

Anonymous Referee #1

We appreciate the time and thoughtful feedback provided by Anonymous Referee #1. The reviewer's comments are shown below in black, with our detailed responses in blue.

This study investigates the potentially important role of carbonyl compounds in wintertime ozone formation using observational data from the Uinta Basin and box model simulations. The comparison among several widely used chemical mechanisms is also a valuable aspect of this work, which could provide useful information for future modelling research. Overall, the topic is scientifically interesting and of significance.

- We thank the reviewer for this summary.

Although chemical budgets have been added to the revised manuscript, the presentation and use of these results could be improved. A large number of tables are provided in the Supplement, listing the top source and sink pathways and their contributions for O₃, HOx and carbonyls. However, the key information is difficult to extract, as readers need to repeatedly consult multiple tables to identify the main controlling processes. A more synthesized presentation in the main text, for example using multi-panel figures to highlight the dominant budget terms, together with a focused discussion of how these budget characteristics differ among chemical mechanisms and relate to the sensitivity results, would greatly enhance the clarity and diagnostic value of the budget analysis.

The manuscript is generally clearly written. However, the Methods section and the final paragraph of the Introduction rely heavily on highly repetitive sentence structures, with many consecutive sentences beginning with similar formulations such as “we did...”. This repetitive writing style substantially reduces readability and makes these sections unnecessarily monotonous. A thorough revision to streamline the text, reduce redundancy, and introduce greater syntactic variety is strongly recommended.

- The Methods section and the final paragraph of the Introduction were thoroughly revised to improve readability and reduce repetitive sentence structures. Consecutive sentences beginning with similar formulations (e.g., “we did...”) were restructured, redundancy was minimized, and greater syntactic variety was introduced using passive and alternative sentence constructions where appropriate.
- We also created two new figures (Figures 3 and 4) to illustrate some aspects of chemical production and loss budgets, and added text surrounding them.

Based on these comments, I believe this paper has scientific merit and the potential to make a useful contribution to ACP. However, substantial revisions are required, particularly to

deepen the chemical analysis, strengthen the mechanistic interpretation and improving readability, before the manuscript can be considered for publication.

More specific comments are as follows (line numbers are denoted as "Lx"):

1) Title: The title is rather vague and does not clearly convey the specific focus or scope of the study. In particular, it is unclear what is meant by "chemical precursors". Clarifying the title to better reflect the main objectives and analyses of the manuscript would improve its clarity.

- The manuscript title has been revised to "Hydrocarbon and Carbonyl Contributions to Wintertime Ozone Formation," which more clearly specifies the chemical species examined and better reflects the scope and objectives of the study.

2) Introduction: When introducing chemical reactions related to O₃ and carbonyls, please indicate in the text that CH₄ and HCHO are presented as example species in Reactions 1-8.

- The text has been clarified to indicate that methane (CH₄) and formaldehyde (HCHO) are presented as representative example species. This clarification has been added immediately after the reaction list in the Introduction section.

3) L121: "Lyman et al. (Lyman et al., 2020)" should be revised to "Lyman et al. (2020)". Please ensure the correct format of references.

- The reference format has been corrected.

4) L134: "followed by" should be "following"

- The wording has been corrected.

5) L137-139: This sentence is vague and should be revised to more precisely describe which aspects of the chemistry are explicitly included.

- The sentence in Section 2.3 has been revised to more clearly describe the chemical processes explicitly represented in MCMv331.

6) L141: Please provide more details on the uptake coefficients, including their parameterizations and approximate values.

- The description of heterogeneous chemistry has been expanded to include uptake coefficients, their parameterization, and approximate values, following the approach of Ninneman et al. (2023). This information has been added at the end of Section 2.3.

7) L143: Since the comparison among results obtained using different chemical mechanisms is one of the highlights in this paper, it would be helpful to give more details on the main differences among these mechanisms and to explicitly link these differences to the relevant discussions. This would provide clearer context for understanding why the mechanisms lead to different sensitivities and identified contributions.

- A paragraph has been added to Section 2.4 describing the fundamental concept of the lumped chemical mechanisms (SAPRC07, RACM2, and CB6). The revised text highlights the key differences between molecule-based and structure-based lumping approaches and explains how these differences influence the representation of NMOC reactivity and oxidation pathways. Later in the Results and Discussion sections, the impact of differences in chemical mechanisms on sensitivity outputs is described.

In addition, a large number of species abbreviations from different chemical mechanisms are used in the main text and the Supplement, which makes cross-mechanism comparison difficult to follow. Providing a summary table in the Supplement that maps analogous species across different mechanisms would greatly improve clarity and facilitate interpretation of the budgets and inter-mechanism comparisons.

- Due to the large number of species explicitly represented in detailed mechanisms such as MCMv331 and the fundamentally different lumping approaches used in mechanisms like SAPRC07, RACM2, and CB6, creating a comprehensive summary table mapping all analogous species across mechanisms would be challenging and would substantially increase the length and complexity of the supplement. Instead, key species are identified by their chemical names in the text, and references to the relevant journal articles and mechanism websites are provided for readers interested in further details. This approach was chosen to maintain clarity while keeping the manuscript and supplement focused and concise.

8) L155-156: The expression “aggregated their mixing ratios as appropriate” is ambiguous and should be clarified.

- The sentence has been revised to clarify that when multiple MCM species correspond to a single lumped mechanism species, their mixing ratios were summed to obtain the lumped species concentration. This information has been added at the end of Section 2.4.

9) Fig 2: Three blue colors are used in this figure, which are difficult to distinguish, particularly when the figure is viewed at reduced size or under low-quality printing conditions. Using more contrasting colors would improve clarity.

- Figure 2 has been revised using a more contrasting and visually distinct color palette.

10) L231-251: This paragraph analyzes the contributions of individual carbonyl species, with most of the discussion focusing on benzaldehyde. While the additional discussion on why benzaldehyde shows positive or negative contributions under different mechanisms is interesting, the current emphasis appears disproportionate. Formaldehyde and acetaldehyde are identified as the dominant contributors to ozone production, yet their roles and the reasons for their varying contributions across different chemical mechanisms are only briefly discussed. It would be useful to discuss them in a dedicated paragraph, with a clearer explanation of why their contributions differ substantially among chemical mechanisms. The discussion of benzaldehyde, which plays a more minor role but shows interesting sign changes across mechanisms, could then be presented separately. Such a reorganization would help clarify the relative importance of different species and improve the overall focus of the discussion.

- The discussion has been reorganized to better reflect the relative importance of individual carbonyl species. A dedicated discussion of formaldehyde and acetaldehyde, identified as the dominant contributors to ozone production, has been added in Section 3.2 with a clearer explanation of the chemical processes controlling their contributions and the reasons for differences among chemical mechanisms. The discussion of benzaldehyde has been revised and presented separately to emphasize its secondary role and its mechanism-dependent behavior. To support this revised discussion, Table 1 and Table 2 have been added, which summarize the contributions of formaldehyde and acetaldehyde to HO₂ and HO_x production across the mechanisms considered.

11) L258: Is the limited contribution of heterogeneous uptake related to low uptake coefficients?

- The relative contributions of each carbonyl compound remained largely unchanged after introducing heterogeneous chemistry into the model (Fig. S4). As stated in the original manuscript, this limited impact is primarily attributed to low specific humidity during the simulation period, which reduces aerosol liquid water content and limits HO_x uptake. The uptake coefficients used in the model were fixed and consistent with values reported in previous studies.

12) Sect 3.3: This section requires further improvement in both analysis and organization. Two key questions need to be clearly addressed: (1) how hydrocarbons influence the

formation of different carbonyl species (based on MCM), and (2) why the simulated responses differ among the four chemical mechanisms. While four figures are used to illustrate the sensitivities of carbonyls to different hydrocarbon classes, the discussion mainly describes the general features of the sensitivity tests rather than providing mechanistic explanations linked to specific reaction pathways. Even a brief indication of the key reactions involved would greatly help readers understand why certain hydrocarbon classes dominate the responses. Without such explanation, several results remain difficult to interpret, particularly for readers who are not specialists in detailed carbonyl chemistry.

In the manuscript, the responses of formaldehyde to hydrocarbons are summarized and explained, but similar explanations are largely missing for other carbonyl species. Specifically, it remains unclear why alkanes dominate the responses of acetaldehyde, methacrolein, benzaldehyde and MEK. An additional paragraph is devoted to explaining the response of benzaldehyde to alkanes. Finally, the differences among the four mechanisms are only briefly mentioned, but the manuscript does not clearly explain why benzaldehyde is more strongly influenced by aromatics in RACM2, or why the results from CB6 are generally distinct from the other mechanisms.

Overall, this section relies heavily on descriptive interpretation of sensitivity results, without sufficiently linking the responses to specific chemical reactions or mechanism structures. As a result, several key questions remain unresolved after reading this section. A clearer summary of the main findings, together with a more balanced and reaction-based discussion across species and mechanisms, would substantially strengthen both the clarity and the scientific depth of this section.

- To address the 1st point regarding how hydrocarbons influence carbonyl formation, reaction-based explanations for each carbonyl species have been added using MCM budget analysis. The balanced sensitivity of formaldehyde to all VOC groups, the alkane-dominated responses of acetaldehyde and MEK, and the indirect HO_x-mediated alkane sensitivity of benzaldehyde and methacrolein are now explained with specific reaction pathways.
- For the second paragraph regarding mechanism differences, clear explanations are now provided for the two main discrepancies. The stronger aromatic influence on benzaldehyde in RACM2 is attributed to an epoxy muconate pathway that is absent in MCM. The distinct CB6 results are explained by its carbon-bond lumping approach, where alkane oxidation does not produce formaldehyde unlike in more explicit mechanisms.

13) Sect 3.4: The authors conclude that “Alkane emissions from oil and gas extraction play a critical role in wintertime O₃ formation” based on the results of O₃ sensitivity to hydrocarbon

emissions. However, the logic between sensitivity analyses and the final source attribution could be further strengthened. While the sensitivity results indicate a strong role of alkanes in modulating O₃ production, this alone does not fully support the conclusion. Firstly, other emission sources in the Uinta Basin may still play a role and are not fully constrained. Secondly, the assumption of zero primary carbonyl emissions in the simulations may not fully reflect real-world conditions, particularly given that oil and gas activities can also emit carbonyls or their immediate precursors.

- In response to the first concern: The intent of this discussion was to place the sensitivity analysis results in the context of previous observational and modeling studies, rather than to perform source attribution based on the box model results alone. To avoid overstating this connection, the text has been revised to clarify that the sensitivity analysis demonstrates the strong chemical influence of alkanes on O₃ production, while references to oil and gas emissions are provided as supporting context from prior studies in the Uintah Basin and similar regions. The revised text also avoids implying that the sensitivity results alone constrain emission sources or exclude contributions from other sources or from primary carbonyl emissions. These changes have been made primarily in Section 3.4.

In addition, the magnitude of the simulated O₃ production response to a 50% increase in alkane emissions (on the order of ~0.2–0.4 ppb h⁻¹) appears small compared to the observed ozone levels (over 100 ppb), suggesting that sensitivity alone may not explain the full amplitude of the pollution events. Clarifying the relative roles of emission strength, chemical amplification, and meteorological accumulation would help close the logical gap between sensitivity results and the final attribution.

- The text in Section 3.4 has been revised to clarify why the simulated O₃ production response to a 50% increase in alkane mixing ratios is modest relative to observed ozone levels. The revised discussion now explicitly addresses the roles of chemical aging, declining NO_x availability, and physical accumulation under persistent inversion conditions, and explains how these factors limit the sensitivity response by the fourth day of the simulation.

14) Sect 3.5: While the addition of chemical budget analyses is appreciated, the way these results are incorporated into the manuscript weakens the overall structure. The main body of the study focuses on the sensitivities of O₃ to carbonyls, carbonyls to hydrocarbons, and O₃ to hydrocarbons. However, the budget analyses are introduced in a separate section at the end, rather than being integrated into the corresponding sensitivity discussions. As a result, the budget results appear disconnected from the main analyses and do not effectively explain the observed sensitivities. Integrating the key budget diagnostics into the relevant sections, and using them directly to interpret the

sensitivity results, would lead to a more coherent structure and a stronger, process-based narrative.

- Section 3.5 has been removed from the main manuscript. Key budget analysis outputs have been integrated into the relevant sensitivity discussion sections and are now used to interpret the O₃ and carbonyl sensitivity results, improving the connection between the analyses and the underlying chemical processes.

15) Conclusion: The Conclusion section is very brief and largely reiterates the content of the manuscript, without sufficiently distilling the key mechanistic insights. Given the complexity of the sensitivity analyses and chemical mechanism comparisons presented in this study, a more substantive conclusion that clearly summarizes the main findings, highlights the dominant controlling processes, and acknowledges remaining uncertainties would strengthen the overall impact of the paper.

- The Conclusion section has been revised to include the dominant chemical processes controlling winter O₃ formation, mechanistic differences among chemical mechanisms, policy implications identifying priority emission targets for O₃ mitigation, and uncertainty related to this study.

Anonymous Referee #2

We appreciate the time and thoughtful feedback provided by Anonymous Referee #2. The reviewer's comments are shown below in black, with our detailed responses in blue.

This study investigates wintertime ozone precursors, focusing on carbonyl compounds, using site measurements and a box model with four popular chemical models in the Uinta Basin, Utah. The authors provide important insight into the formation of ozone in an area that has struggled to meet the EPA's standard for the pollutant. This study addresses a significant knowledge gap and has scientific merit. Some revisions are recommended to help clarity and presentation.

- We thank the reviewer for this summary.

The manuscript is clearly written, but it may be helpful to mention for each referenced study, if they were looking at summertime or wintertime, as was done in the discussion on Figure 1. That can quickly help the reader with context for other studies.

Line 43: Do oil and gas operations have the same emissions output in winter compared to summer?

- No, oil and gas operations do not have the same emissions output in winter compared to summer. Emissions are generally higher during winter because cold temperatures directly increase pollutant release at the source. Nitrogen oxide emissions rise in winter as vehicles and heavy equipment emit more during cold starts, and emission control systems are less effective at low temperatures. In addition, some stationary equipment, such as heaters fuelled with natural gas, is used mainly in winter and adds extra emissions that are not present in summer.
- Methane and volatile organic compound emissions also tend to be higher in winter. Cold weather operations like thawing frozen lines, venting pipelines, and conducting well blowdowns release methane and VOCs into the atmosphere, whereas these activities are minimal or absent during warmer months. Although winter weather can trap pollutants near the surface, the key difference is that the actual emissions themselves are higher in winter, not just their concentrations in the air.
- A sentence has been added to the introduction addressing the seasonal variability of emissions from oil and gas operations and the factors contributing to higher wintertime releases.

Line 117: Why are noon and midnight selected as the start times for measurements? Is it the best representation of the mixing ratios/diurnal patterns for these compounds?

- Noon and midnight were chosen as the measurement times because they capture key points in the daily cycle of these compounds. Midday generally represents the highest mixing ratios due to increased emissions and stronger photochemical activity, while midnight represents the lowest mixing ratios when emissions and chemical production are reduced. Because of limited funding, measurements were collected within a three-hour window around these times to still capture the main diurnal pattern using a targeted sampling approach.
- A note has been added to Section 2.2 explaining the reasoning behind selecting noon and midnight as measurement start times.

Line 210: What was the study area for Shareef et al. (2022)? It's interesting that the summertime study lined up better with this than the wintertime study, so it might be useful to mention directly in the text where they conducted their study.

- The study areas have been added where appropriate.

Line 244: More discussion on these supplement tables would be helpful, i.e. highlighting some specific numbers or cases that show the behavior you mention.

- Additional details on the chemical processes, along with budget analyses, have been included throughout the Results section to support the sensitivity analysis outputs.

Figures 3-7: For all of these figures, several shades of blue are used, which in my opinion may not have adequate contrast and could make it difficult to distinguish the groups. Using different colors with more contrast would be helpful.

- The color schemes of Figures 3–7 and Figures S6–S10 have been revised to reduce the use of similar blue shades and to improve visual contrast among the different groups.