Response to comments on "Wintertime photochemistry of acyl peroxynitrates and ozone in South Korea during the ASIA-AQ campaign."

We very much appreciate the careful reading and the detailed comments provided by the reviewers. The responses to the comments of the reviewers in our direct reply (shown below). The figure and line numbers indicated in the responses correspond to those in the marked copy. Comments from the reviewers are shown in black italics and responses in blue.

Response to Reviewer 1

This is a well written and well-cited paper describing data of PAN and a range of different PAN-type compounds taken over aircraft flights over S. Korea in the winter of 2024. It contains novel data that will contribute to the literature of these compounds, especially photochemical production during the wintertime. The collection of measurements allows model calculations to be well constrained and to address questions of precursors in ways that were hard to imagine in the recent past. I think that the paper mostly stands on its own without need for significant revisions, although I have some concerns and suggestions.

We thank the reviewer for the positive assessment of this work and for recognizing the value of the observations and analysis presented here.

General Comments

As is common with these papers, there are a lot of abbreviations and acronyms used. I would urge the authors to clearly define all terms. For example, what exactly does "OH exposure" (first mentioned on Line 320) mean? It is described later in the text of Section 4, but without sufficient explanation. Also, how is the term χ being used in this manuscript? And is "zero-out sensitivity analysis (Line 434) explained somewhere?

We agree with the reviewer that several abbreviations and technical terms required clearer definition. In response, we revised the manuscript throughout to define abbreviations and acronyms more clearly at first use and to provide more explicit explanations of key terms, including OH exposure, χ, and zero-out sensitivity analysis, in the relevant sections.

We have added the following texts to lines 325–326 to define OH exposure:
"defined as the product of OH concentration and time over the photochemical age of an air amass"

We have also modified the texts in lines 354 for clarity:
"which provides an observation-based proxy for the extent of photochemical processing by OH radical"

In addition, we revised the texts in lines 575–577 and 595 to clarify the use of χ_{PANs} based on observations, kinetic calculations, and model simulations:

"Using a similar kinetic approach to Romer et al. (2020), we investigate the fractional contribution of PANs to total NO_x loss (χ_{PANs}). Here, observation-based χ_{PANs} ($\chi_{PANs-obs}$) is defined as the ratio of observed PANs to the sum of observed PANs, HNO_3, and particulate inorganic nitrate ($pNO_3^-{}_{\mathrm{inorganic}}$)."

"(χ_{PANs} based on kinetic calculations; $\chi_{\mathrm{PANs-kc}}$)"

We have removed "zero-out sensitivity analysis" from line 444 and Figure 6 caption to minimize confusion.

Perhaps the strongest comment I have is about the density of information crammed into the figures in this manuscript. There are sub-figures within sub-figures within sub-figures that sometimes serve more to obscure than enlighten the significant story the authors are telling. In some cases (e.g. Figures 4 & 6) legends actually cover up some of the data because the figures are so crammed. It's also not always apparent how the sub-figures are grouped together. I understand the desire to convey as much information as possible, but I wonder if the authors would consider simplifying the figures either by separating them into more individual figures or summarizing their points in the text (for example by creating a table with correlation parameters in lieu of all the scatterplots) and/or putting some of the figures into the supplemental materials. I would encourage the authors to consider which graphics are essential for conveying their story and which are not. This would have the additional benefit of simplifying the captions to be more readable.

We agree with the reviewer that the density of information in several figures reduced their clarity. In response, we streamlined the figures to better emphasize the main findings, improved designs, adjusted legend positions in figures such as Figs. 4 and 6 so that the data are more clearly visible, and moved Fig. 8 b–d to the Supporting Information (SI). We also revised the figure captions throughout the manuscript accordingly.

<u>Specific comments</u>

Line 304 – I would delete the first sentence of this paragraph as it seems redundant.

We removed the first sentence of the paragraph and revised the text in line 307 to read:
"Although significant pollution over the MS was observed during ASIA-AQ, this region is understudied."

Line 307 – What is the reference for the short atmospheric lifetime of APAN?

We added Orlando and Tyndall (2002) as a reference in line 280, where we first discuss the short atmospheric lifetime of APAN due to OH oxidation.

Orlando, J. J., and Tyndall, G. S.: Mechanisms for the Reactions of OH with Two Unsaturated Aldehydes: Crotonaldehyde and Acrolein, J. Phys. Chem. A., 106, 12252–12259, https://doi.org/10.1021/jp021530f, 2002.

Line 326 – Also, give a reference for the attribution of biomass burning with HCN and CH3CN.

We have added Holzinger et al. (1999) as a reference in lines 332–333.

Holzinger, R., Warneke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., Schade, G., and Crutzen, P. J.: Biomass Burning as a Source of Formaldehyde, Acetaldehyde, Methanol, Acetone, Acetonitrile, and Hydrogen Cyanide, Geophys. Res. Lett., 26, 1161–1164, https://doi.org/10.1029/1999GL900156, 1999.

Line 370 – It would be good to explain why Figure 4a is on a log scale

We thank the reviewer for pointing this out. Figure 4a is not shown on a logarithmic scale. Instead, the y axis is split to more clearly show the contributions of the minor PAN homologues, given the dominant contribution of PAN (~80%). We revised the figure design and caption to avoid confusion.

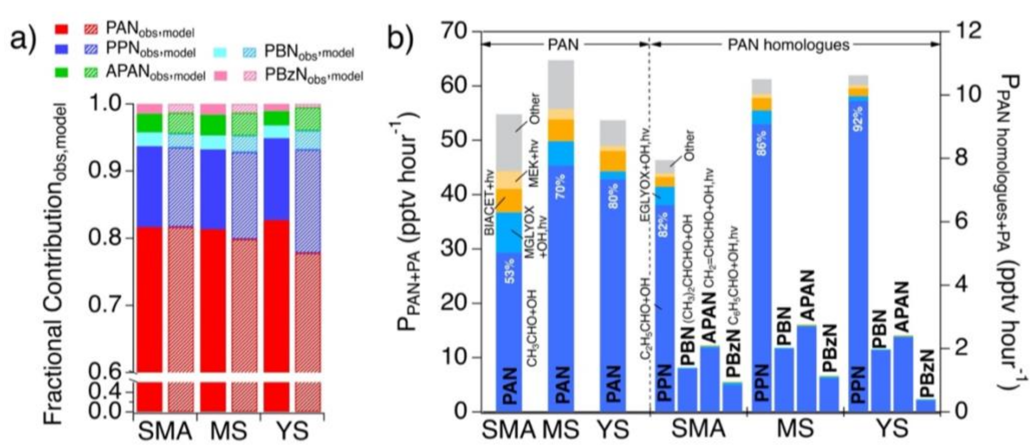

Figure 4. (a) Averaged fractional contributions of observed PANs compounds (bright colored bars) and those of modeled instantaneous production rates of PANs, *P*(PANs), (colored bars with patterns) over the SMA, MS, and YS. The split y-axis is used to improve visibility of the homologue contributions. (b) Averaged *P*(PANs) over the SMA, MS, and YS along with precursor contributions. The left three bars correspond to *P*(PAN) and other bars corresponds to *P*(PAN homologues).

Line 399 – I would replace the word "increased" with "higher"

We have made the suggested change.

Line 540 - I might add at the end of the paragraph something along the lines of "…especially given the importance of anthropogenic VOC like aromatics, as shown above."

Following the reviewer's suggestions, we have modified texts to line 555–556:
"suggest that VOC reductions, especially anthropogenic aldehydes, alkenes and aromatics, would be more effective than NO_x controls"

Line 542 – Why is the heterogeneity so "marked" given the geographic range of the flights? Is heterogeneity the best term to describe what the authors are saying?

We revised the text in lines 559 and 563 from "heterogeneity" to "variability."

Line 550 – Can the authors address the deviation of the green and purple traces at low RNO2/RALD?

The deviation between OPE derived from the model simulations (purple) and kinetic calculations (green) at low RNO_2/RALD is mainly attributable to the higher $P(O_3)$ estimated by kinetic calculation. The kinetic calculation is based on observed VOC reactivity and prescribed ozone yields, whereas modeled $P(O_3)$ is calculated from the reactions of simulated peroxy radicals, including HO_2 and RO_2, with NO. Despite this simplified formulation, the kinetic calculations show reasonable agreement with model simulations.

At the end of the paper I was left wanting to have more closure on the comparison of wintertime chemistry to summertime chemistry and how that can be applied to management strategies.

To maintain the scope and focus of the manuscript, and given the scarcity of summertime PANs observations, we limited our revision to a brief statement highlighting the need for future airborne observations and analysis of PANs during summer in South Korea.

We added the following text to lines 657–659:

"Together with prior springtime observations from KORUS-AQ, future studies of summertime PANs in South Korea would improve understanding of seasonal differences in their chemistry and inform broader control strategies for photochemical pollution."

Response to Reviewer 2

The paper describes measurements of PAN and its homologues over South Korea in wintertime during the ASIA-AQ campaign. It shows how the measurements of PAN homologues can be used as tracers for industrial emissions, which do not have long atmospheric lifetimes and it provides further understanding of wintertime oxidation of complex VOC mixtures. I would recommend publishing the paper after minor corrections as suggested below.

We thank the reviewer for the careful reading of the manuscript and the helpful comments.

General comments

A lot of the figures contain a lot of information (and a lot of panels and sub-panels) and for some of them I wonder if it would be easier to follow the story if the figures were split into smaller ones when the different panels are not directly linked. However, I'm also aware that it would bring the total amount of figures to a quite high amount.

We agree with the reviewer that the density of information in several figures reduced their clarity. In response to both reviewers' comments, we streamlined the figures to better emphasize the main findings, improved the organization of subpanels, adjusted legend positions in figures such as Figs. 4 and 6 so that the data are more clearly visible, and moved Fig. 8b–d to the Supporting Information (SI). We also revised the figure captions throughout the manuscript to improve accordingly.

Minor comments

Line 142 – How much isotopically labelled PAN do you calibrate with? Could there be any problems with overlaps between PAN at m/z 59 and your calibration at m/z 61 when adding isotopic PAN continuously?

We added isotopically labeled PAN continuously at approximately 200 pptv during flights. The high mass resolution of the ToF analyzer (~5000 m/Δm) resolves the isotopic acetate anion signal at m/z 61.016 ($^{13}C_2$-acetate) from the non-isotopic signal at m/z 59.010 ($^{12}C_2$-acetate), with no measurable overlap between the two signals. This is consistent with our previous experience using flight instruments with quadrupole filters at unit mass resolution, where the 2 Da separation between m/z 59 and m/z 61 was also sufficient to prevent interference.

Line 312 – 314: You observed higher APAN towards the boundaries of your investigation area and explain the increase to the southeast by local influence from the Gumi Industrial Complex through northeasterly winds. However, when looking at figure 2, the Gumi Complex looks like it is to the southeast of your southeast measurements. Does that mean the emissions from the Gumi Complex is transported north and then west or does Figure 2 not show all the data? Could it be other industrial areas further to the east that causes the increase in the southeast?

We thank the reviewer for this helpful comment. We agree that the original wording could overattribute the southeastern enhancement to the Gumi Industrial Complex alone. Our interpretation is that the elevated APAN and APAN/PAN ratios were primarily associated with transport under west and northwesterly winds, while the southeastern enhancement may also reflect contributions from industrial sources to the south and east, including but not limited to the Gumi Industrial Complex. We therefore revised the final sentence of this paragraph to clarify this point.

We modified lines 316–319 as follows:
"In addition to the major influence of industrial sources from the northwest, the southeastern enhancements may also reflect secondary contribution from sources to the south and east, including the Gumi Industrial Complex, associated with variable winds."

Line 486 – 487: You write "The general increase in P(O3) is due to increasing OH reactivity with NOx, as the calculation does not account for suppression of OH at high NOx levels." Does that mean the calculated increase is significantly overestimated?

As stated in Sect. 4.3, $P(O_3)$ from the kinetic calculations uses a constant OH concentration and is therefore likely overestimated at high NO_x levels, where OH is suppressed primarily through nitric acid production. We report absolute $P(O_3)$ values from the kinetic calculations because they provide a useful observation-based measure of ozone production, comparable in purpose to OH reactivity but incorporating additional chemical constraints, including ozone yields, alkyl nitrate branching ratios, and OH reactivity. However, because the calculation does not fully represent radical suppression and feedbacks under elevated NO_x conditions, our main discussion focuses on the relative contributions of different precursor classes rather than the interpretation of absolute ozone production rates. In addition, this approach also allows analysis of a broader observational dataset, whereas the model simulations require fully synchronized inputs. We use the comparisons in Figs. 7b–d to evaluate the absolute $P(O_3)$ values from the kinetic calculations against the model simulations, with modeled OH used in the kinetic calculations for this comparison.

Line 488 – 494: If ketones and alcohols are important contributors, how come alkanes, alkenes and aromatics are not, when they all have similar contributions according to the pie charts when over South Korea (SMA and MS) and alkanes and alkenes are at least double that of ketones and alcohols over the yellow sea?

We revised the text in lines 500–501 to improve clarity by more clearly comparing the contributions from oxygenated compounds, including aldehydes, ketones, and alcohols, with those from alkanes, alkenes, and aromatics, rather than discussing individual VOC classes separately. This also improves consistency with the later discussion of modeled oxygenates in line 519.

We revised the text as the following:
"$P(O_3)$ from kinetic calculations is more effective for evaluating relative precursor contributions independent of OH. The pie charts in Fig. 7a show substantial contributions of oxygenates, especially C_{2+} aldehydes to $P(O_3)$, second in importance to CO. Other important oxygenated contributors include formaldehyde as well as ketones and alcohols such as MEK, methanol, ethanol, and isopropanol, which together account for ~95% of this category."

Line 508 – Does "episodic enhancements of alkenes" refer to the one "spike" observed in Figure 7d at around 55 data points? Or are there more episodes in data not shown here since it is attributed to petrochemical plumes? I also think that some clarification on what is used for the x-axis in this figure would be good.

The reviewer is correct that the episodic enhancement of alkenes refers to the spike observed in Fig. 7d. We revised the text in line 520–522 to read:

"In addition, peak ozone production over the YS occurred during episodic enhancements of alkenes that dominated P(O3), which was attributed to sampling of relatively fresh petrochemical plumes, as also described in Sect. 3.1."

We also revised the x-axis label in Fig. 7b–d and the corresponding caption text from "Data points" to "Sequential model step" to improve clarity.

Line 523 – The percentage of the radical loss due to reactions with NOx sounds like it only includes the production of HNO3 and PANs, however, it also includes the small contributions leading to the formation of alkyl nitrates and aromatic nitrates. Could you make that clear in the text? Although later these pathways are mentioned as minor radical termination pathways (line 525), so I would suggest choosing one place to include them.

We agree with the reviewer that the original wording could imply that radical loss by reaction with NO_x included only HNO_3 and PANs. In response, we revised the text to clarify that this category is dominated by HNO_3 and PANs but also includes smaller contributions from alkyl nitrates and nitroaromatic compounds. For the kinetic calculations in Sect. 4.4, we continue to focus on PANs and HNO_3 because they are dominant NO_x oxidation products, their production rates can be constrained by observations, and they are directly relevant to the diagnostic framework developed here.

We have modified the text in line 535–542 as the following:
"The modeled instantaneous radical loss indicates that radical loss by reaction with NOx dominates over the SMA (88%) and MS (80%), with nitric acid (HNO_3) and PANs as the major products and smaller contributions from alkyl nitrates and nitroaromatic compounds (Fig. 8a). It should be noted that the chemistry of nitroaromatics in the MCM mechanism may be uncertain and needs further investigation (Bates et al., 2021; MacFarlane et al., 2025). The dominant contributions of HNO_3 and PANs to radical loss are consistent with wintertime observations in Beijing based on direct radical measurements (Tan et al., 2018; Lu et al., 2019). Other minor radical termination pathways include formation of peroxides, HONO, and pernitric acid (HO_2NO_2)."

Line 530 – Is the median of 0.9 a median across all the measurements over land or are each data point a median of a group of measurements? If the median of all the measurements is 0.9, then I would suggest writing "Figure 8a shows a median Ln/Q value of 0.9 over South Korea, …".

We have made the suggested change.

Figure 8, panel b-d – What do the numbers in the legend after base describe in these three panels?

We thank the reviewer for pointing out that the legend description was incomplete. The numbers shown after "base" in Fig. 8b–d represent the PANs production rate, ozone production rate, and ozone production efficiency, respectively, for the base-case simulations. To address this comment, and consistent with both reviewers' suggestions regarding figure density, we moved Fig. 8b–d to the SI and modified the legends.

Figure S6 – It looks like there are multiple very different population densities plotted for some of the longitudes, can you explain that? Is that from flying over the same longitudes, but different latitudes and then averaging the aromatics across the latitudes? And across the five flights used for this analysis?

The shaded areas represent the median $PD_{5\text{-km}}$ values for the selected regions in 0.02º longitude bins. As pointed out by the reviewer, overlap in the shaded regions reflects sampling at the same longitude bins but at different latitudes. The $PD_{5\text{-km}}$ values include data from all five research flights conducted over South Korea and the Yellow Sea.

<u>Technical comments</u>

Abstract – O3 and NO2 are written without the numbers in subscript

We have made the suggested change.

Figure S1 – The orange square is very difficult to see under the red flight tracks. Could you make it a different color?

As suggested, we changed the marker color from orange to yellow and added a black outline to improve visibility.

Section 2.3.1 – There are some inconsistencies whether things are written in italics or not. For example, in line 185 you write RXi, however, in equation (1) it says RXi. OH is written in italics in equation (3). In line 203 OVOC is written both in italics and normal. I would suggest reading through the section to check for these inconsistencies.

We thank the reviewer for pointing out these inconsistencies in font style. We revised the text throughout Sect. 2.3.1 for consistency in notation and formatting.

Line 171 – The Seoul Metropolitan Area has been defined as SMA in the introduction, but here SMA is given as Seoul and Suburban, which is probably the same as the Metropolitan area, but I would suggest choosing one definition.

We modified the text in line 174 from "Seoul and Suburban" to "Seoul Metropolitan Area" for consistency.

Line 193 – In equation (3) RVOCi represent the OH reactivity for VOCs i, but in line 193 it is defined as RVOCs.

We modified the text in line 196 from "RVOCs" to "RVOCi."

Line 199 – I would add commas or brackets around P(HNO3) and P(PANs).

We have made the suggested change.

Line 200 – Add an s after radical.

We have made the suggested change.

Line 201 and equation 5 – Do you want to call it αHA or αHydrogen Abstraction?

We use $\alpha_{\text{Hydrogen Abstraction}}$ throughout the main text for consistency.

Line 277 – A punctum is missing after environments.

We have made the suggested change.

Line 282 – add "the" to write "and the sum of…"

We have made the suggested change.

Line 314 – Do you mean the PANs distribution in Figure 1a?

We have modified the text from "Figure 1b" to "Figure 1a".

Line 339-340 – "During ASIA-AQ" is repeated in the sentence.

We removed the repeated phrase "during ASIA-AQ" in line 346.

Line 381 – Add an s to contribution

We have made the suggested change.

Line 391 – I think you mean assess instead of access

We have modified the texts from "access" to "assess".

Line 485 – insert "an" before OH concentration

We have made the suggested change.

Line 499 – add "the" in front of "VOC classes"

We have made the suggested change.

Line 558 – Is the Romer et al. reference the same as the one mentioned in line 545 or is it actually a different study?

We thank the reviewer for pointing out the incorrect reference to Romer et al. We have modified the texts from "2018" to "2020."

Line 620 – Maybe add "other" in front of precursors

We have made the suggested change.

Equation S1-S6 – Molecules are usually not written in italics.

We have made the suggested change.