

We thank the reviewers for taking the time to review our work and leave constructive comments. In the text below, the bold text is the comment from the reviewer, the normal text is our response, and any underlined text is new additions to either the main manuscript or the SI. One major change that we would like to point out early on is that the name of the “vertical mixing” factor has been changed to the “aged-transported” factor, and the “aged air” factor has been changed to the “aged-local” factor, based on suggestions from one of the reviewers.

Reviewer 1

1. Section 3.3 compares the results with another VOC source apportionment study conducted in Fairbanks. For readers unfamiliar with the VOC source apportionment study by Ketcherside et al. (2025) and the PM source apportionment study by Ijaz et al. (2024), including a figure (e.g., Fig. S14 and S15 alongside a corresponding figure from Ijaz et al.) or a summary table highlighting the main differences between the PMF results (CTC versus residential site) would strengthen the discussion and improve readability.

Figure 5 has been added to the main paper, which compares our work, Ketcherside et al., and Ijaz et al. together in one figure.

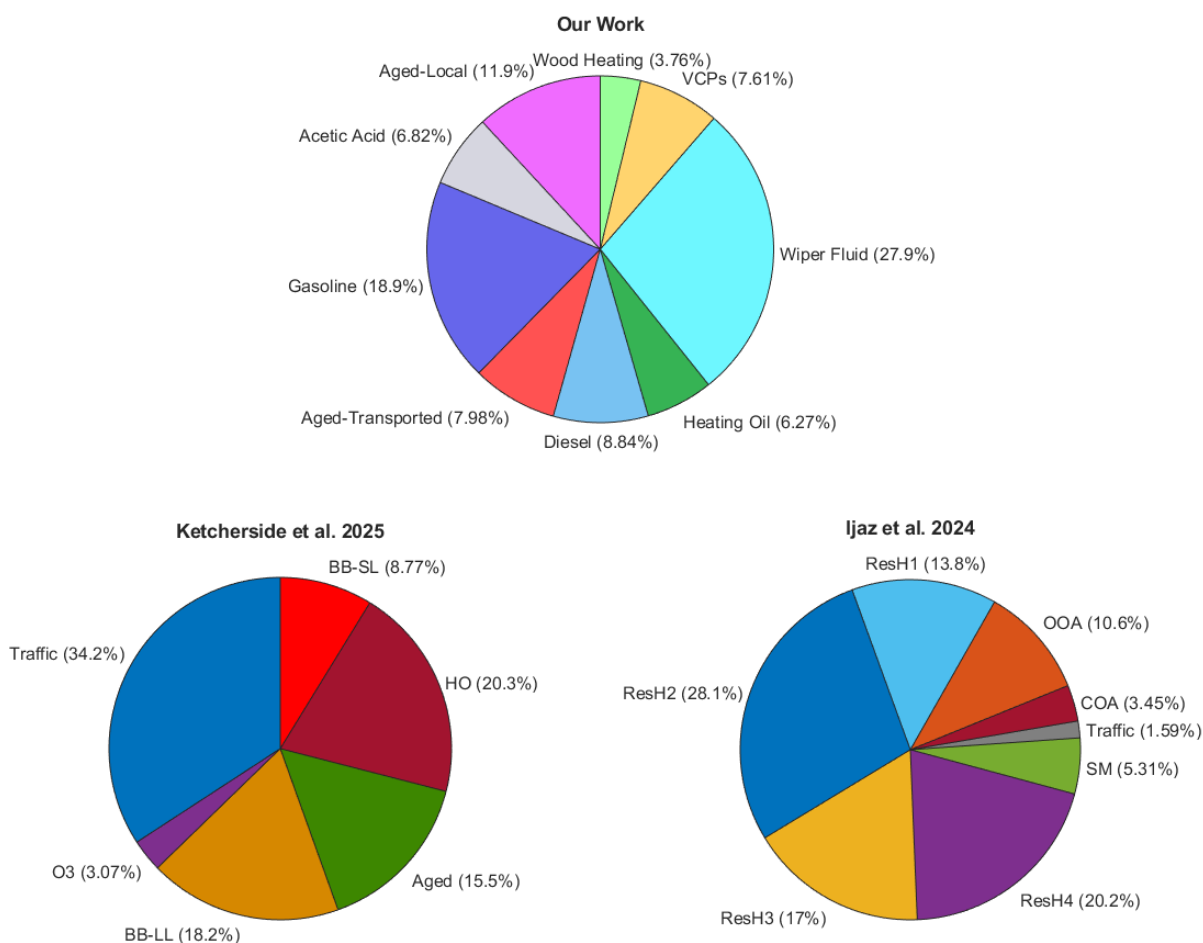


Figure 5. Comparison of the PMF factor solutions used in this work, Ketcherside et al. (2025), and Ijaz et al. (2024). In Ijaz et al. (2024), the factors ResH1, ResH2, and ResH4 originate from biomass burning, while ResH3 originates from heating oil.

Figure S15 (now Figure S18) now includes a direct comparison of the factors in our work and Ketcherside et al.

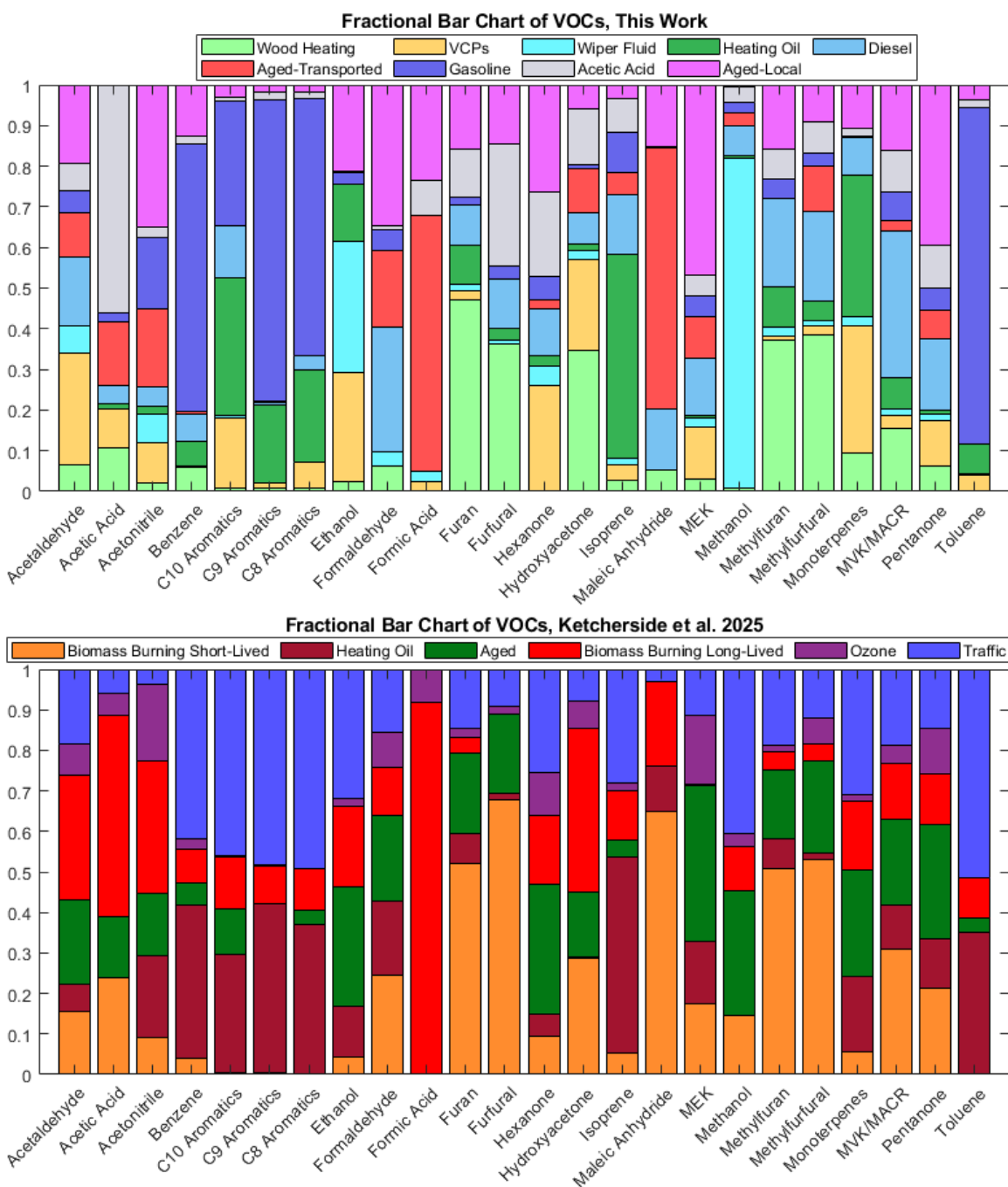


Figure S18. Top: fractional bar chart of VOC species assigned to each factor in this work. Bottom: recreation of Figure S5 in Ketcherside et al. (2025) for comparison with our work.

2. Beyond describing the differences in VOC sources observed at two sites within the same city, it would add value to further discuss, either at the end of this section or in the conclusion, the potential implications for SOA and ozone formation, as well as the variability occurring at such a local scale. Are the observed differences significant enough to affect secondary pollutant formation?

We think that ozone formation is likely not affected, because photochemistry is limited with lack of sunlight, and ozone that does form is titrated quickly by high concentrations of NO in Fairbanks. Oxidant levels are also generally low, so we do not expect much variation in SOA formation between the two sites. However, differences in S(IV) formation are possible. This paragraph has been added to the Section 4, line 983 about the residential site vs downtown: “Since the site in Ketcherside et al. (2025) is residential, we expect VOC species related to vehicle emissions to be lower compared to our downtown site. This is true for formaldehyde, which is on average 60% lower at the residential site compared to downtown. Assuming the same is true for total ammonia, secondary aerosol formation of S(IV) and other species may be lower at the residential site than downtown.”

3. Furthermore, only a few of the 9 scatter plots presented in Figure 3 appear directly relevant to the discussion. I would suggest replacing them with the Pearson correlation heatmap shown in Fig. S16, which provides more comprehensive information supporting the overall interpretation. Although this figure is discussed in the Supplementary Information, including correlations with external factors in the main manuscript would better support the source attribution analysis.

Figure 4 has been replaced with the heatmap in Figure S16. Some correlations that are not mentioned in the paper (dN, CO₂) have been removed from the figure. We have also deleted various plots that showed basic correlation since they are redundant. In some cases where correlation was mentioned but no figure was referenced, we referenced Figure 4 in the text. For example:

Line 597: “Figure 4 shows a weak negative correlation between temperature and wood heating.”

Line 664: “Figure 4 and S16 show that the aged-transported factor is the only factor to have a positive correlation with wind speed.”

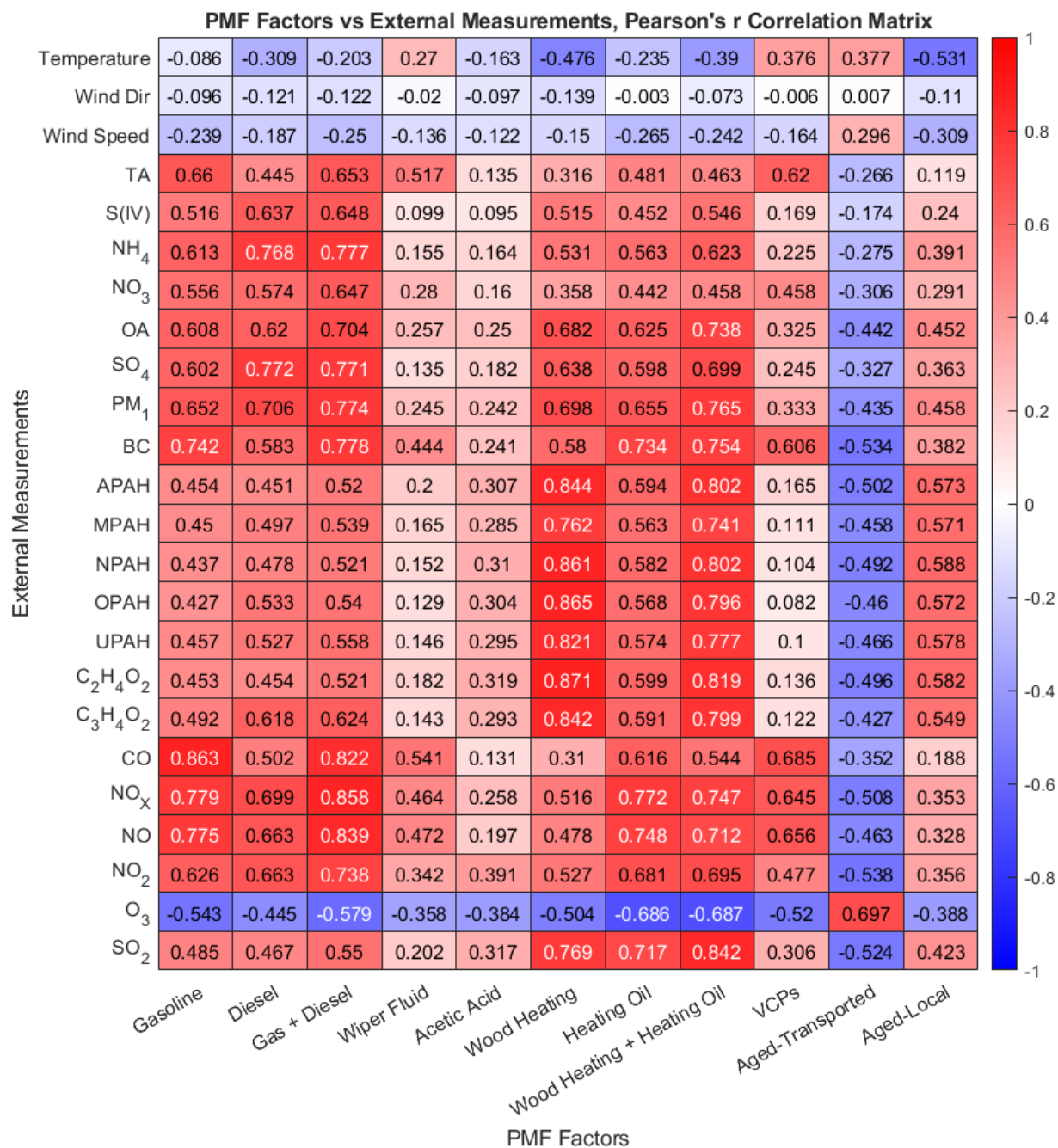


Figure 4. Correlation matrix of PMF factors versus external species. TA (total ammonium) includes both gas-phase and aerosol-phase measurements. Species from S(IV) to C₃H₄O₂ are all measurements in the aerosol phase. Species from CO to SO₂ are all measurements in the aerosol phase.

4. The wiper fluid factor accounts for 28% of the measured VOCs, exceeding the combined contributions from traffic and diesel sources. Does this interpretation seem reasonable? This factor also appears highly site-specific, as it was not observed at the Fairbanks residential site. If the number of factors were reduced, would methanol and ethanol instead be redistributed into other sources?

Even as low as the four factor solution, the windshield wiper fluid was resolved, so we expect this to be a real factor. The Q/Qexp value also decreases dramatically from one factor to four factors, so we rule out the 1-3 factor solutions. Further discussion was added to Section S2, line 123, about the possible reasons for the difference between the two sites: “This could be why a wiper fluid factor is not observed in Ketcherside et al. (2025), since a large proportion of cars are parked inside garages when cars are started in the morning, and because most cars started in the afternoon will be outside of residential areas. They observe a similar mixing ratio of methanol to our measurements, and although they did not observe a windshield wiper fluid factor, methanol was still largely associated with traffic. This factor stands out for the high time-resolution data and should not be combined with traffic in our analysis.”

5. Page 3, line 72: It would be useful to provide quantitative values after “a significant fraction of PM2.5 in Fairbanks” to better emphasize the importance of investigating their sources and formation pathways.

Sentence has been edited to include percent values (line 77): “HMS and other S(IV) species can account for up to 41% sulfur PM2.5 mass and 6.8% of total PM2.5 mass in Fairbanks, a larger fraction than in other urban environments (Campbell et al., 2022, 2024).”

6. Was no cooking-related factor identified?

We have added this paragraph (starting at line 332) and Table S7 to the SI:

Not Assigned: Cooking Factor

We did not see evidence of a cooking factor in our PMF analysis of VOCs, in contrast to Ijaz et al. (2024) who resolved a cooking factor in the particle phase. Long-chain aldehydes like hexanal, octanal, and nonanal have been used in previous work as tracers for cooking emissions (Coggon et al., 2024; Peng et al., 2017; Wernis et al., 2022). Table S7 shows the percent of the total signal at $C_6H_{12}OH^+$, $C_8H_{16}OH^+$, and $C_9H_{18}OH^+$ (corresponding to protonated hexanal, octanal, and nonanal, respectively) assigned to each of the nine factors. None of these species are strongly associated to any factor. The VCP factor contains the most cooking tracers overall but the weekend diurnal cycle, which peaks at around 1-3 am and is lowest around 7-10 am, does not follow what we would expect from a cooking factor. The aged-transported factor contains 22% of the octanal and 34% of the nonanal, but it is unlikely for the cooking factor to be correlated with ozone and wind speed. No other factor contains 20% or more of two cooking tracers. Therefore, we do not assign a cooking factor here.

Table S7. Percent apportionment of cooking tracers hexenal, octanal, and nonanal to each factor.

Factor	$\text{C}_6\text{H}_{12}\text{OH}^+$ (Hexanal)	$\text{C}_8\text{H}_{16}\text{OH}^+$ (Octanal)	$\text{C}_9\text{H}_{18}\text{OH}^+$ (Nonanal)
VCP	26.2%	20.2%	33.7%
Acetic Acid	20.6%	2.2%	2.3%
Methanol	4.2%	2.1%	4.2%
Heating Oil	1.5%	7.0%	1.3%
Aged-Transported	2.0%	21.5%	33.5%
Diesel	10.5%	20.3%	15.4%
Aged-Local	26.9%	6.1%	0.0%
Wood Heating	0.0%	14.7%	9.6%
Gasoline	8.1%	5.8%	0.0%

7. For the VCP factor, were no siloxane fragments observed?

We have added this to Section 2, line 217 for clarification: “Based on post-campaign calibration measurements using D₃-D₅ siloxane standards and comparison of their main fragmentation patterns with the closest matching ions observed in the campaign data, only ions at m/z 297.098 and 299.066, which are consistent, within the instrument mass accuracy, with ions previously reported for pure D4 siloxane were detected (m/z 297.083 and m/z 299.062 corresponding to $\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4\text{H}^+$ and $\text{C}_7\text{H}_{22}\text{O}_5\text{Si}_4\text{H}^+$). However, the fact that both ions are mainly associated with the biomass burning factor (50 and 42% versus 3 and 8% for the VCP) indicates that their assignment to D4 siloxane remains uncertain. Other plausible assignments, including $\text{C}_{20}\text{H}_{10}\text{O}_3\text{H}^+$ (297.091) and $\text{C}_{21}\text{H}_{12}\text{O}_2\text{H}^+$ (299.071), corresponding to compounds that are more likely to be associated with biomass burning emissions, cannot be excluded.”

8. Both the VCP and wiper fluid factors appear to increase with warmer temperatures (Fig. S25 and Fig. S29). Do the authors have a possible explanation for this behavior?

We had discussed these in Section S1, but have moved it to the main paper in Section 3.

Wiper fluid (line 571): “The periods with the highest mixing ratio of the wiper fluid factor are the warmer periods at the beginning (Jan 21st-26th) and end (Feb 21st-27th) of the ALPACA campaign, where temperatures are often greater than -15 °C (Figure S13). It is 2.9 times higher on average in the warm polluted period than the cold polluted period. In warmer periods, slush and mud on the road from snow melt would be more common, necessitating more use of windshield wiper fluid.”

VCP (line 623): “The VCP factor is highest during the warmer periods at the beginning (Jan 21st-26th) and end (Feb 21st-27th) of the ALPACA campaign (Figure S14), and 3.3 times higher on average in the warm polluted period than the cold polluted period. This could be due to more off-gassing of VCP products at higher temperatures.”

9. Page 17 – line 457: “This is large difference likely due”, please rephrase.

Fixed

10. Page 19 – line 495-496: ”Ijaz et al. (2024) contribute about 1.6% (0.06 µg/m³) of measured OA to traffic [...] we contribute”, here “attribute” may be more appropriate than “contribute.”

Fixed

Reviewer 2

1. Justification of the PMF factor solution. No section explains why the nine-factor solution is chosen over the neighbouring solutions. The wood-heating and heating-oil factors look like a split of a single space-heating factor, and the aged-air and vertical-mixing factors are almost the same, with shared secondary signatures. The supplement only notes that Q/Q_{exp} decreased monotonically and that the solution was chosen for its interpretability, while the bootstrap criteria (Table S6) test each factor against the same tracer used to define it, which is circular. Please add a clear, solution-by-solution explanation (ideally in a dedicated section; this is currently placed in S2 and would be better as S1), state whether the factor pairs above merge at lower factor numbers, and report the rotational and statistical uncertainty of the factor contributions, because the paper depends strongly on exact apportionment percentages.

Section S2 (now S1) has been greatly expanded to explain our process in choosing the nine-factor solution:

“We use the Q/Q_{exp} values to help eliminate some solutions. The Q/Q_{exp} value decreases dramatically up to the four factor solution (Figure S23), so we rule out the 1-3 factor solutions.

The four-factor and five-factor solutions do not appear to be representative of Fairbanks because it appears that the vehicle-related and heating oil factors are mixed. In the four factor solution, we define a gasoline, driving/wiper fluid, heating, and aged-transported factor. The driving/wiper fluid factor separates into the windshield wiper fluid factor and another factor that appears to be a mixture of heating oil and diesel in the five factor solution. The heating oil factor and the diesel factor then separate again in the six factor solution.

In the six factor solution, acetic acid is assigned mainly (in decreasing order) to the heating oil, diesel, and aged-transported factor, but in the seven factor solution it is assigned to its own factor. This is consistent with the observations, since measurements of acetic acid contain many large spikes that are not seen with other factors. The VCP factor is defined in the eight factor solution. The aged-local factor is defined in the nine-factor solution. Neither the VCP factor nor the aged-local factor appear to be splits of other factors.

In the 10 factor solution, a new factor emerges which has a similar diurnal cycle to the aged-transported factor, but the peak occurs one hour earlier (Figure S24). The new 10 factor also contains oxygenated species that were previously abundant in the aged-transported factor. This includes $\text{C}_3\text{H}_4\text{O}_2\text{H}^+$ (51% of total assigned to 9 factor solution aged-transported; 50% assigned to new 10th factor), $\text{C}_3\text{H}_4\text{O}_3\text{H}^+$ (76% aged-transported; 44% new factor) $\text{C}_4\text{H}_4\text{O}_3\text{H}^+$ (59% aged-transported; 41% new factor) $\text{C}_6\text{H}_4\text{O}_3\text{H}^+$ (61% aged-transported; 41% new factor). It is not correlated to wind speed. Therefore, this appears to be another local aged factor. We find it unlikely that there would be two locally aged factors. Especially because the diurnal cycle of the new factor has a diurnal cycle that increases early in the morning, peaks midday, and decreases in the afternoon, the factor appears to be related to photooxidation, but in an extremely dark environment like Fairbanks this assignment would be doubtful. Therefore, we assess that this is a split of the aged-transported factor, and stop at the 9 factor solution.

The assignments for factors 2-10 are shown in Table S5. 100 bootstrap results for the nine factor solution, and all runs passed the evaluation criteria. The evaluation criteria are shown in Table S6. The rotational and statistical uncertainty (also referred to as the PMF error) of the factors range from 2.8-5.4% (Figure S25).“

A figure showing PMF error has been added to the SI as Figure S25.

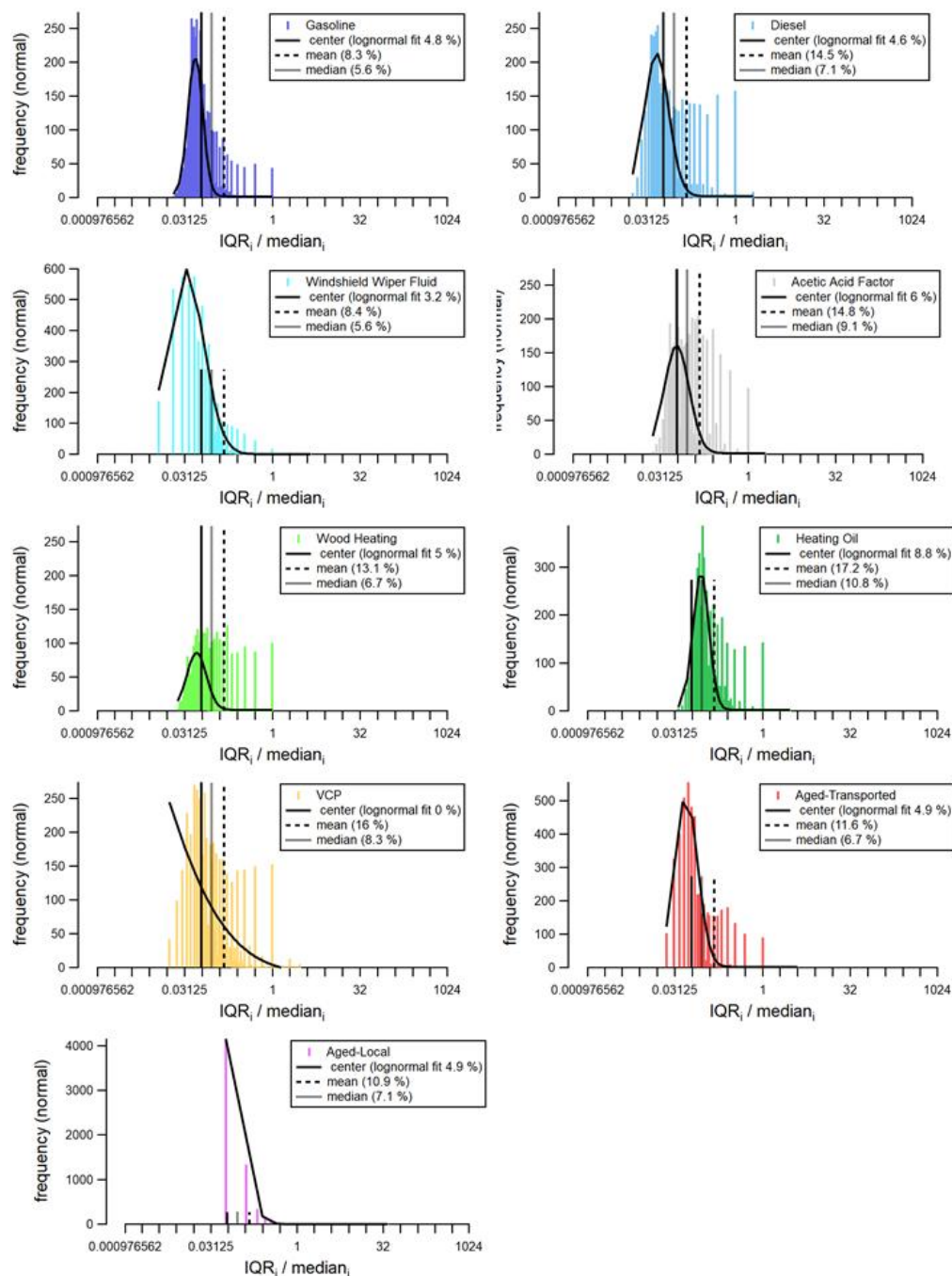
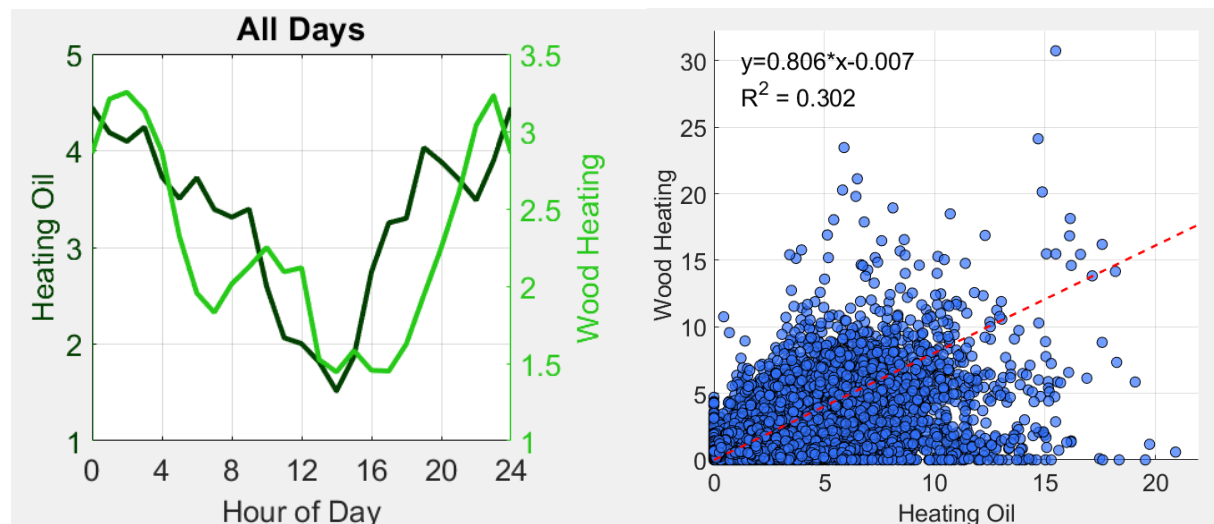


Figure S25. The statistical and rotational uncertainty (also known as PMF error) of each factor from the 100 bootstrap runs. The SoFi 9 manual describes the PMF error as $\pm$ one half of the median value shown in the plots above.

Similar temporal patterns are expected for the wood-heating and heating-oil factors because both are associated with residential heating, but the heating oil factor is associated with aromatics (consistent with Ketcherside et al.) and the wood heating factor is associated with biomass burning species. Furthermore, differences in the diurnal profiles, together with the weak correlation between the two factors, indicate that they are distinct rather than the result of the splitting of a single factor.



We are not sure about the meaning of the comment “the bootstrap criteria (Table S6) test each factor against the same tracer used to define it, which is circular.” In SoFi Pro, the bootstrap criteria are used to sort the factors of each bootstrap into the same order for further analysis. We use the most prominently correlated VOC species or external measurement with each factor to sort the bootstrap runs, and in the text we mention that “all runs passed the bootstrap criteria”, meaning all runs were consistent enough to be sorted with the criteria we defined.

We address the point about aged-air vs vertical mixing in the next comment.

2. Interpretation and naming of the secondary factors. “Vertical mixing” is a meteorology-based name for a factor whose chemical composition (mostly formic acid, maleic anhydride, formaldehyde, and several C_xH_yO₃ species) is clearly secondary/aged. The authors also show that the factor depends on wind direction, which points to transport rather than only vertical exchange. The vertical-mixing and aged-air factors share strong secondary-chemistry and transport signatures; please justify keeping them separate, or merge them into secondary-chemistry factor(s) and discuss the primary emissions that feed them. The attribution would be much stronger with wind-rose plots for each factor and back-trajectory analysis showing the factor origins.

We understand that “vertical mixing” is not a descriptive name of the factor. In the text, we have changed instances of “vertical mixing” to “aged-transported” and “aged air” to “aged-local”.

We have addressed why we think the aged-local and aged-transported factors should be separate:

“Conceptually, the aged-local factor and the aged-transported factor are similar. Both describe aged air masses that undergo secondary chemistry. The main difference between the two factors is that the aged-transported factor corresponds to weakly stable conditions (with mixing from aloft), and aged-local corresponds to strongly stable and stagnant conditions. Weakly vs strongly stable conditions are discussed in Brett et al. (2025). The aged-local factor includes emissions local to Fairbanks when the inversion layer is strong and O_3 is completely titrated by high mixing ratios of NO_x , whereas the aged-transported includes aged sources, such as wood heating plumes, that interact with O_3 . Therefore, we would expect secondary reaction mechanisms to depend more on NO_3 radicals than O_3 . The positive correlation of the aged-transported factor with ozone vs the negative correlation of the aged-local factor with ozone (Figures 4, S29, S30), and the nearly opposite trends in the diurnal cycles between aged-transported and aged-local (Figure 3) are evidence that these are two independent factors.”

With regard to air mass origins and pollutant dispersion, we make use of the detailed analysis carried out by Brett et al. (2025) who examined pollutant dispersion and sources during ALPACA. They compared tracer simulations run forwards from emission sources to observations, including at the CTC site. The results show clear differences in pollutant dispersion and emission influences between stable conditions with strong surface-based temperature inversions trapping pollutants local to the CTC site below 20m and weakly stable conditions with enhanced vertical exchange and pollutant dispersion. This is reflected in the wind-roses that are now included for each sector in Figure S16.

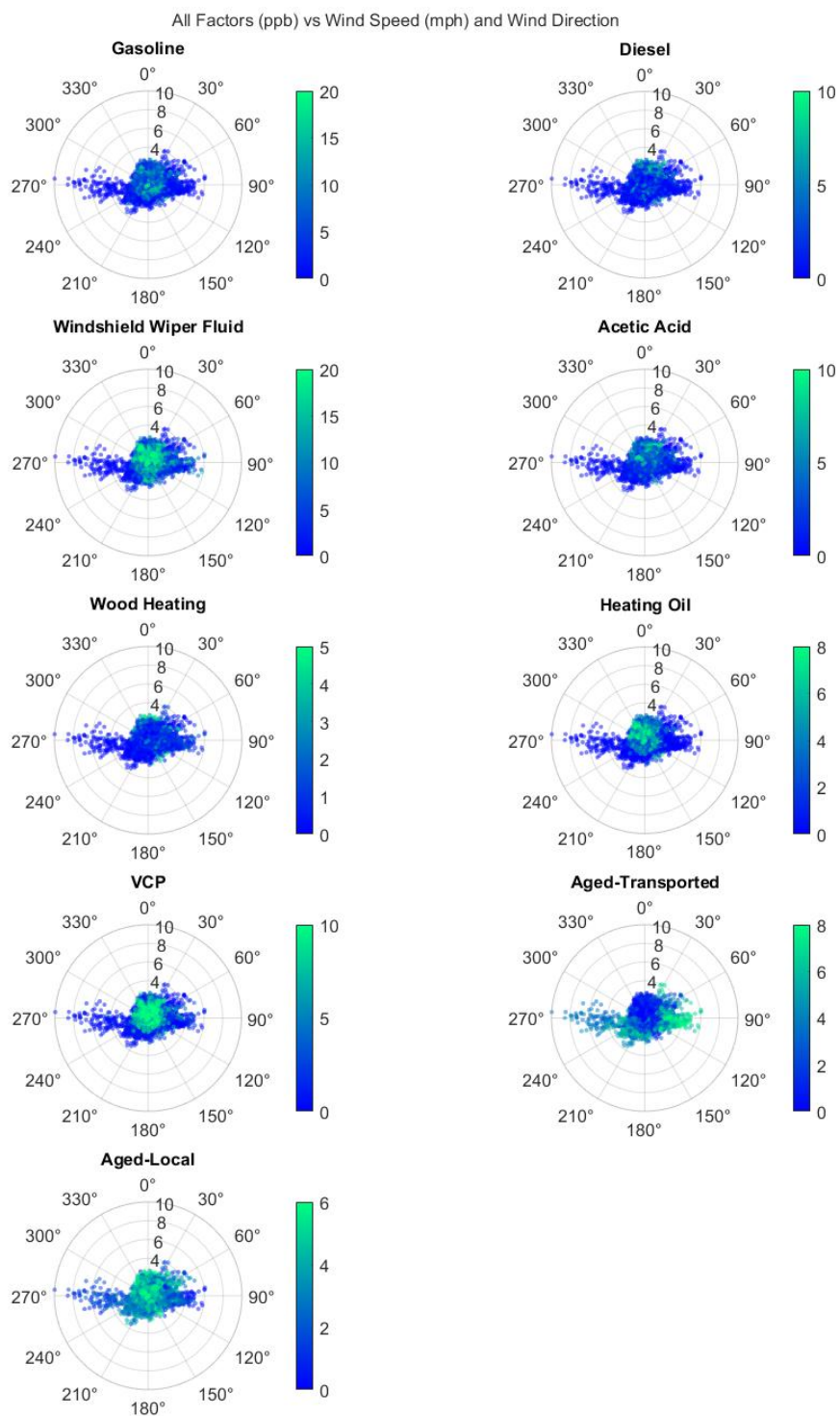


Figure S16. Windrose plots of all factors. The colorbar was reduced between 1/4 to 1/2 the maximum mixing ratio of the factor in order to better highlight the relationship with wind.

3(a). The diesel toluene/benzene ratio of zero is used as a diagnostic, but a zero assigned by PMF is an artifact, not a real emission ratio; the claim that gasoline/diesel differences explain a four-order-of-magnitude carbonyl/aromatic contrast should be checked against a mass-based source comparison, because the roughly two-fold difference suggested by Table S3 cannot explain it and more likely shows that PMF has difficulty separating these sources.

First, we would like to acknowledge that the ratio values listed in the SI were calculated with the pre-bootstrap results, so they don't reflect the average value from 100 runs. We have replaced these values with the values from the bootstrap runs. The other numbers in the SI are correct. The conclusions are largely unchanged. The new values are:

Gasoline: toluene/benzene = 3.1 ppb/ppb, formaldehyde/toluene = 0.033 mg/mg, acetaldehyde/toluene = 0.026 mg/mg, formaldehyde/C8 aromatics = 0.038 mg/mg, acetaldehyde/C8 aromatics = 0.030 mg/mg

Diesel: toluene/benzene = 0.003 ppb/ppb, formaldehyde/toluene = 1967 mg/mg, acetaldehyde/toluene = 834 mg/mg, formaldehyde/C8 aromatics = 36.1 mg/mg, acetaldehyde/C8 aromatics = 15.3 mg/mg

Acetic acid: toluene/benzene = 2.6 ppb/ppb

Wood heating: toluene/benzene = 1E-4 ppb/ppb

Aged-transported: toluene/benzene = 0.36 ppb/ppb

Aged-local: toluene/benzene = 0.73 ppb/ppb

We acknowledge that an assignment of 0 is an artifact of PMF. Using the bootstrap runs, these ratios are no longer zero, but we still mention this in the paper:

Line 94 SI: "The toluene/benzene ratio of the diesel factor is 0.003 ppb/ppb. This low value is partially because the PMF software assigned no toluene to the diesel factor in some of the bootstrap runs, which is an artifact of the PMF software assignment."

Line 212 SI: "Very little toluene was assigned to this factor, which leads to a toluene/benzene ratio of 1.0×10^{-4} ppb/ppb. Such low values of toluene are partially due to some bootstrap runs assigning no toluene to the biomass burning factor, which is an artifact of the PMF software. However, the low toluene/benzene ratio could indicate biomass burning (Zhang et al., 2016)."

The gasoline factor has a formaldehyde/C8 ratio of $0.25 \mu\text{g m}^{-3}/6.5 \mu\text{g m}^{-3} = 0.038$ mg/mg and formaldehyde/C8 ratio of $0.19 \mu\text{g m}^{-3}/6.5 \mu\text{g m}^{-3} = 0.030$ mg/mg. The diesel factor has a formaldehyde/C8 ratio of $1.47 \mu\text{g m}^{-3}/0.042 \mu\text{g m}^{-3} = 36.1$ mg/mg and formaldehyde/C8 ratio of $0.62 \mu\text{g m}^{-3}/0.042 \mu\text{g m}^{-3} = 15.3$ mg/mg. This leads to an approximate 1E3 magnitude difference between the ratios for their respective species.

3(b). Windshield wiper fluid is, by definition, a volatile chemical product and not a tailpipe emission (Coggon et al., 2018, on in-cabin D5 siloxane, which is still classified as a VCP even though it is vehicle-associated); the “vehicle-related ≈56%” framing therefore mixes use behaviour with combustion emissions and should be revised. The acetic-acid factor, assigned to “old vehicles” based on indirect evidence and a “may be related to vehicle emissions” argument, is also included in the vehicle total and needs a sensitivity range.

We agree that windshield wiper fluid is a VCP, however due to the broad nature of the VCP factor vs the specific nature of the wiper fluid factor, we consider it more fitting to include it with vehicles. We describe this in section 3.2.2, line 566: “Since the windshield wiper fluid is only associated with vehicles but is not a direct tailpipe emission, it is technically a volatile chemical product (VCP). However, we feel it is more fitting to include the wiper fluid factor as a vehicle-associated factor, since the VCP factor (discussed in 3.2.4) is a broad grouping that includes cleaning products, personal care products, solvents, and other similar products.”

We have made the text clearer in the abstract (line 35): “Positive matrix factorization (PMF) analysis indicates that up to 56% of VOCs are vehicle-associated, with 29-36% from direct emissions and 21% from windshield wiper fluid.”

We have edited the conclusion as well (line 934): “We attribute 29-36% of total VOCs to direct vehicle emissions and 21% to windshield wiper fluid, for a maximum of 56% of vehicle-related VOCs.”

We have also reworded “old vehicles” to be more specific (line 170 SI): “We are leaning towards emissions from vehicles with old engine oil for two main reasons. First, acetic acid has been measured in emissions from vehicles with old engine oil....”

3(c). The analysis reports the species that dominate each factor; it would be more useful to also identify tracer masses whose signal is mostly explained by a single factor, for all factors, which would test how well PMF separated the sources.

We do include some low concentration species, for example $C_5H_4O_2H^+$ and $C_6H_{12}OH^+$ in the acetic acid factor, $C_8H_8O_3H^+$ and $C_7H_8O_2H^+$ in the wood heating factor. It is not that common for the majority of one tracer species to be explained by a single factor. This may be due to similarities in factor composition (like diesel fuel and heating oil), or similarities on diurnal cycles (like wood heating and heating oil). We have included low-concentration tracers where we could.

4. Make fuller use of the PTR-ToF-MS data. Although the PMF used over 300 ions, the interpretation in the main text is based on a small set of species, and the full chemical range of the solution is never shown. Plots of the factors in O/C–H/C and OSC–log C space, and stacked views of intensity by carbon number and oxygen content, would show what

contributes to each factor across the spectrum and would clearly improve the source naming. A low individual signal does not mean low information content.

We respectfully disagree with the reviewer in this case. Plots of O/C-H/C and OSC-logC are mainly intended to show how aerosols age over time. Fairbanks is a unique environment because it is so cold and dark, there is not much typical oxidation that occurs. We are also not aware of studies that have associated VOC PMF factors with oxidation state metrics. Gas-phase PMF factors are not expected to follow what is observed in OA PMF where oxidation generally decreases volatility. VOC concentrations can span several orders of magnitude, from ppt to ppb levels. A single compound present at substantially higher concentrations than the other species within a factor may dominate the elemental ratios, limiting the usefulness of O/C as an indicator of the overall oxidation state of that factor. In addition, the presence of oxygenated compounds does not necessarily imply secondary formation, as some oxygen-containing VOCs are primarily emitted. For example, acetic acid is often associated with primary emission sources.

5. Inter-campaign comparison should be shown, not left to the reader. Several parts of the text ask the reader to compare the manuscript's figures with those of other papers; showing these differences quantitatively is the job of this paper. Please give factor-profile correlations against Ketcherside et al. (2025) and bring the main comparison into the main text. The current main-text figures are few and not very informative. Where time resolution or the inclusion of external species (O₃, NO_x) is suggested as the reason for the difference with Ketcherside et al. (lines 484–487), this can be tested directly by running PMF with those species included; explaining the difference by a factor that was deliberately left out, without testing it, is not convincing.

Figure 5 has been added to the main paper, which compares our work, Ketcherside et al., and Ijaz et al. together in one figure.

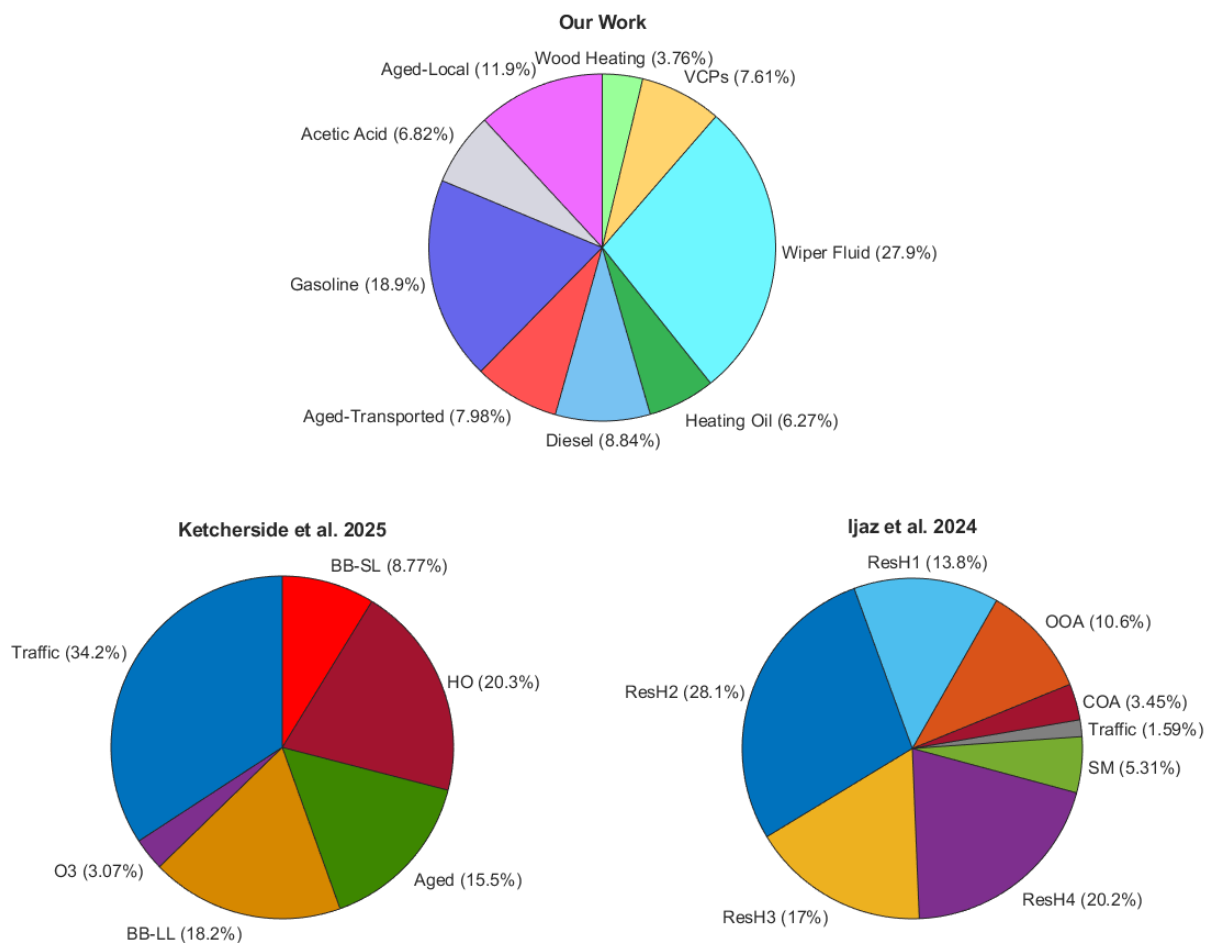


Figure 5. Comparison of the PMF factor solutions used in this work, Ketcherside et al. (2025), and Ijaz et al. (2024). In Ijaz et al. (2024), the factors ResH1, ResH2, and ResH4 originate from biomass burning, while ResH3 originates from heating oil.

Figure S15 (now Figure S18) now includes a direct comparison of the factors in our work and Ketcherside et al.

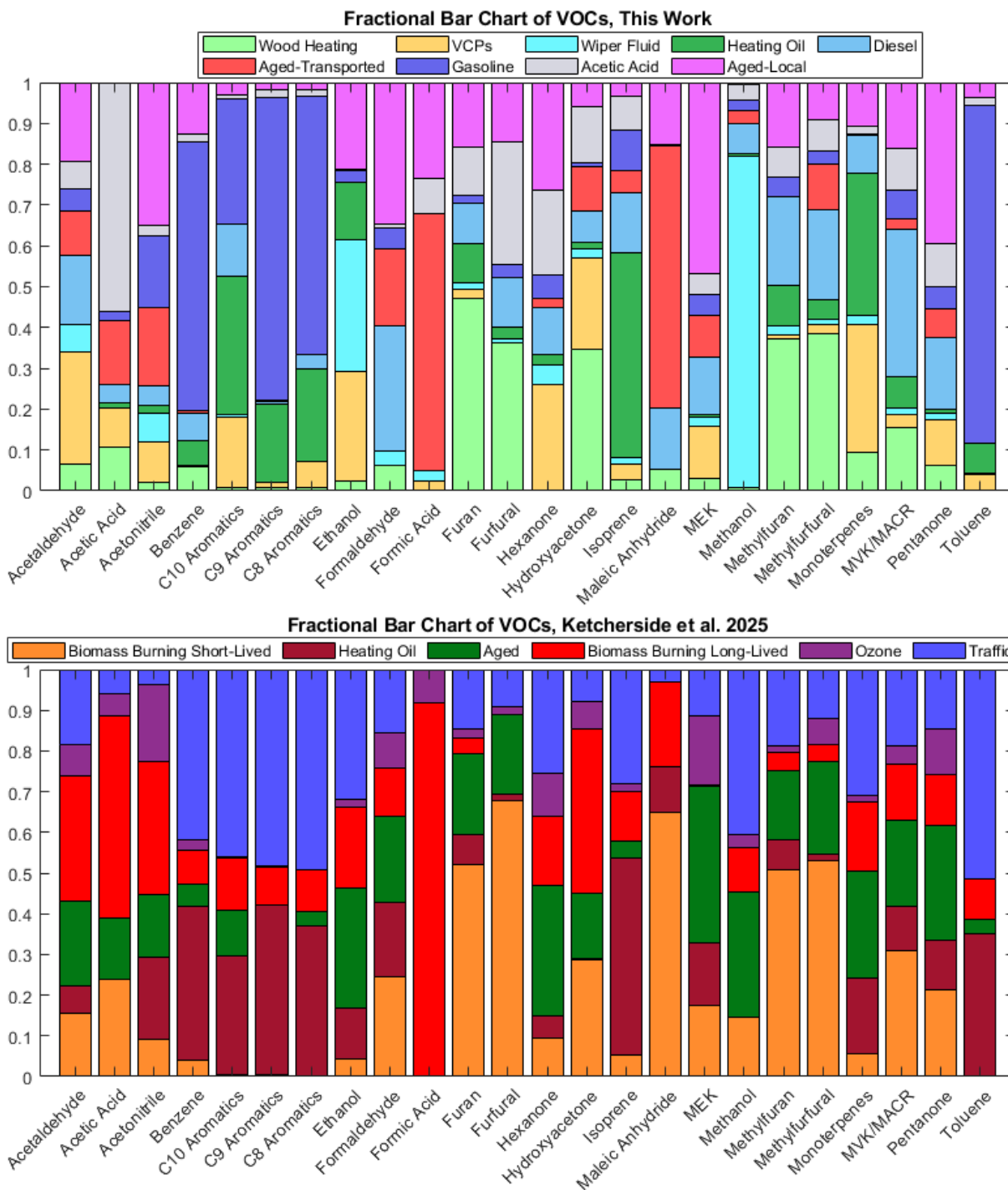


Figure S18. Top: fractional bar chart of VOC species assigned to each factor in this work. Bottom: recreation of Figure S5 in Ketcherside et al. (2025) for comparison with this work.

We agree that including additional external tracers such as O_3 and NO_x in the PMF analysis could help assess their influence on the factorization and potentially provide further insight into the differences with Ketcherside et al. However, performing a new PMF analysis with an expanded input dataset would constitute a substantial extension of the present work and

is beyond the scope of this study. Our intention here was not to attribute the observed differences solely to the exclusion of these species, but rather to highlight methodological differences that may contribute to the different outcomes.

6. Related to this, please state whether cooking tracers such as long-chain aldehydes (e.g. Coggon et al., 2024; Klein et al., 2019) were included, given that Ijaz et al. (2024) resolved a cooking factor in the same airshed but this study did not.

We have added this to the SI, line 332:

Not Assigned: Cooking Factor

We did not see evidence of a cooking factor in our PMF analysis of VOCs, in contrast to Ijaz et al. (2024) who resolved a cooking factor in the particle phase. Long-chain aldehydes like hexanal, octanal, and nonanal have been used in previous work as tracers for cooking emissions (Coggon et al., 2024; Peng et al., 2017; Wernis et al., 2022). Table S7 shows the percent of the total signal at $C_6H_{12}OH^+$ $C_8H_{16}OH^+$ $C_9H_{18}OH^+$ corresponding to protonated hexanal, octanal, and nonanal respectively, assigned to each of the nine factors. None of these species are strongly associated to any factor. The VCP factor contains the most cooking tracers overall but the weekend diurnal cycle, which peaks at around 1-3 am and is lowest around 7-10 am, does not follow what we would expect from a cooking factor. The aged-transported factor contains 22% of the octanal and 34% of the nonanal, but it is unlikely for the cooking factor to be correlated with ozone and wind speed. No other factor contains 20% or more of two cooking tracers. Therefore, we do not assign a cooking factor here.

Table S7. Percent apportionment of cooking tracers hexenal, octanal, and nonanal to each factor.

Factor	$C_6H_{12}OH^+$ (Hexanal)	$C_8H_{16}OH^+$ (Octanal)	$C_9H_{18}OH^+$ (Nonanal)
VCP	26.2%	20.2%	33.7%
Acetic Acid	20.6%	2.2%	2.3%
Methanol	4.2%	2.1%	4.2%
Heating Oil	1.5%	7.0%	1.3%
Aged-Transported	2.0%	21.5%	33.5%
Diesel	10.5%	20.3%	15.4%
Aged-Local	26.9%	6.1%	0.0%
Wood Heating	0.0%	14.7%	9.6%
Gasoline	8.1%	5.8%	0.0%

7. Formaldehyde treatment and the S(IV)/HMS conclusion. The PTR formaldehyde is about four times lower than the MIRA and COFFEE instruments and is corrected by a single constant scale factor. Because the stated cause is a humidity-dependent back-

reaction, a constant factor cannot correct a bias that changes with time, and the reported r^2 of 0.69–0.81 together with a four-fold offset is consistent with—not evidence against—such a dependence. Please clarify whether the scaled or the unscaled formaldehyde series was used as PMF input (a constant scale keeps the percentages unchanged but biases the shape of the time series), and discuss the humidity dependence directly, because formaldehyde is the basis of the diesel-source and HMS arguments. Finally, the abstract states that vehicle-related ammonia and formaldehyde “likely play a key role” in HMS formation; this causal claim is based on weak correlations ($R^2 \approx 0.4$) among combustion factors that vary together and without any ammonia measurement (as the authors admit). The careful wording used in the body (“this first look seems to indicate”) should also be used in the abstract and conclusions.

Although the ionization back reaction of formaldehyde makes its response factor dependent on the water vapor content, we find no correlation between relative humidity and the scale of difference of the PTR-ToF-MS HCHO compared to the other instruments, shown in the figure below (added as Figure S2). This is most likely because wintertime Fairbanks is exceptionally dry, with ambient specific humidities outside most PTR-MS observations. Any variation in ambient humidity can be significant in a relative sense, but in absolute terms the conditions remain very dry and therefore a single scalar to correct the PTR-MS data is appropriate. Discussion has been added to the methods, line 206: “Although the PTR-ToF-MS measurements of formaldehyde were underestimated due to back-reactions with water vapor, we find no relationship between relative humidity or dew point and the magnitude of difference of PTR-ToF-MS compared to other instruments (Figure S2). Therefore, the formaldehyde measured by the PTR-ToF-MS was scaled up by a constant factor of four to match these instruments, and the scaled data was used in the PMF input.”

In the abstract and conclusion, the wording has been made less strong. “Likely play a key role” has been changed to “could play a role” in the abstract. “May be largely linked” has been changed to “may be linked” in the conclusion. The last two sentences in the conclusion have been edited, line 988: “Although this is an important step in understanding secondary S(IV) formation, the lack of ammonia measurements during the ALPACA campaign prevent conclusive statements from being made. Simultaneous VOC, ammonia, and S(IV) measurements combined with pH modeling would strengthen these results.”

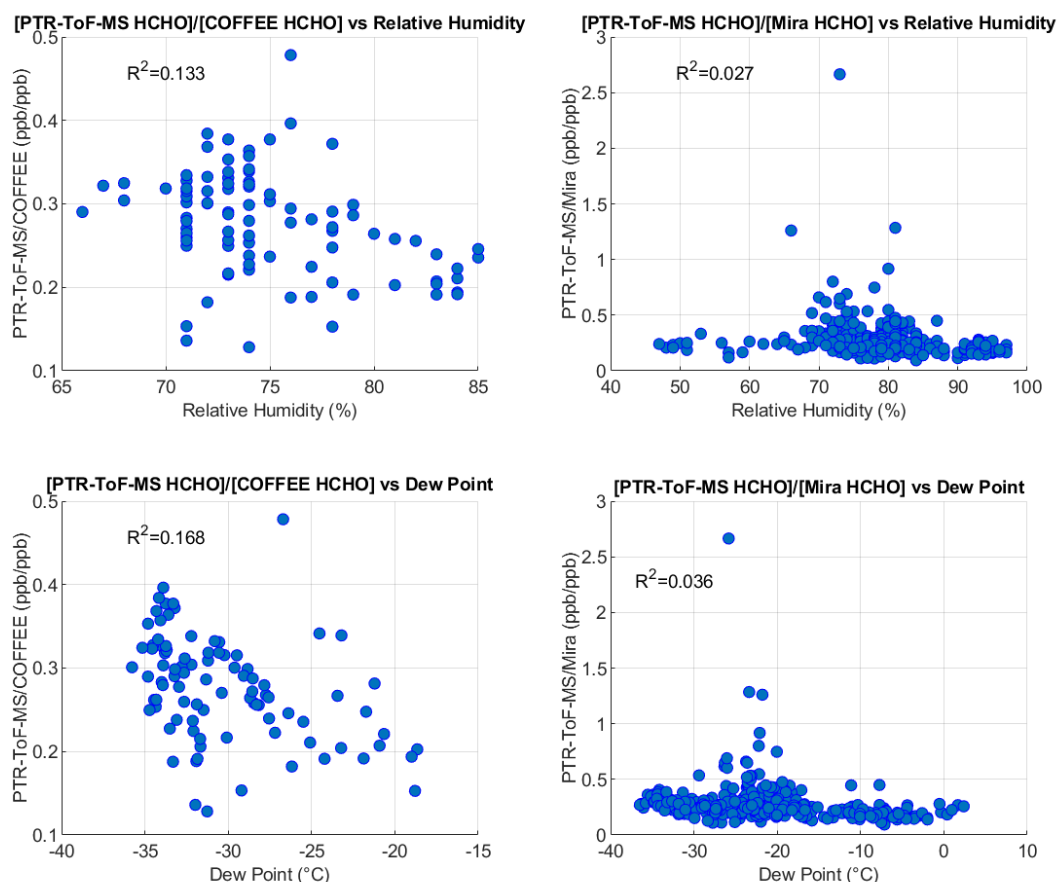


Figure S2. Comparison of the difference between PTR-ToF-MS/COFFEE formaldehyde measurements and PTR-ToF-MS/Mira formaldehyde measurements with relative humidity and dew point.

8. Lines 91, 102–103, 114–116: The campaign location and naming are introduced in a confusing way. The residential site of the earlier ALPACA publications (≈ 3 km away) and the downtown site of this study should be named, dated, and clearly separated early in the text, since both are called “ALPACA.” As written, lines 102–103 read as if PMF was done for the campaign in general rather than only for the downtown site.

Edits have been made to the introduction for clarity, including adding the date and more obvious naming of the sites, starting at line 98: “Several studies conducted PMF analysis during the 2022 ALPACA field campaign. Ijaz et al. (2024), conducted in downtown Fairbanks, used PM1 measurements from both a PTR-ToF-MS with a CHARON inlet and an AMS to conduct PMF; they found that most PM1 OA at the downtown site was attributed to residential heating when using the CHARON PTR-ToF-MS measurements. Ketcherside et al. (2025) combined PTR-ToF-MS VOCs, PM2.5, and gaseous measurements of SO₂, CO, ozone, and NO_x to

examine sources of gases and aerosols in a residential neighborhood approximately 3 km away from the downtown ALPACA site. They find that aromatic VOCs make up 50% of the total VOC mixing ratio, which are mainly attributed to traffic and heating oil. Formaldehyde was found to come from various sources, and many other VOCs were mainly attributed to residential wood combustion. As the VOC measurements in their work were conducted in a residential area about 3 km away from downtown Fairbanks, their analysis is likely more influenced by residential factors like space heating. The role of VOCs in secondary aerosol chemistry has not been addressed in these studies.”

Additions have been made in the methods to explain the two site, line 121: “Measurements were conducted in a trailer in downtown Fairbanks next to the University of Alaska Fairbanks Community and Technical College (64.84064°N, 147.72677°W, elevation 136 m above sea level) from 17 January to 25 February 2022 as part of the 2022 ALPACA campaign, unless stated otherwise. This location is referred to as the downtown site throughout the paper, which was co-located with Ijaz et al. (2024). Ketcherside et al. (2025) took place in a residential neighborhood (referred to as the residential site) approximately 3 km away from the downtown site.”

Further, mentions of “CTC site” have been changed to “downtown site”, and “house site” to “residential site”, since these names more accurately reflect the location of the site.

9. Lines 105–106: The claim of being “the first study to have two sets of PTR-MS measurements under the same airshed” is a weak novelty claim and is weakened by the 2.6 km separation, the different instruments, and the different time resolution. Consider starting instead with the truly new aspects (non-ethanol fuel, extreme cold, the VOC–S(IV) link).

We agree that this statement is not important compared to our main findings or the aspects that make Fairbanks unique. We have removed that line and edited the introduction, line 112: “Here, we report VOC measurements from an online PTR-MS in downtown Fairbanks during the ALPACA campaign in 2022. We use PMF to identify VOC sources in the uniquely cold and dark conditions of Fairbanks, and we note the uncommon aspect that gasoline in Fairbanks contains no ethanol.”

10. Lines 33, 135–136: PTR identification of compound categories is sensitive to fragmentation. Please describe how possible fragmentation interferences were handled, especially for masses that are known to be affected, both in the compound identification and in the mixing-ratio conversion.

We thank the reviewer for this comment and agree that fragmentation can influence both compound identification and mixing-ratio quantification. We have added this to the methods section, line 171:

“In this study, no general fragmentation correction was applied. As demonstrated by Pagonis et al. (2019), the absence of such corrections may lead to an underestimation of oxygenated and nitrogen-containing compound families. The magnitude of this bias is difficult to assess for the present dataset, as it depends on the fragmentation behavior of individual compounds. However, the PTR-ToF-MS was operated at a low E/N (60 Td), which minimizes fragmentation, and the resulting bias is therefore expected to be limited. It is worth noting that fragmentation corrections are only feasible when the protonated molecular ion is detected and can be uniquely assigned to the compound of interest. This is not the case for some O-containing compounds (e.g., >C3 alcohols, >C3 linear aldehydes) or for N-containing compounds, for which the protonated molecular ion is generally not observed in ambient air, and whose main fragments ions are not specific and overlap with fragment ions from abundant atmospheric hydrocarbons, such as alkanes and alkenes (Brown et al., 2010; Buhr et al., 2002; Duncianu et al., 2017).”

11. Time resolution is inconsistent. The Methods describe 2-minute averaging (lines 124, 433), the Conclusions state one-minute resolution (line 543), and line 118 describes a 15-minute-per-hour duty cycle that is not explained. Please make these consistent and clarify the sampling scheme and how it feeds into the diurnal cycles and the PMF input.

The one-minute time resolution in the conclusion was a typo, which has been fixed. More explanation has been added about the 15 minute cycle in the methods, line 148: “A proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF 6000 X2, Ionicon Analytik GmbH, Austria) was used to monitor VOCs. As described in Ijaz et al. (2025), the PTR-ToF-MS was equipped with an inlet to switch between gas-phase and aerosol-phase species. The gas-phase was measured for 15 minutes every hour, and the aerosol-phase species for 45 minutes every hour. Both were measured at a 20-second time resolution. Only the gas-phase data was used for the PMF analysis in this work.”

12. Lines 139–141: The ethanol mixing ratios are corrected by a factor of nine for fragmentation, based on post-campaign laboratory calibration. As ethanol is the second-largest species and feeds the wiper-fluid and VCP factors, please report the uncertainty of this correction.

We have added more explanation to the methods section, line 192: “Post-campaign ethanol calibration was conducted using a certified 20-component gas reference mixture, for which the certified concentration uncertainty was 10.1%. Instrument drift between campaign and post-campaign calibration was corrected using acetaldehyde, a compound common to both the campaign and post-campaign calibration cylinders with certified relative uncertainties of 5% and 5.4%, respectively. Therefore, the relative uncertainty obtained by uncertainty propagation by transferring the ethanol calibration to the post-campaign period is estimated as 12.5%.”

13. Line 189 and throughout: Please report uncertainties (e.g. standard deviation of the mean) on the campaign averages. In addition, the 0.05 ppb campaign-mean threshold is reasonable for the overview, but it may remove short, source-specific plumes whose campaign mean is below the cutoff but which still represent a separate source; it would be useful to check for such cases.

We have added the standard deviation to values in section 3.1.

We think there may be a misunderstanding about how PMF was ran. We included all VOC species, regardless of concentration, in the PMF runs. Therefore, these short plumes would be included and considered when the PMF software is determining sources.

14. Short-chain alkanes (<C8) are undetected by PTR. The manuscript itself notes that ethane, propane, and butane can represent a large fraction of carbon (7.5–37% in other campaigns). This unmeasured, vehicle-heavy pool is a caveat for every reported apportionment percentage and should be stated clearly wherever fractions are given.

These have been added to the main text:

Line 536: “The mean VOC mixing ratios for the gasoline and diesel factor are likely underreported because the PTR-ToF-MS used in this study was not able to measure hydrocarbon species with less than 8 carbons. Ferrarese et al. (2024) shows that gasoline vehicle emissions of hydrocarbons (in mg/km) between 2-5 carbons are higher than aromatic emissions, and that hydrocarbon emissions increase as temperature decreases. Diesel emissions of short-chain hydrocarbons are overall smaller, but also increase as temperature decreases.”

Line 936: “The mean mixing ratios of the gasoline and diesel factors are likely underreported since we were unable to measure short-chain alkanes.”

15. Line 149–150: See Major Comment 6 on the formaldehyde–humidity tension.

We believe this has been addressed in comment 6.

16. Line 290: Please clarify that values such as benzene (65.8%), toluene (82.6%), etc., are the fraction of the total measured amount of each compound that is assigned to that factor.

-This sentence has been reworded in Section 3, line 529: “The gasoline factor is by far the largest source of aromatic species, with 65.8% of the total measured benzene, 82.6% of toluene, 74.1% of C8 aromatics, and 63.4% of C9 aromatics assigned to the factor.”

17. Lines 345–346: Several statements about temperature dependence (e.g. the warm/cold ratios of wiper fluid, VCP, wood heating) would be supported by showing factor–temperature correlations.

Figure 4 has been replaced with a heatmap, which includes the correlation of temperature with all factors.

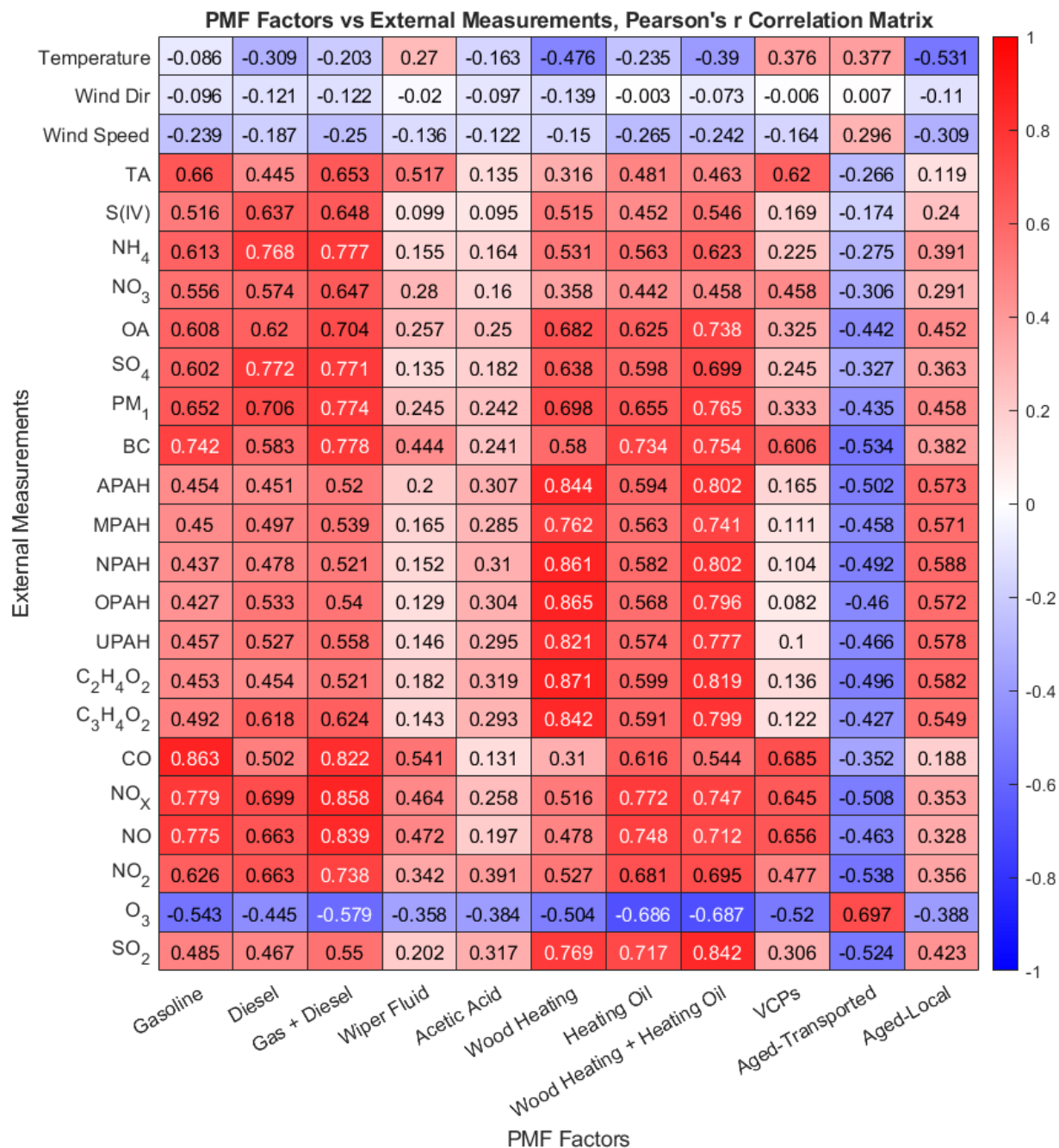


Figure 4. Correlation matrix of PMF factors versus external species. TA (total ammonium) includes both gas-phase and aerosol-phase measurements. Species from S(IV) to C₃H₄O₂ are all measurements in the aerosol phase. Species from CO to SO₂ are all measurements in the aerosol phase.

18. Supplement (diesel section): See Major Comment 3(a) on the toluene/benzene = 0 diagnostic and the mass-based check.

We believe we have addressed this in comment 3.

19. Supplement (wiper fluid): Did the authors observe glycols associated with these emissions? Their presence or absence would help support the wiper-fluid assignment.

Identification of glycols is complicated by the fact that their protonated ions undergo dehydration fragmentation reaction in the drift tube, yielding fragments that interfere with VOC commonly found in ambient air ($\text{C}_2\text{H}_5\text{O}^+$ corresponding to acetaldehyde for ethylene glycol and $\text{C}_3\text{H}_7\text{O}^+$ corresponding to acetone for propylene glycol (10.1021/acs.est.5b00557)). No protonated ethylene glycol ion ($\text{C}_2\text{H}_6\text{O}_2\text{H}^+$) was detected during the campaign and contribution of $\text{C}_2\text{H}_5\text{O}^+$ from the wiper fluid factor to the total signal was small (6.5%). Signal at $\text{C}_3\text{H}_8\text{O}_2\text{H}^+$ corresponding to protonated propylene glycol was measured but contribution of the wiper fluid factor to the total ion signal was small (2.5%), like the one corresponding to $\text{C}_3\text{H}_7\text{O}^+$ (2.9%). This is not surprising, as the safety data sheets (SDSs) for winter personal-vehicle windshield washer fluids marketed in Alaska indicate that they contain little or no ethylene glycol and no propylene glycol. This latter is mostly used in plane deicing, and we did not see any association between the wiper fluid factor and wind.

20. Line 358: See Major Comment 3(b) on the VCP-versus-traffic categorisation of wiper fluid.

We believe we have addressed this in comment 3.

21. Figure 1: A stacked bar chart would show the category concentrations directly and allow error bars, instead of using pie charts that hide the absolute values.

We have replaced Figure 1 and figure S4 with bar charts. We have added this sentence in the methods, line 166: “The average relative uncertainty regarding the concentration derived from the propagation of the relative uncertainties on the transmission and the k is estimated to be within $\pm 30\%$.”

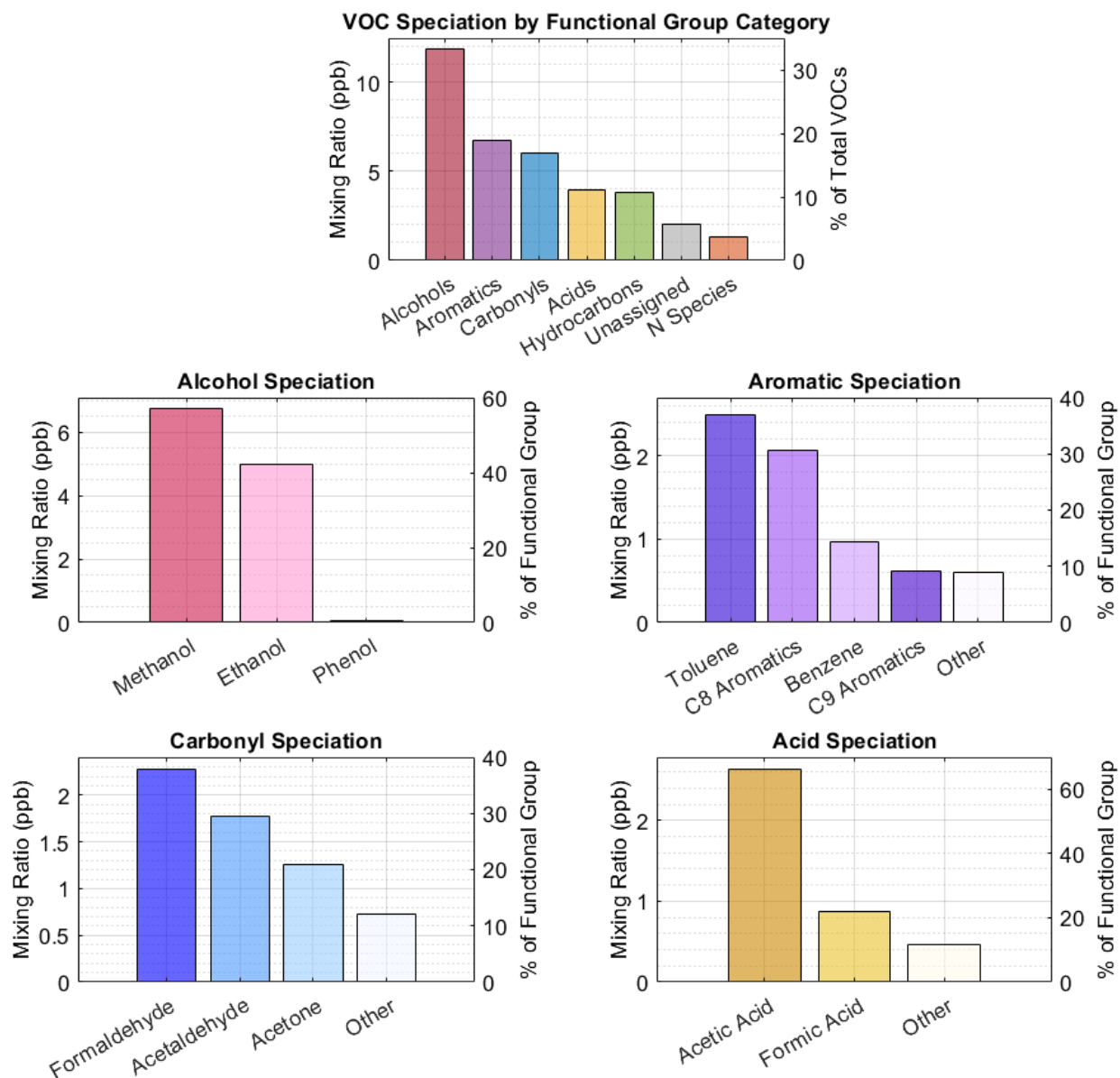


Figure 1. Mean composition of VOCs categorized by their functional groups during ALPACA campaign. The “Unassigned” group is made of up of about 290 species whose individual campaign means are all less than 0.05 ppb.

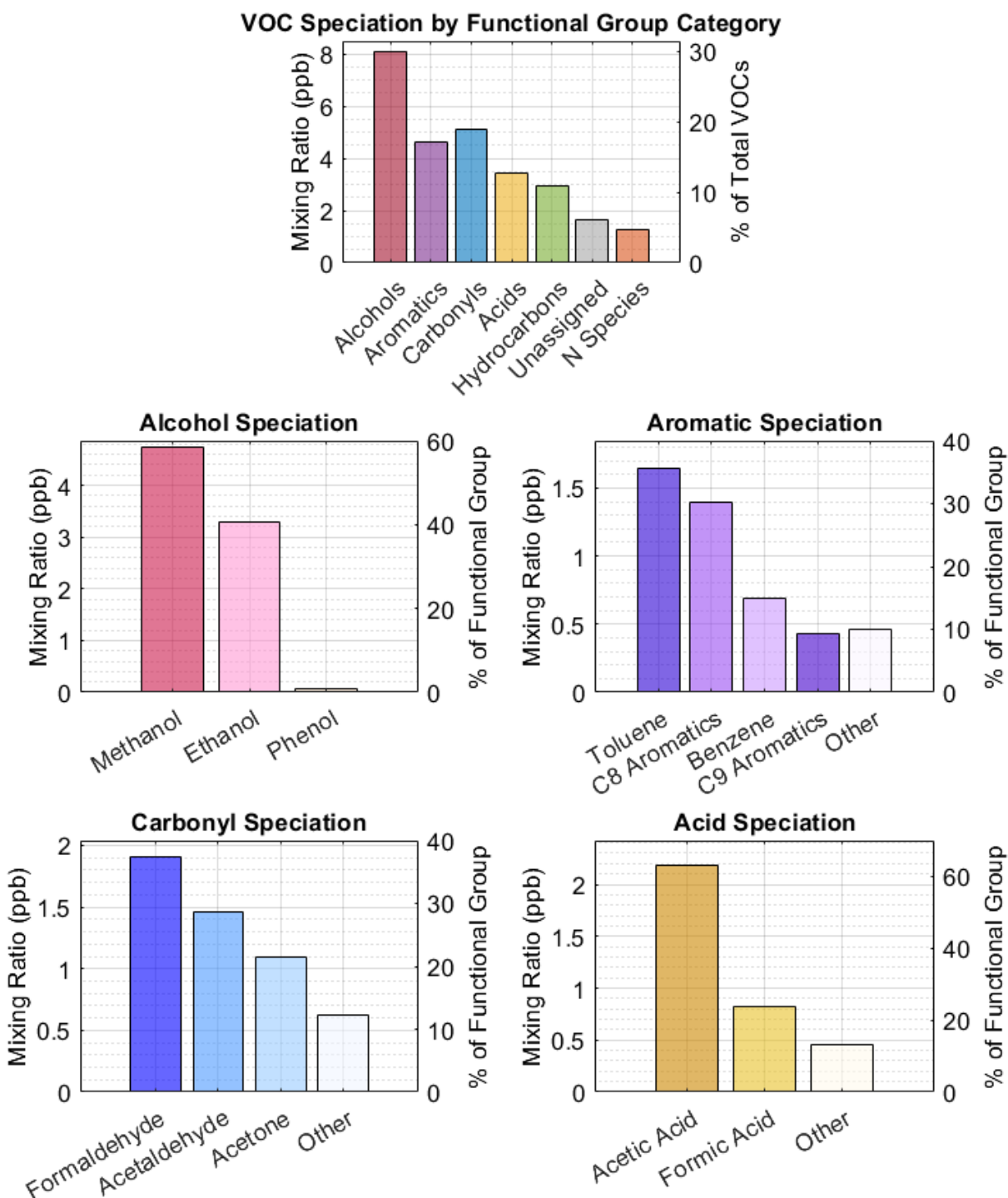


Figure S4. Median composition of VOCs categorized by their functional groups during ALPACA campaign. The “Unassigned” group is made up of up of about 290 species whose individual campaign means are all less than 0.05 ppb.

32. Figure 3: Factor names are not consistent with the text (e.g. a panel labelled “Methanol” for the wiper-fluid factor), and the panels do not have clear axis labels and units. Please also report correlations for physically reasonable factor combinations (gasoline + diesel, wiper fluid + VCP, wood heating + heating oil) against total ammonium and consider whether diurnal-cycle comparisons are more informative than the scatter correlations, which are all weak.

Figure 3, now Figure 4 (per comments from other reviewer) has been replaced with a correlation heatmap. The names have been corrected.

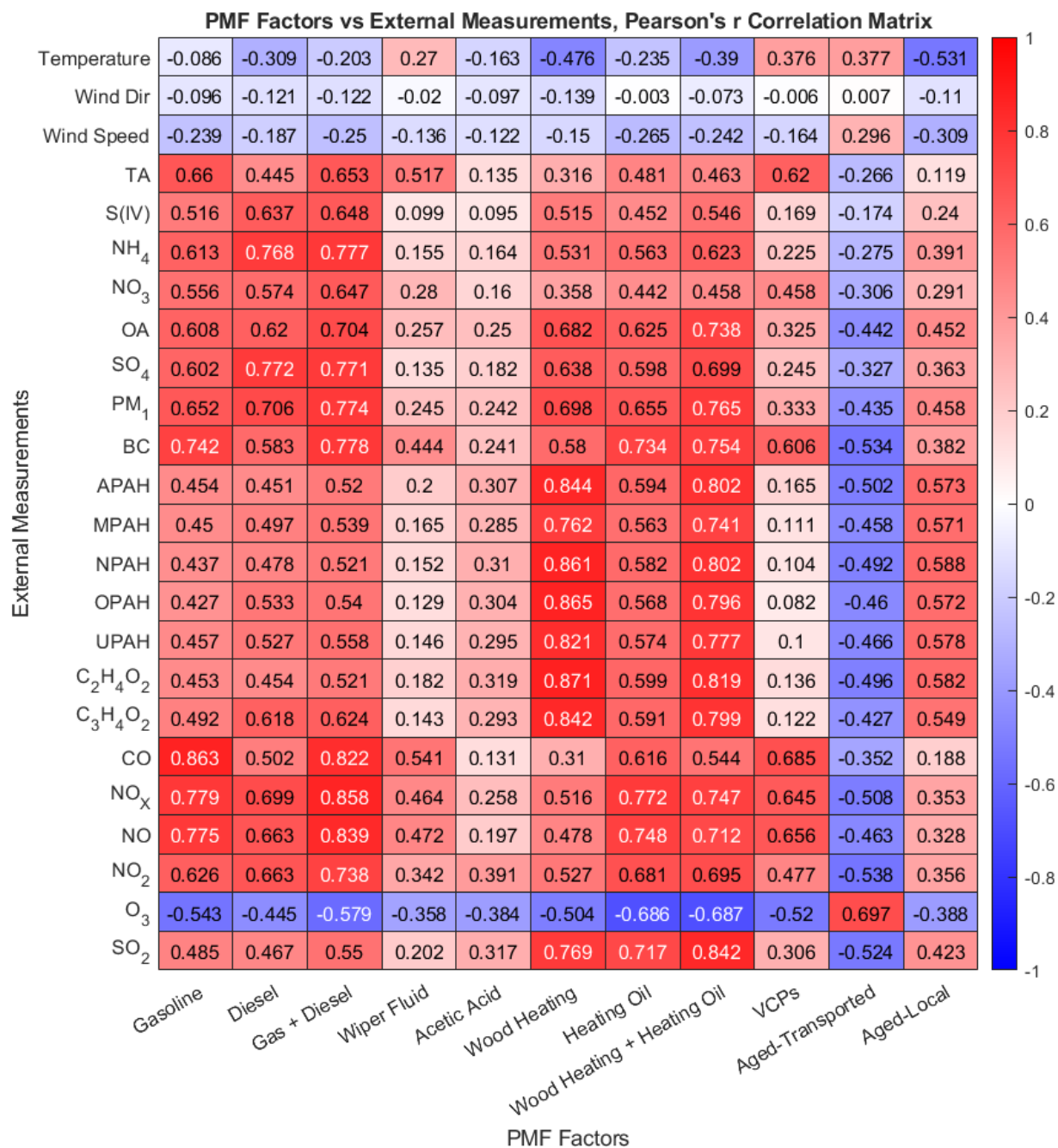


Figure 4. Correlation matrix of PMF factors versus external species. TA (total ammonium) includes both gas-phase and aerosol-phase measurements. Species from S(IV) to C₃H₄O₂ are all measurements in the aerosol phase. Species from CO to SO₂ are all measurements in the aerosol phase.

Gas + diesel and wood heating + heating oil have been added to the heatmap. However, although we agree that windshield wiper fluid should be classified as a VCP, we do not think it makes sense to combine it with the VCP factor since the wiper fluid factor is directly associated with vehicles, while the VCP factor is a broad category covering care products, cleaning products, solvents, etc.

We have reordered the paragraph at line 835 to talk about the diurnal cycles first, and emphasized the similarities between the diurnal cycles of TA and the gasoline factor: “Gasoline vehicles may be a large source of total ammonium in wintertime Fairbanks. The diurnal cycle of TA has many similarities to the gasoline factor, including an early morning increase and 5pm peak on weekdays. We find that TA correlates best with the gasoline factor ($r = 0.659$), followed by the VCP factor ($r = 0.620$) as shown in Fig. 4. TA is also correlated to external factors CO ($R^2 = 0.47$), NO_x, ($R^2 = 0.42$), and somewhat with BC ($R^2 = 0.36$), which are commonly associated with vehicle emissions (Fig. S20).”

33. Lines 24 and 70: Define S(IV) at first use.

Fixed.

34. Line 255: Correct to “Europe.”

Fixed