- Atmos.* 109, doi:10.1029/2004JD004769.
- 35
- (2015). 2015, from <http://www.rockymountainenergyforum.com/topics/wattenberg-field>.
- Rutter, A. P., R. J. Griffin, B. K. Cevik, K. M. Shakya, L. W. Gong, S. Kim, J. H. Flynn and B. L. Lefer (2015). "Sources of air pollution in a region of oil and gas exploration downwind of a large city." *Atmospheric Environment* 120: 89-99, doi:10.1016/j.atmosenv.2015.08.073.
- 40
- Sather, M. E. and K. Cavender (2012). "Update of long-term trends analysis of ambient 8-hour ozone and precursor monitoring data in the South Central U.S.; encouraging news." *Journal of Environmental Monitoring* 14(2): 666-676, doi:10.1039/c2em10862c.
- Shrivastava, M., J. Fast, R. Easter, W. I. Gustafson, R. A. Zaveri, J. L. Jimenez, P. Saide and A. Hodzic (2011). "Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach." *Atmospheric Chemistry and Physics* 11(13): 6639-6662, doi:10.5194/acp-11-6639-2011.
- 45



- Sullivan, J. T., T. J. McGee, A. O. Langford, R. J. A. II, C. J. Senff, P. J. Reddy, A. M. Thompson, L. W. Twigg, G. K. Sumnicht, P. Lee, A. Weinheimer, C. Knote, R. W. Long and R. M. Hoff (2016). "Quantifying the contribution of thermally driven recirculation to a high-ozone event along the Colorado Front Range using lidar." *J. Geophys. Res.- Atmospheres* 121, doi:10.1002/2016JD025229.
- 5 Swarthout, R. F., R. S. Russo, Y. Zhou, A. H. Hart and B. C. Sive (2013). "Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources." *Journal of Geophysical Research-Atmospheres* 118(18): 10614-10637, doi:10.1002/jgrd.50722.
- 10 Swarthout, R. F., R. S. Russo, Y. Zhou, B. M. Miller, B. Mitchell, E. Horsman, E. Lipsky, D. C. McCabe, E. Baum and B. C. Sive (2015). "Impact of Marcellus Shale Natural Gas Development in Southwest Pennsylvania on Volatile Organic Compound Emissions and Regional Air Quality." *Environmental Science & Technology* 49(5): 3175-3184, doi:10.1021/es504315f.
- 15 Tsimpidi, A. P., V. A. Karydis, M. Zavala, W. Lei, L. Molina, I.M.Ulbrich, J. L. Jimenez and S. N. Pandis (2010). "Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area." *Atmos. Chem. Phys.* 2010: 525-546, doi:10.5194/acp-10-525-2010.
- Ulbrich, I. M., M. R. Canagaratna, Q. Zhang, D. R. Worsnop and J. L. Jimenez (2009). "Interpretations of organic components from Positive Matrix Factorization of aerosol mass spectrometric data." *Atmos. Chem. Phys.* 9: 2891-2918.
- 20 U.S. Energy Development Corporation. (2015). "Natural gas: dry vs. wet." 2015, from [http://www.usenergydevcorp.com/media\\_downloads/Natural%20Gas%20Dry%20Vs%20Wet\\_050913.pdf](http://www.usenergydevcorp.com/media_downloads/Natural%20Gas%20Dry%20Vs%20Wet_050913.pdf).
- 25 Vu, K. T., J. H. Dingle, R. Bahreini, P. J. Reddy, T. L. Campos, G. S. Diskin, A. Fried, S. C. Herndon, R. S. Hornbrook, G. Huey, L. Kaser, D. D. Montzka, J. B. Nowak, D. Richter, J. R. Roscioli, S. Shertz, M. Stell, D. Tanner, G. Tyndall, J. Walega, P. Weibring, A. J. Weinheimer, G. Pfister and F. Flocke (2016). "Impacts of the Denver Cyclone on Regional Air Quality and Aerosol Formation in the Colorado Front Range during FRAPPÉ 2014." *Atmos. Chem. Phys.* 2016: 1-40, doi:10.5194/acp-16-12039-2016.
- 30 Warneke, C., J. A. de Gouw, P. M. Edwards, J. S. Holloway, J. B. Gilman, W. C. Kuster, M. Graus, E. Atlas, D. Blake, D. R. Gentner, A. H. Goldstein, R. A. Harley, S. Alvarez, B. Rappenglueck, M. Trainer and D. D. Parrish (2013). "Photochemical aging of volatile organic compounds in the Los Angeles basin: Weekday-weekend effect." *Journal of Geophysical Research-Atmospheres* 118(10): 5018-5028, doi:10.1002/jgrd.50423.
- 35 Warneke, C., J. A. deGouw, J. S. Holloway, J. Peischl, T. B. Ryerson, E. Atlas, D. Blake, M. Trainer and D. D. Parrish (2012). "Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions." *J. Geophys. Res.* 117, doi:10.1029/2012JD017899.
- 40 Warneke, C., F. Geiger, P. M. Edwards, W. Dube, G. Petron, J. Kofler, A. Zahn, S. S. Brown, M. Graus, J. B. Gilman, B. M. Lerner, J. Peischl, T. B. Ryerson, J. A. de Gouw and J. M. Roberts (2014). "Volatile organic compound emissions from the oil and natural gas industry in the Uintah Basin, Utah: oil and gas well pad emissions compared to ambient air composition." *Atmospheric Chemistry and Physics* 14(20): 10977-10988, doi:10.5194/acp-14-10977-2014.
- 45 Warneke, C., S. A. McKeen, J. A. deGouw, P. D. Goldan, W. C. Kuster, J. S. Holloway, E. J. Williams, B. M. Lerner, D. D. Parrish, M. Trainer, F. C. Fehsenfeld, S. Kato, E. L. Atlas, A. Baker and D. R. Blake (2007) "Determination of urban volatile organic compound emission ratios and comparison with an emissions database." *J. Geophys. Res.- Atmos.* 112, doi:10.1029/2006JD007930.
- Williams, B. J., J. T. Jayne, A. T. Lambe, T. Hohaus, J. R. Kimmel, D. Sueper, W. Brooks, L. R. Williams, A. M. Trimborn, R. E. Martinez, P. L. Hayes, J. L. Jimenez, N. M. Kreisberg, S. V. Hering, D. R. Worton, A. H. Goldstein and D. R. Worsnop (2014). "The First Combined Thermal Desorption

Aerosol Gas Chromatograph-Aerosol Mass Spectrometer (TAG-AMS)." *Aerosol Science and Technology* 48(4): 358-370, doi:10.1080/02786826.2013.875114.

5 Yatavelli, R. L. N., F. Lopez-Hilfiker, J. D. Wargo, J. R. Kimmel, M. J. Cubison, T. H. Bertram, J. L. Jimenez, M. Gonin, D. R. Worsnop and J. A. Thornton (2012). "A Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer Coupled to a Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS) for Analysis of Gas and Particle-Phase Organic Species." *Aerosol Science and Technology* 46(12): 1313-1327, doi:10.1080/02786826.2012.712236.

10 Zhang, Q., J. L. Jimenez, M. R. Canagaratna, J. D. Allan, H. Coe, I. Ulbrich, M. R. Alfarra, A. Takami, A. M. Middlebrook, Y. L. Sun, K. Dzepina, E. Dunlea, K. Docherty, P. F. DeCarlo, D. Salcedo, T. Onasch, J. T. Jayne, T. Miyoshi, A. Shimono, S. Hatakeyama, N. Takegawa, Y. Kondo, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, P. Williams, K. Bower, R. Bahreini, L. Cottrell, R. J. Griffin, J. Rautiainen, J. Y. Sun, Y. M. Zhang and D. R. Worsnop (2007). "Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes." *Geophys. Res. Lett.* 34(13), doi:10.1029/2007GL029979.

15 Zhang, Q., J. L. Jimenez, M. R. Canagaratna, I. M. Ulbrich, N. L. Ng, D. R. Worsnop and Y. Sun (2011) "Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review." *Anal. Bioanal. Chem.*, doi:10.1007/s00216-11-5355-y.

20 Zheng, W., F. M. Flocke, G. S. Tyndall, A. Swanson, J. J. Orlando, J. M. Roberts, L. G. Huey and D. J. Tanner (2011). "Characterization of a thermal decomposition chemical ionization mass spectrometer for the measurement of peroxy acyl nitrates (PANs) in the atmosphere." *Atmospheric Chemistry and Physics* 11(13): 6529-6547, doi:10.5194/acp-11-6529-2011.

Zhou, W., D. S. Cohan and B. H. Henderson (2014). "Slower ozone production in Houston, Texas following emission reductions: evidence from Texas Air Quality Studies in 2000 and 2006." *Atmospheric Chemistry and Physics* 14(6): 2777-2788, doi:10.5194/acp-14-2777-2014.

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# Sources and Characteristics of Summertime Organic Aerosol in the Colorado Front Range: Perspective from Measurements and WRF-Chem Modeling

Roya Bahreini <sup>1,2</sup>, Ravan Ahmadov <sup>3,4</sup>, Stu A. McKeen <sup>3,4</sup>, Kennedy T. Vu <sup>2</sup>, Justin H. Dingle <sup>2</sup>, Eric C. Apel <sup>5</sup>, Donald R. Blake <sup>6</sup>, Nicola Blake <sup>6</sup>, Teresa L. Campos <sup>5</sup>, Chris Cantrell <sup>7</sup>, Frank Flocke <sup>5</sup>, Alan Fried <sup>8</sup>, Jessica B. Gilman <sup>3</sup>, Alan J. Hills <sup>5</sup>, Rebecca S. Hornbrook <sup>5</sup>, Greg Huey <sup>9</sup>, Lisa Kaser <sup>5</sup>, Brian M. Lerner <sup>3,4,10</sup>, Roy L. Mauldin <sup>7</sup>, Simone Meinardi <sup>6</sup>, Denise D. Montzka <sup>5</sup>, Dirk Richter <sup>8</sup>, Jason R. Schroeder <sup>6,11</sup>, Meghan Stell <sup>5</sup>, David Tanner <sup>9</sup>, James Walega <sup>8</sup>, Peter Weibring <sup>8</sup>, Andrew Weinheimer <sup>5</sup>

<sup>1</sup> Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

<sup>2</sup> Environmental Toxicology Graduate Program, University of California, Riverside, CA 92521, USA

<sup>3</sup> Earth Systems Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305, USA

<sup>4</sup> Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80301, USA

<sup>5</sup> Atmospheric Chemistry Observations & Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO 80301, USA

<sup>6</sup> Department of Chemistry, University of California, Irvine, CA 92697, USA

<sup>7</sup> Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO 80303, USA

<sup>8</sup> Institute for Arctic and Alpine Research, University of Colorado, Boulder, CO 80303, USA

<sup>9</sup> Department of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30033, USA

<sup>10</sup> Now at Aerodyne Research, Inc., Billerica, MA, 01821

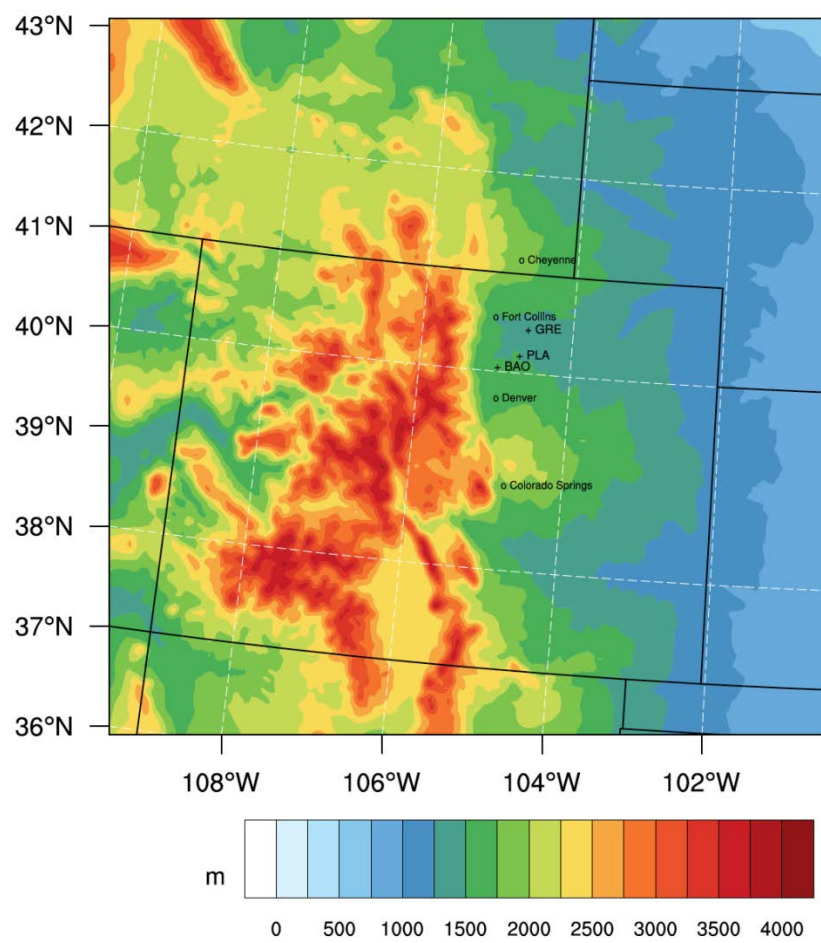
<sup>11</sup> Now at NASA Langley Research Center, Newport News, VA, 23666

*Correspondence to:* Roya Bahreini ([Roya.Bahreini@ucr.edu](mailto:Roya.Bahreini@ucr.edu))

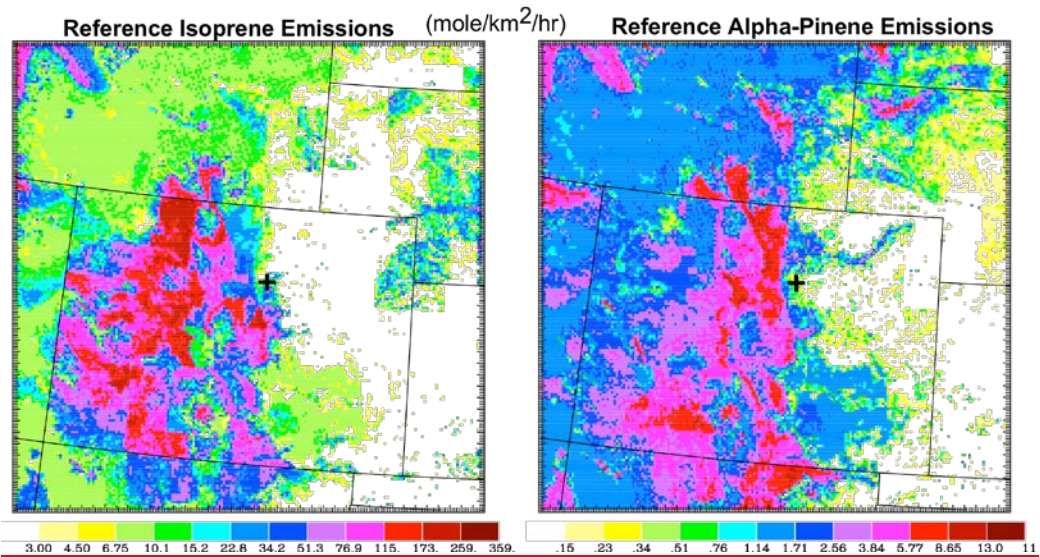
## Supplemental Information

VOC specie	Mean (ppbv)	R coefficient CH <sub>4</sub> regress	R coefficient C <sub>2</sub> H <sub>2</sub> regress	R coefficient C <sub>3</sub> H <sub>8</sub> regress	Oil/Gas CH <sub>4</sub> emission ratio
CH <sub>4</sub>	1975.7	1	0.52	0.678	1
CO	146	0.303	0.854	0.186	0
NO <sub>x</sub>	5.03	0.369	0.68	0.231	0
C <sub>2</sub> H <sub>6</sub>	13.8	0.72	0.44	0.987	0.185
C <sub>3</sub> H <sub>8</sub>	11.1	0.678	0.414	1	0.17
N-Butane	5.76	0.68	0.41	0.994	0.0905
Iso-Butane	2.33	0.676	0.406	0.997	0.0379
N-Pentane	2.27	0.701	0.44	0.985	0.036
Iso-Pentane	1.97	0.702	0.452	0.987	0.0297
2methyl-Pentane	0.215	0.73	0.496	0.966	0.00257
Hexane	0.668	0.731	0.472	0.965	0.00872
Heptane	0.207	0.736	0.497	0.941	0.00236
Octane	0.0583	0.739	0.531	0.894	0.000583
Nonane	0.00668	0.64	0.5	0.726	8.65e-05
Decane	0.0174	0.668	0.732	0.65	6.25e-05
Undecane	0.0115	0.571	0.698	0.513	3.44e-05
Cyclopentane	0.119	0.712	0.452	0.973	0.00186
1m-Cyclopentane	0.741	0.723	0.48	0.963	0.00997
Cyclohexane	0.187	0.724	0.474	0.96	0.00271
1m-Cyclohexane	0.193	0.712	0.464	0.952	0.00267
1e-Cyclohexane	0.0226	0.654	0.483	0.881	0.000325
11dm-Cyclopentane	0.014	0.717	0.463	0.955	0.000196
c13dm-Cyclohexane	0.0232	0.683	0.452	0.927	0.000382
t12dm-Cyclohexane	0.00899	0.704	0.478	0.921	0.000139
t13dm-Cyclohexane	0.00426	0.714	0.521	0.922	5.61e-05
113tm-Cyclohexane	0.00659	0.637	0.47	0.783	7.92e-05
1e1m-Cyclohexane	0.00308	0.708	0.621	0.846	3.45e-05
Benzene	0.166	0.746	0.658	0.904	0.00114
Toluene	0.234	0.722	0.723	0.781	0.00126
m+p Xylenes	0.0882	0.712	0.749	0.722	0.000423
1ethyl-Benzene	0.025	0.639	0.836	0.591	6.7e-05
o Xylene	0.0311	0.677	0.799	0.646	0.000113
ipropyl-Benzene	0.0013	0.681	0.783	0.662	5.43e-06
npropyl-Benzene	0.00321	0.615	0.834	0.548	7.66e-06
1e-3,4m-Benzene	0.0174	0.608	0.798	0.53	3.61e-05
1e-2m-Benzene	0.0023	0.565	0.827	0.468	4.11e-06
123tm-Benzene	0.00504	0.581	0.793	0.471	1.04e-05
124tm-Benzene	0.0201	0.621	0.793	0.546	5.76e-05
135tm-Benzene	0.00841	0.654	0.762	0.606	3.6e-05
C <sub>2</sub> H <sub>2</sub>	0.177	0.52	1	0.414	0
C <sub>2</sub> H <sub>4</sub>	0.32	0.594	0.798	0.508	0.000561
C <sub>3</sub> H <sub>6</sub>	0.079	0.567	0.653	0.502	0.00021
1-Butene	0.00884	0.558	0.741	0.496	1.68e-05
1,3-Butadiene	0.00336	0.443	0.687	0.346	5.55e-06

**Table S1.** Statistical summary of VOC and NO<sub>x</sub> measurements at the BAO tower during the 2012 SONNE study. Shown are means from ~780 samples, r-coefficients from linear regressions relative to CH<sub>4</sub>, acetylene and propane, and the derived emission ratios relative to CH<sub>4</sub> specifically from oil/gas activities (ppbv/ppbv).



**Figure S1.** Terrain height (above sea level, in m) in the WRF-Chem model domain, 4 km resolution



**Figure S2.** Isoprene and alpha-pinene emissions at reference temperature (30° C) and photosynthetic photon flux density (PPFD = 1000  $\mu\text{mole}/\text{m}^2/\text{s}$ ) from the BEIS inventory over the 4-km model domain. Dark crosses show the location of Denver, CO.

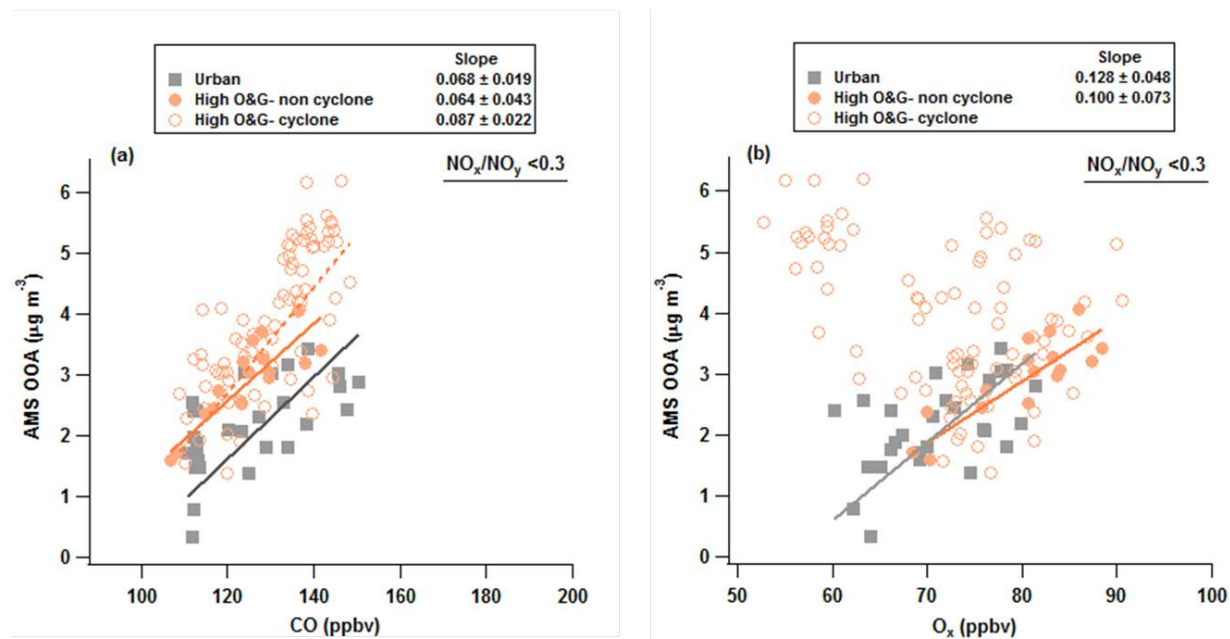
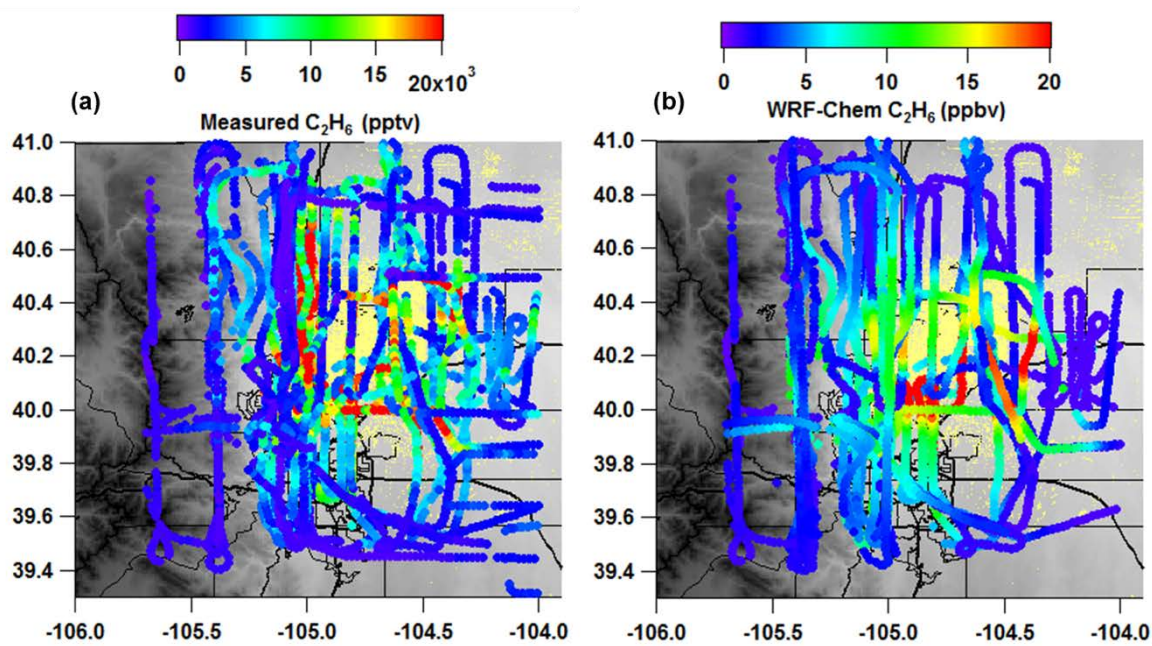


Figure S2S3. Correlation plots of PMF-derived OOA vs. CO (a) and odd oxygen,  $\text{O}_x$  defined as  $\text{O}_3 + \text{NO}_2$  (b) in aged plumes.



**Figure S3S4.** Flight tracks of C130 in the Front Range BL, color coded with ethane values from measurements (a) and BC-tdOG scenario (b). Locations of the O&G wells are shown with yellow dots.