

Hydrocarbon and Carbonyl Contributions to Wintertime Ozone Formation

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Abstract: Using the Framework for 0-D Atmospheric Modeling (F0AM), a zero-dimensional box model designed for simulating atmospheric chemistry, we simulated winter ozone (O₃) formation in the Uinta Basin, Utah, with four chemical mechanisms: the Master Chemical Mechanism (MCMv331), Statewide Air Pollution Research Centre Mechanism (SAPRC07), Regional Atmospheric Chemistry Mechanism (RACM2), and Carbon Bond Mechanism (CB6). Our purpose was to (1) identify carbonyls that act as important precursors to winter O₃ formation and determine how they form, (2) determine the extent to which carbonyl compounds were primarily or secondarily produced, (3) assess O₃ production potential, and (4) analyze how different hydrocarbon groups influence both carbonyl and O₃ formation. The final emission flux for carbonyls was near zero, indicating that they were mostly secondary photochemical products. MCMv331 identified formaldehyde and acetaldehyde as the dominant O₃ precursors, contributing 0.20 and 0.06 ppb/h, respectively, to the O₃ production rate. SAPRC07 and RACM2 showed similar trends, while CB6 emphasized the generic group “ketones” as key contributors. Across all mechanisms, alkanes were the most influential precursor group for the formation of carbonyls and O₃. Including heterogeneous chemistry in the model resulted in a modest (1 ppb) decrease in O₃ levels without altering the relative importance of precursors. This study highlights the importance of primarily emitted organic groups in winter O₃ production and provides insights into O₃ reduction strategies in the Uinta Basin and similar regions.

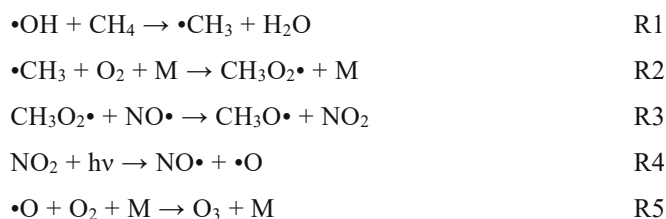
1. Introduction

Elevated tropospheric O₃ levels have raised serious concerns over the past decades due to their harmful effects on human health and the environment. High ground-level O₃ can cause respiratory issues, eye irritation, and chest discomfort (Soares et al., 2022; Filippidou et al., 2011). It also negatively impacts ecosystems (Ashmore et al., 2000) and contributes to climate change in the long term (Barnes et al., 2019; Simpson et al., 2014). Tropospheric O₃ forms through photochemical reactions involving precursors like nitrogen oxides (NO_x) and non-methane organic compounds (NMOC), and is highly influenced by meteorological and topographical conditions. Although tropospheric O₃ is typically considered a summertime problem, high O₃ during winter conditions has been reported worldwide. Notable examples include Wyoming, USA (2008) and Lanzhou, China (2018), where high O₃ levels were observed despite cold winter conditions (Yang et al., 2024). Weak vertical mixing and high NMOC mixing ratios existed in all of these cases. Mansfield and Hall (2018) and Mansfield and Lyman (2024) showed that wintertime O₃ can only form in high-NMOC environments (Mansfield et al., 2018; Mansfield et al., 2024).

In the Uinta Basin, Utah, USA, high levels of ground-level O₃ were initially observed in December 2009, drawing attention to wintertime O₃ pollution in the region (Mansfield et al., 2020). This phenomenon is primarily attributed to a combination of strong temperature inversions with snow cover and emissions from oil and gas operations. Geographically, the Uinta Basin is surrounded by high mountains, creating a bowl-shaped terrain that traps local pollution. This topography provides ideal conditions for creating strong thermal inversions that form at the lowest elevations and expand daily until disrupted by a significant storm (Lyman et al., 2015; Oltmans et al., 2014). Snow cover plays an important role in stabilizing inversions by reducing the mixed-layer height (Edward et al., 2014). Snow cover also increases the surface albedo, which leads to a higher actinic flux for photolysis reactions (Mansfield et al., 2013). Under these conditions, precursors emitted from oil and gas operations accumulate in the basin and undergo photochemical reactions in the presence of sunlight to produce O₃, and O₃ itself accumulates day after day (Lyman et al., 2015). Additionally, oil and gas operations exhibit seasonal variability in emissions, with wintertime activities often associated with higher releases of NO_x, methane, and volatile organic compounds due to increased cold-start emissions, reduced efficiency of emission control systems at low temperatures, and additional sources such as natural gas-fired heaters and cold-weather maintenance activities that are largely absent during warmer months (Mansfield et al., 2024).

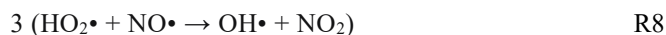
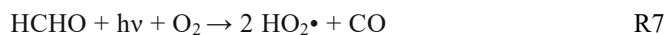
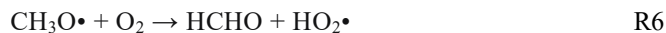
The photochemical process starts with the reaction of hydroxyl (OH) radicals with hydrocarbons, forming alkyl radicals (R1). In Reactions 1–8, methane (CH₄) and formaldehyde (HCHO) are used as representative examples to demonstrate key reaction pathways relevant to ozone (O₃) formation. These radicals rapidly react with oxygen to form peroxy radicals (R2), which, in the presence of nitrogen monoxide (NO), convert into alkoxy radicals while generating nitrogen dioxide (NO₂) (R3). The NO₂ then undergoes photolysis (R4), producing an oxygen atom that reacts with molecular oxygen to form O₃ (R5) (Wilkes, 2020).

In this whole process, radicals play a crucial role in initiating and sustaining the oxidation cycles of O₃ production by driving the interaction between NMOC and NO_x in the troposphere (Carter et al., 2012; Seinfeld et al., 1989).



During the summer, radicals mostly come from the photolysis of O₃ and the subsequent reaction of O(¹D) with water vapor (Levy, 1971). However, this mechanism becomes less efficient in winter due to decreased ultraviolet light and water vapor, leading to a 15-to-60-fold reduction in primary radical production (Lehi et al., 1971; Edward et al., 2013). Photolysis of carbonyl compounds and other photolabile oxygenated NMOC (ONMOC) is another source of radicals that can lead to O₃ production (Carbajo et al., 2008). These carbonyls can originate from the oxidation of primarily

emitted, non-oxygenated NMOC (as shown in R6 through R8). In the Uinta Basin, the winter conditions and the high mixing ratio of NMOC originating from oil and gas operations enhance the role of carbonyl photolysis as the dominant source of oxidants (Edward et al., 2014).



Radical amplification is a chemical process in which a small number of atmospheric radicals (OH or HO₂) initiate reaction chains that generate additional radicals, greatly increasing their overall mixing ratio. In the sequence of reactions R1, R2, R3, R6, R7, and R8, this chain leads to the formation of three OH radicals from a single initial OH, demonstrating the multiplying effect of radical amplification and showing how a high-NMOC wintertime atmosphere can still produce adequate radicals for significant O₃ production. These unique and complex interactions between geographical, meteorological, and chemical conditions create an ideal environment for winter O₃ formation in the Uinta Basin.

Previous studies on O₃ pollution have primarily focused on the relationship between O₃ and its precursors during the summertime (Yang et al., 2024). However, studies such as Edwards et al. (2014) highlight the important role of carbonyl compounds in winter, emphasizing their contribution to radical production and subsequent O₃ formation. Despite this progress, the detailed chemical mechanisms driving winter O₃ events remain underexplored. Addressing this knowledge gap is critical for understanding the unique conditions driving winter O₃ production in regions like the Uinta Basin.

A zero-dimensional (0-D) box model like the Framework for 0-D Atmospheric Modeling (F0AM) simplifies the atmosphere into a single, well-mixed "box," isolating chemical processes from transport effects, which allows controlled experimentation with precursor emissions and environmental parameters, enabling a detailed analysis of chemical processes. It is also capable of simulating winter-specific conditions such as low temperatures, limited sunlight, and stagnant boundary layers, which makes it ideal for studying winter O₃ formation (Wolfe et al., 2016). Researchers have previously utilized F0AM to simulate wintertime O₃ (Lyman et al., 2022, and Mansfield et al., 2024).

In this study, the chemistry of carbonyl compounds and a range of primarily emitted organic compounds was investigated, with a particular focus on their role in winter O₃ formation in the Uinta Basin. The sensitivity of primarily emitted organic groups such as alkanes, alkenes, alkynes, alcohols, and aromatics to carbonyl formation and their overall impact on winter O₃ production was examined using the F0AM box model coupled with Master Chemical Mechanism version 331 (MCMv331). The MCM is a near-explicit chemical mechanism that represents detailed gas-phase degradation of various NMOCs, leading to the formation of O₃ and other secondary pollutants (Saunders et al., 2003). To establish a solid understanding of the chemical processes driving winter O₃ formation, we compared the outputs of MCMv331 with lumped mechanisms, including the Regional Atmospheric Chemistry Mechanism version

2 (RACM2), Statewide Air Pollution Research Center Chemical Mechanism version 07 (SAPRC07), and Carbon Bond Chemical Mechanism version 6 (CB6). Our goal in these comparisons was to identify a chemical mechanism that balances computational efficiency with chemical accuracy for future 3D photochemical modeling.

2. Method

2.1 Site Description and Study Period

Measurement data were collected at the Horsepool atmospheric monitoring station in the central Uinta Basin, Utah (40.143°N, 109.469°W; 1569 m above sea level). This remote desert site has minimal influence from urban emissions and is primarily impacted by nearby oil and gas operations, making it an ideal location for investigating their effects on regional air quality and wintertime O₃ formation (Lyman et al., 2015; Neemann et al., 2015; Mansfield et al., 2020).

The simulation period (24–27 February 2019) was notable for a strong thermal inversion and the buildup of winter O₃. These inversion episodes were characterized by persistent snow cover from January through early March 2019, which contributed to multiday stagnation episodes and the accumulation of O₃ near the surface. The inversion layer acted as a barrier, limiting vertical mixing and trapping O₃ precursors close to the ground, thereby enhancing local photochemical O₃ production (Lyman et al., 2022).

2.2 Instrumentation

Trace gases were measured at the Horsepool site by drawing ambient air through an unheated PTFE filter pack inlet into an indoor PFA manifold at a flow rate of 10 L min⁻¹. O₃, NO_x, NO_y, and CO were measured using Ecotech analyzer models 9810, 9841, 9843, and 9830, respectively; methane and total nonmethane hydrocarbons were measured using a Chromatotec Chroma THC Analyzer; and PM_{2.5} was measured using a Met One BAM 1020. Weekly calibrations were performed using an Ecotech GasCal system and a Thermo 701H zero air generator. Meteorological parameters, including snow depth (MaxBotix MB7092), total solar radiation (Kipp and Zonen CNR4), wind speed and direction (RM Young 05108-45-L), temperature and humidity (Vaisala HMP155), and barometric pressure (Vaisala PTB101B) were recorded with a Campbell CR1000 datalogger, which was checked annually against NIST-traceable standards (Lyman et al., 2022).

Speciated nonmethane organic compounds were also measured, including C₂–C₁₀ hydrocarbons, C₁–C₃ alcohols, and 12 carbonyl compounds. Carbonyl measurements were not available for 2019; therefore, average values from inversion periods in other seasons were used (Lyman et al., 2022). Air samples were collected in Silonite-coated whole-air canisters for hydrocarbons and alcohols and on DNPH (2,4-dinitrophenylhydrazine) cartridges for carbonyls. One 3-hour sample was collected daily, with start times alternating between midnight and noon to capture the diurnal extremes of mixing ratios, as midday typically reflects higher concentrations driven by emissions and photochemical activity, while midnight represents lower values when these processes are reduced. DNPH cartridge samples were analyzed by eluting the absorbed carbonyl compounds using a mixture of 75% acetonitrile and 25% dimethyl sulfoxide. The resulting extracts were then injected into a high-performance liquid chromatography (HPLC)

system equipped with a UV detector to separate, identify, and quantify the carbonyl–DNPH derivatives based on retention times and peak areas. Additional methodological details are provided in Lyman et al. (2020). Whole-air canister samples were preconcentrated using an Entech 7200 with a cold-trap dehydration method and analyzed by gas chromatography with flame ionization detection for C1–C3 hydrocarbons and by gas chromatography–mass spectrometry for the remaining compounds (Lyman et al., 2022; Lyman et al., 2020).

2.3 Box Model

The Framework for 0-D Atmospheric Modeling (F0AM) box model version 4.1 (Wolfe et al., 2016; Xiong et al., 2023) was used with an average diurnal cycle configuration to simulate winter O₃ production, similar to Lyman et al. (2022). Average hourly meteorological data, CO, and total NO_x from the 4-day modeling period were used as inputs for each modeled day, with NO_x speciation determined internally by the model. Model inputs included study period average mixing ratios of all organic compounds, including methane, as well as individual hydrocarbons, alcohols, and carbonyls. An albedo of 0.7 was applied for winter conditions, consistent with observations during the study period, and an O₃ column of 275 Dobson units was used based on data from the OMI satellite (OMDOAO3e v003) accessed through NASA’s Giovanni application (NASA Giovanni, 2024). Variable boundary layer heights were prescribed following Edwards et al. (2014). The same variable dilution constant (kdil) as in Edwards et al. (2014) was initially applied and subsequently adjusted until modeled O₃ concentrations were consistent with observed values, following Ninneman et al. (2023).

A subset of the MCMv331 was used, consisting of 3423 chemical species and 10309 chemical reactions (Saunders et al., 2003; Bloss et al., 2005). This explicit mechanism represents detailed oxidation pathways of measured organic compounds, including stepwise degradation of NMOCs, formation of intermediate carbonyls, radical cycling involving OH, HO₂, and RO₂, and their interactions with NO_x that drive winter O₃ production.

For a subset of model runs, we introduced heterogeneous chemistry to understand the impact on winter O₃ formation due to OH and HO₂ uptake onto aerosol surfaces, following the method of Ninneman et al. (2023). In this approach, the uptake of OH and HO₂ was represented using a fixed uptake coefficient (γ) of 0.2. The heterogeneous loss rates were calculated as a function of aerosol surface area using observed PM_{2.5} concentrations and an assumed specific surface area, consistent with the parameterization described in Ninneman et al. (2023).

2.4 Comparison with Lumped Chemical Mechanisms

The output of MCMv331 was compared with several lumped mechanisms, including the RACM2, SAPRC07, and CB6, which consist of fewer species and reactions. Lumped mechanisms simplify atmospheric chemical modeling by aggregating similar species and reactions into fewer representative categories, which reduces computational complexity and enhances efficiency, making them ideal for large-scale air-quality models. Lumped mechanisms allow for faster computation while still capturing essential chemical processes, which is very important for the computational efficiency of large 3-D photochemical models. (Zaveri et al., 1999).

SAPRC07 and RACM2 use a molecule-based lumping approach. In these mechanisms, organic compounds with similar molecular structure, functional groups, and gas-phase reactivity are grouped into a single surrogate species. The reaction rate constants of each surrogate are typically calculated as weighted averages of the individual compounds included in the lump, based on their chemical reactivity and atmospheric importance. As a result, each surrogate species represents the overall chemical behavior of a group of similar compounds rather than any individual molecule. SAPRC07 consists of 134 surrogate species and 698 chemical reactions, while RACM2 includes 124 surrogate species and 363 chemical reactions. In contrast, the CB6 mechanism follows a structure-based lumping approach. Instead of representing whole molecules, CB6 conserves carbon-carbon bond types and functional carbon groups. Organic compounds are decomposed into carbon bond fragments such as alkyl groups, double bonds, and aromatic rings, which are then assigned to surrogate species based on bond type. Chemical reactions track the transformation of these carbon bonds during oxidation processes, allowing CB6 to represent organic carbon chemistry with fewer species while maintaining carbon conservation. The CB6 mechanism includes 77 surrogate species and 216 chemical reactions. All three of these lumped mechanisms retain some explicit organic species, including formaldehyde. SAPRC07 and RACM2 retain more explicit species than CB6.

To compare these mechanisms with MCMv331, species mapping was performed to aggregate and convert measured organic chemical species into the corresponding species in the lumped mechanisms. Species properties from the United States Environmental Protection Agency (EPA) SPECIATE database version 5.2 were used, along with a species conversion database provided by Ramboll (EPA, 2024). The conversion database is included in the Supplementary Information. When more than one MCM species corresponded to a single lumped mechanism species, their mixing ratios were summed to obtain the lumped species concentration.

2.5 Emission Flux

Hydrocarbons in the Uinta Basin are primarily emitted from oil and gas activities (Lyman et al., 2015; Mansfield et al., 2020; Warneke et al., 2014). Because the hydrocarbon dataset was temporally limited, their mixing ratios were held constant throughout the simulation period. On the other hand, carbonyl compounds can be emitted directly or formed secondarily through photochemical reactions of hydrocarbons. To accurately represent atmospheric conditions and allow for realistic secondary carbonyl production, optimized emission fluxes (EFs) were developed for carbonyl compounds. Initial mixing ratios were set to measured values, while subsequent modeled mixing ratios were allowed to vary over time. Emission flux values were iteratively adjusted to achieve minimal increasing or decreasing trends in mixing ratios across the four modeled days. If the Day 4 mixing ratio of a given carbonyl compound was lower than the Day 1 value, the initial EF was considered too low and was incrementally increased until the trends aligned as closely as possible. Conversely, if mixing ratios increased throughout the simulation, the EF was considered too high and was reduced, in some cases to zero. An EF of zero implied no local emissions and that all carbonyls, except those initially present, were formed from atmospheric photochemical reactions (Maasakkers et al., 2019). Through systematic adjustment of EF values, the modeled carbonyl mixing ratios were constrained to reflect observed atmospheric behavior, thereby improving the reliability of the simulation results.

2.6 Determination of the Influence of Selected Carbonyls on O₃ Production

To investigate the influence of individual carbonyl compounds on winter O₃ production, the F0AM box model was initially run without any modifications to establish baseline O₃ production. The initial mixing ratio of a selected carbonyl compound was then set to zero and constrained to remain at zero in a subsequent model run. The average O₃ production rate (ppb h⁻¹) between 09:00 and 16:00 on the fourth day of the simulation was compared between the two scenarios. This time window was selected to capture periods of consistent photochemical activity, during which carbonyl compounds contribute to radical production and daytime O₃ formation (Pang et al., 2006). Differences in O₃ production rates resulting from forcing the mixing ratio of a given carbonyl compound to zero were used to quantify its influence. This procedure was systematically repeated for all measured carbonyl compounds, and the resulting outputs were compared to determine compound-specific contributions to O₃ production.

2.7 Determination of the Influence of Primarily Emitted Organics on Carbonyl and O₃ Production

A sensitivity analysis was conducted to assess the impacts of primarily emitted organic groups (alkanes, alkenes, alkynes, alcohols, and aromatics) on carbonyl production. The analysis focused on selected carbonyl compounds, including formaldehyde, acetaldehyde, methacrolein, benzaldehyde, and methyl ethyl ketone, which were chosen based on their significant influence on winter O₃ formation. Initial mixing ratios of the primary organic groups were varied by ±50%, while maintaining constant speciation within each group, and the corresponding percentage changes in average mixing ratios of carbonyls were evaluated between 13:00 and 17:00 on the fourth day of the simulation. This time window was selected to avoid rapid morning changes in boundary layer height that could introduce variability in pollutant mixing ratios (Lapworth, 2006; Mahrt, 1981). During the afternoon period, the atmosphere is more homogeneous, allowing for an even distribution of precursors and reaction products. It also represents a steady-state condition for radical species (•OH, •HO₂, and •RO₂), ensuring a balanced production and loss cycle (Lew et al., 2020; Heard et al., 2004). This approach allowed us to evaluate the sensitivity of carbonyl formation to fluctuations in levels of primary organic groups.

A similar sensitivity analysis was performed to determine the influence of primarily emitted organic groups on the O₃ production rate, which allowed us to identify the individual impact of each organic compound group on winter O₃ production.

3. Results and Discussion

3.1 Winter O₃ Pollution in the Uinta Basin

Figure S1 represents the diurnal variation of the hourly average O₃ mixing ratio during the simulation period in the Uinta Basin. On the fourth day, the daily maximum 8-h average O₃ mixing ratio reached 94 ppb, exceeding the U.S. Environmental Protection Agency standard of 70 ppb; the maximum hourly value was 102 ppb. The negative relationship between O₃ and relative humidity is shown in Figure S2. In comparison, the F0AM Box model with the explicit chemical mechanism MCMv331 estimated a maximum O₃ mixing ratio of 107 ppb on the fourth day of the

simulation (Figure 1). After incorporating heterogeneous chemistry based on MCMv331, the O₃ level decreased by 1 ppb. The SAPRC07 lumped mechanism estimated the O₃ level at 111 ppb, while RACM2 predicted slightly lower than the measured value at 100 ppb, and CB6 provided the highest estimation of 122 ppb. Liu et al. (2023) conducted a Box model study with commonly used chemical mechanisms during summertime in multiple cities of China and identified that RACM2 showed the best agreement with observation during the polluted period, followed by MCMv331 and SAPRC07. These findings aligned with our studies. On the other hand, Shareef et al. (2022) evaluated different lumped chemical mechanisms with CMAQ (3D photochemical model) on winter O₃ prediction in Alberta, Canada, and found no significant differences in SAPRC07, RACM2, and CB6 output.

The O₃ budget on Day 4 shows a consistent pattern across all four mechanisms (Tables S8.1–S8.4). O₃ production is controlled almost entirely by the reaction between ground-state oxygen atoms and molecular oxygen, contributing 99–100% of total formation, while reactions involving organic peroxy radicals and HO₂ contribute less than 0.01%. O₃ loss is driven mainly by photolysis, which accounts for 75–78% of total removal, followed by the reaction of NO with O₃, which contributes 18–21%.

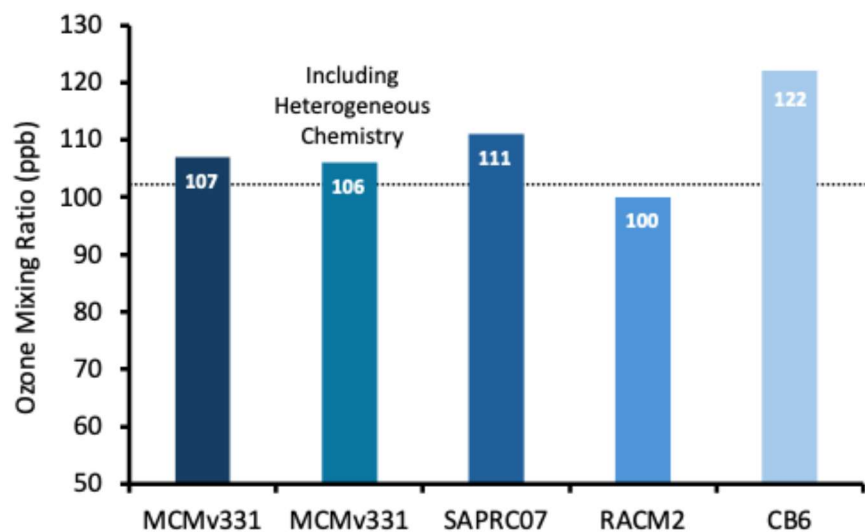


Figure 1: Comparative analysis of maximum hourly O₃ mixing ratio using different chemical mechanisms. The dotted line represents the observed maximum hourly O₃ level (102 ppb).

3.2 Contribution of Carbonyls to Winter O₃ Formation

Figure 2 shows that O₃ was more sensitive to changes in carbonyl mixing ratios in the lumped mechanisms compared to MCMv331. Master Chemical Mechanism (MCM) employs an explicit representation of reactions, wherein carbonyl compounds degrade through multi-generational, branched pathways that distribute radical formation across several intermediate species and slower reaction steps (Saunders et al., 2003). On the other hand, with simplified chemical mechanisms, carbonyl chemistry is formulated to produce O₃, forming radicals like HO₂ rapidly and directly, often in

a single reaction step. This fundamental difference in mechanism structure may explain the higher O₃ sensitivity to carbonyls observed with the lumped mechanisms compared to MCMv331 (Goliff et al., 2013; Yarwood et al., 2010).

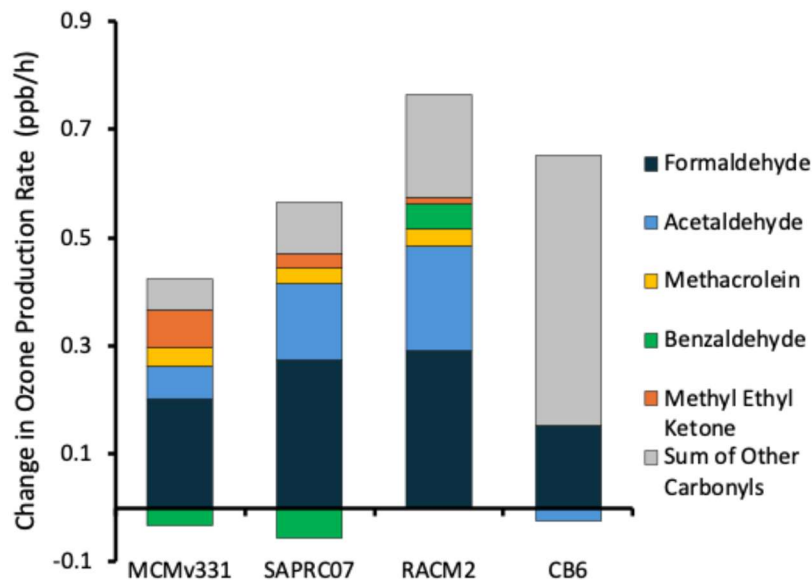


Figure 2: Change in O₃ production rate on Day 4 of the modeled period in response to a 50% increase in the mixing ratio of the indicated carbonyls. Each bar represents the overall change in O₃ production rate for a specific chemical mechanism. The sections within each bar illustrate the contributions of individual carbonyl compounds.

Figure 3 illustrates modeled day 4 HO_x production and loss budgets across the four chemical mechanisms, expressed as percentages of each mechanism's total (Table S9 provides more information). Across all mechanisms, thermal decomposition of peroxyacetyl nitrate (PAN, in CB6) is the single largest HO_x production pathway, accounting for 23–38% of total production. Organoperoxy radical (RO₂)+NO reactions were far more important for the lumped mechanisms compared to MCMv331, but this is likely an artifact of collapsing multi-step reaction sequences in lumped mechanisms, leading to higher budget percentages from fewer reaction pathways. In the HO_x loss budget, HO₂ + NO₂ termination dominates in all mechanisms (25–40%), and OH reactions with alkanes represent the second-largest sink (9–33%), consistent with the dominance of alkane emissions in the Uinta Basin. OH-alkane reactions appear less important for MCMv331 in the figure because it catalogs reactions with specific alkanes, so most OH-alkane reactions were not among the top five most important reactions and were instead included as Other. Notably, the OH + benzaldehyde loss term appears in the MCMv331 top-5 reactions (approximately 3% of total HO_x loss) but is absent from the RACM2 and CB6 budgets, providing a direct

mechanistic basis for the negative O₃ sensitivity to benzaldehyde observed in MCMv331 and SAPRC07 but not in the lumped mechanisms (Fig. 2; Table 3).

Notwithstanding these caveats, all four mechanisms have fairly similar HOx production budgets. Total HOx production rates were similar for MCMv331, SAPRC07, RACM2 (21.2, 23.7, and 22.1 molecules cm⁻³, respectively), while CB6 radical production was notably higher, at 38.7 molecules cm⁻³. Higher radical production in CB6 may explain the higher ozone mixing ratios modeled by CB6, as shown in Figure 1.

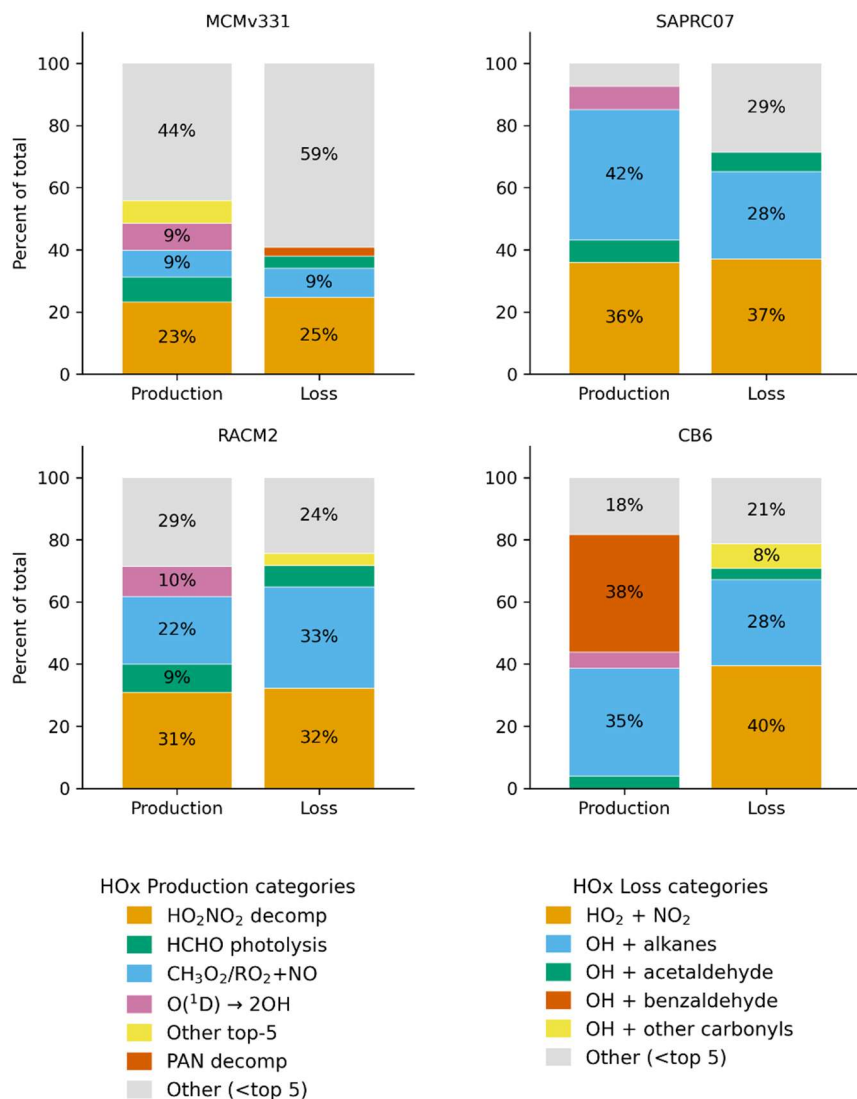


Figure 3: Modeled day 4 HOx production and loss budgets for each of the four chemical mechanisms evaluated in this study. For each mechanism, the left bar shows the percentage contribution of each reaction pathway to total HOx production, and the right bar shows the percentage contribution to total HOx loss. Only the top five reactions by integrated reaction rate are categorized individually; remaining reactions are grouped as "Other." See Tables S8 through S10 for detailed budget information for O₃, HOx, and individual carbonyls.

287

288 The F0AM box model with MCMv331 identified formaldehyde as the dominant contributor to the O₃ production rate,
 289 accounting for a change of 0.20 ppb h⁻¹, or approximately 50% of the total contribution from carbonyl compounds.
 290 This finding aligns with Edwards et al. (2014), who reported formaldehyde as the primary daytime radical source in
 291 the Uinta Basin, contributing 30% of radical formation from carbonyls, with the remainder attributed to larger carbonyl
 292 species. Across all chemical mechanisms examined, both the production and loss of formaldehyde lead to substantial
 293 HO₂ radical formation through reactions R6 and R7, which play a critical role in O₃ production. The combined HO₂
 294 production from formaldehyde accounts for approximately 8 to 20% of total hydrogen oxide radicals (HOx)
 295 production across the mechanisms considered (Table 1). In MCMv331, acetaldehyde was found to be the second-
 296 highest contributor in our study, causing a change of 0.06 ppb/h in the O₃ production rate, with SAPRC07 and RACM2
 297 following a similar trend. Overall, acetaldehyde contributes roughly half of the HO₂ produced by formaldehyde
 298 (Tables 1 and 2). In addition, reactions with acetaldehyde lead to a substantially greater loss of OH, an important
 299 radical in O₃ production, compared to formaldehyde. Oxidation of acetaldehyde by OH forms the acetyl peroxy
 300 radical, which can be sequestered as peroxyacetyl nitrate under cold conditions. This compound is thermally stable at
 301 low temperatures and can transport NO_x and radicals over long distances, thereby reducing their availability for local
 302 O₃ production (Fischer et al., 2014).

303 In CB6, most medium and high molecular weight carbonyls are lumped into the single “KET” species (Yarwood et
 304 al., 2010), so KET represents a much larger carbon pool than any individual carbonyl. As shown in Table S10.4, almost
 305 all KET is formed through the alkoxy-radical pathway (ROR → KET, ~99%), which strongly promotes radical
 306 propagation. At the same time, formaldehyde in CB6 undergoes a substantial HO₂ removal reaction (FORM + HO₂,
 307 ~31% of its loss; Table S10.4), limiting its radical yield. As a result, KET has a much stronger effect on O₃ production
 308 than formaldehyde in CB6.

309 The relative contributions of each carbonyl compound remained largely unchanged after introducing heterogeneous
 310 chemistry into the model (Figure S4). This is likely due to low specific humidity during the simulation period, which
 311 limits the uptake of HOx radicals by aerosols. As a result, the radical budget and hence O₃ production potential were
 312 not significantly altered (Figure 1), preserving the dominance of formaldehyde and acetaldehyde among carbonyl
 313 precursors.

314

315 Table 1: Contribution of formaldehyde to HO₂ production by process across chemical mechanisms.

Mechanism	HO ₂ from Formaldehyde Production (% of total HOx)	HO ₂ from Formaldehyde Photolysis (% of total HOx)	Total Formaldehyde Related HO ₂ (% of total HOx)
MCMv331	8.6%	8.0%	16.6%

SAPRC07	8.1%	7.1%	15.2%
RACM2	10.5%	9.0%	19.5%
CB6	4.0%	4.0%	8.0%

Table 2: Contribution of acetaldehyde to HO₂ production by process across chemical mechanisms.

Mechanism	HO ₂ from Acetaldehyde Production (% of total HOx)	HO ₂ from Acetaldehyde Photolysis (% of total HOx)	Total Acetaldehyde Related HO ₂ (% of total HOx)
MCMv331	7.5%	0.8%	8.3%
SAPRC07	-	1.3%	~1.3%
RACM2	8.7%	1.5%	10.2%
CB6	-	0.5%	~0.5%

Table 3: Contribution of benzaldehyde to the HOx budget across chemical mechanisms.

Mechanism	OH Consumption Rate (molecules cm ⁻³)	HO ₂ Production Rate (molecules cm ⁻³)	Net HOx
MCMv331	-0.61	+0.2	-0.41
SAPRC07	-0.52	0	-0.52
RACM2	-0.08	+0.01	-0.07
CB6	-	-	-

The impact of benzaldehyde on O₃ production differs across chemical mechanisms. In MCMv331, benzaldehyde shows a negative contribution of -0.03 ppb h⁻¹, indicating that increasing benzaldehyde reduces the O₃ production rate, with a similar negative response observed in SAPRC07. In both MCMv331 and SAPRC07, benzaldehyde undergoes detailed aromatic degradation that consumes radicals or forms less reactive products. As a result, benzaldehyde competes for OH and acts as a radical sink, leading to increased HOx loss (Table 3). In MCMv331, phenoxy radicals formed from benzaldehyde directly consume O₃, further contributing to the negative impact on O₃ production. In contrast, in RACM2, the OH + benzaldehyde reaction is much less important relative to the total HOx budget, so increasing benzaldehyde does not significantly increase HOx loss. Instead, oxidation of benzaldehyde in RACM2 forms peroxybenzoyl radicals that enhance NO to NO₂ cycling, resulting in net positive O₃ production.

Edwards et al. (2014) attributed 85% of radical production to the photolysis of carbonyl compounds during a 2013 winter O₃ episode at the same Uinta Basin location. However, studies have shown that the emissions in the Uinta Basin have declined since the Edwards et al. study (Mansfield et al., 2020; Lin et al., 2021), and during our study, we found that the initial mixing ratios of several carbonyls were lower compared to those of Edwards et al. on the fourth day of the simulation period (Table S1). Furthermore, the emission flux required to simulate representative carbonyl mixing ratios was minimal or zero. The addition of carbonyl emissions in the box model led to an overestimation of their mixing ratios, indicating that carbonyls were mostly secondary pollutants, created in the atmosphere from

photochemistry, rather than emitted directly from sources. Stockwell et al. (2011) and Nogueira et al. (2017) also identified carbonyl compounds mainly as secondary pollutants generated through the oxidation of hydrocarbons from anthropogenic or biogenic emissions.

3.3 Contribution of Hydrocarbons to Carbonyl Compound Formation

Figure 4 shows the production pathways for formaldehyde and acetaldehyde — the two dominant carbonyl O₃ precursors — across the four mechanisms (additional carbonyl production and loss budgets are available in Table S10). For formaldehyde, the methyl peroxy radical + NO reaction ($\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{HCHO} + \text{HO}_2$) accounts for 55–60% of production in MCMv331, SAPRC07, and RACM2. CB6 shows a notably different pattern, with the $\text{CH}_3\text{O}_2 + \text{NO}$ contribution falling to 36% while alkene oxidation rises to nearly 20%. For acetaldehyde, all four mechanisms show strong dominance of alkyl peroxy and alkoxy radical pathways derived from alkane oxidation, with ethoxy radical decomposition ($\text{C}_2\text{H}_5\text{O}\cdot \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$) accounting for approximately 75% of production in MCMv331 and similar lumped pathways dominating in SAPRC07 and RACM2. CB6 is again distinctive, with a significant contribution from its lumped ketone species ($\text{KET} \rightarrow \text{ALD2}$, approximately 17%; denoted as aldehyde photolysis in the figure), reflecting the broader lumping of C₃+ alkane oxidation intermediates into a single ketone pool in that mechanism. Also, Figure 4 shows 99% of acetaldehyde production in the SAPRC07 mechanism comes from ethoxy radical decomposition, while the other mechanisms show a significant contribution from larger organic oxy or peroxy radical species. SAPRC07 actually uses a system of “yield tokens” as outcomes of upstream reactions, obscuring the radical species that generated acetaldehyde. In the absence of information about radical species, we assigned all to ethoxy radical decomposition in the figure. Total formaldehyde production rates were 3.31, 3.25, 3.88, and 4.28 molecules cm⁻³ for MCMv331, SAPRC07, RACM2, and CB6, respectively; total acetaldehyde production rates were 2.12, 3.77, 4.02, and 2.86 molecules cm⁻³ for the same mechanisms.

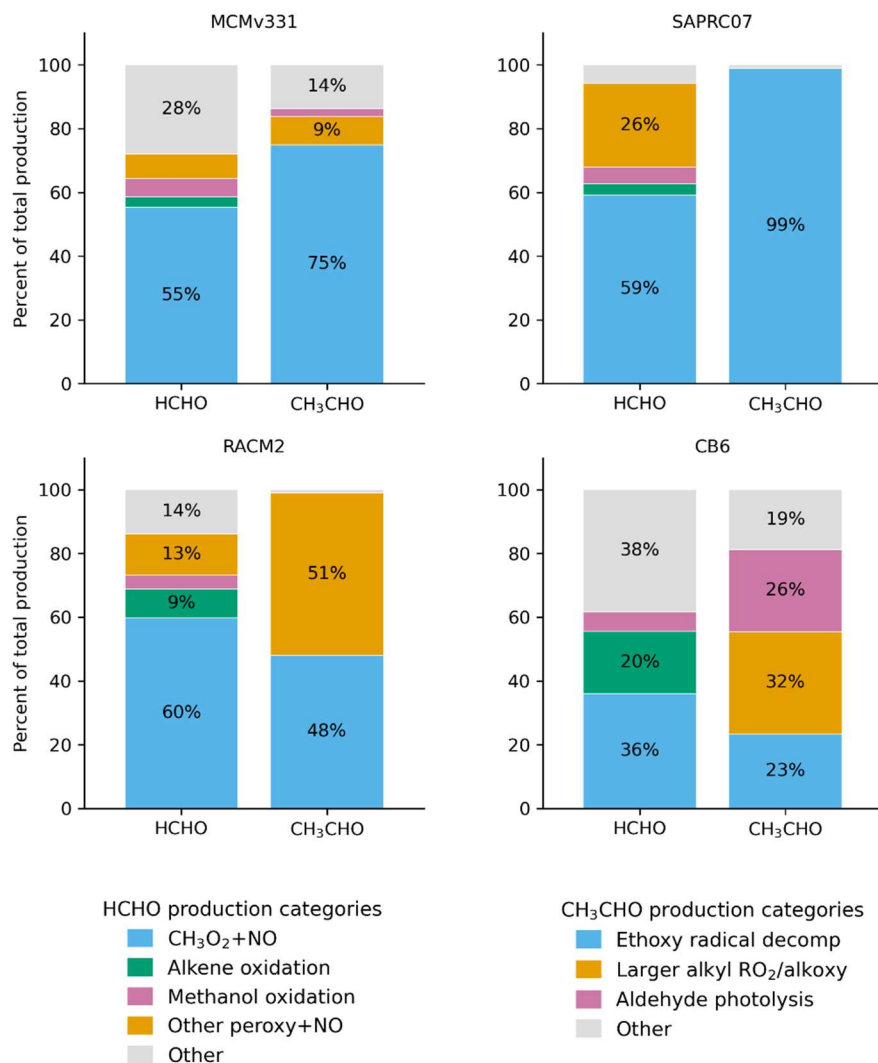
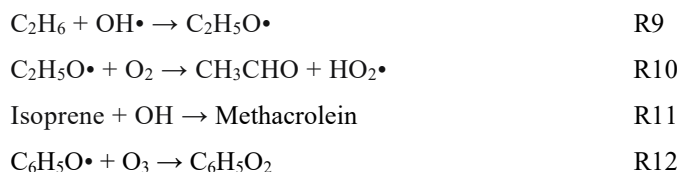


Figure 4. Modeled day 4 production budgets for formaldehyde (HCHO) and acetaldehyde (CH₃CHO) across the four chemical mechanisms. For each mechanism, bars show the percentage contribution of each reaction pathway to total production of the indicated carbonyl species. Only the top five reactions by integrated reaction rate are categorized individually; remaining reactions are grouped as "Other." See Tables S8 through S10 for detailed budget information for O₃, HOx, and individual carbonyls.

Figure 5 illustrates the contribution of various hydrocarbon groups to the formation of key carbonyl compounds, including alkanes, alkenes, alkynes, aromatics, and alcohols. The MCMv331 results indicated that formaldehyde formation is influenced by a wide variety of NMOC groups (4-7% each) because, as shown in Figure 4, its dominant production pathway (R6, 55.3%) relies on the methyl peroxy radical (CH₃O₂) (R1-R3), a universal intermediate generated from oxidation of multiple organic classes, including alkane oxidation via fragmentation of larger alkoxy radicals, alkene ozonolysis through Criegee intermediate decomposition, and aromatic ring-opening reactions. In

addition, formaldehyde is produced through several direct pathways independent of CH_3O_2 , such as terminal alkene ozonolysis, methanol oxidation, and glyoxal photolysis (Saunders et al., 2003).

Alkanes are generally less reactive than other NMOC groups; however, due to their prominence in the Uinta Basin atmosphere, they still play a dominant role in the formation of formaldehyde and other carbonyl compounds. The mixing ratios of acetaldehyde, benzaldehyde, and methyl ethyl ketone increased by 24%, 28%, and 20%, respectively, in response to a 50% increase in the initial mixing ratio of total alkanes. Ethane reacts with the OH radical to form the ethoxy radical ($\text{C}_2\text{H}_5\text{O}\cdot$) (R9), which is then oxidized to produce acetaldehyde (R10). This reaction pathway is the dominant source of acetaldehyde, accounting for 74.9% of its total formation. Isopentane also acts as a significant contributor to acetaldehyde formation (Table S4), feeding into the same pathway. Its branched structure promotes alkoxy radical decomposition, which releases ethyl radicals that subsequently produce acetaldehyde through the same ethoxy radical pathway (R9–R10) as ethane. There are no such comparable pathways available for other NMOC groups, making alkane oxidation the primary contributor to acetaldehyde production. Ethanol oxidation forms some acetaldehyde, but ethanol mixing ratios were low in the model, and Figures 4 and 5 show this to be a minor pathway.



Methacrolein production is typically associated with isoprene oxidation (R11); however, isoprene mixing ratios are negligible in the wintertime Uinta Basin due to plant dormancy. Budget analysis confirms that methacrolein is introduced almost entirely through primary emissions (Table S10.1). A 50% increase in alkane mixing ratios resulted in an 83% increase in methacrolein mixing ratio in MCMv331, the largest response among all carbonyl compounds (Figure 5). This sensitivity arises because OH radicals account for 80% of total methacrolein destruction, and alkane oxidation is simultaneously the largest OH sink in the system. Increasing alkane concentrations enhances OH consumption, reducing steady state OH and suppressing methacrolein destruction. Other carbonyls such as formaldehyde and acetaldehyde are less affected because their chemical production also decreases when OH is reduced, partially offsetting the slower destruction. Methacrolein, with no chemical production source, lacks this counterbalance. A 50% increase in aromatics reduced methacrolein by 9% due to phenoxy radical-driven HO_x suppression. The O_3 budget reveals that phenoxy radicals directly destroy O_3 (R12, $2.31 \text{ molecule cm}^{-3}$, 0.19% of total O_3 loss), reducing the primary OH source ($\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) \rightarrow 2\text{OH}$). Additionally, phenoxy radicals react with NO_2 to form nitrophenols ($\text{C}_6\text{H}_5\text{O} + \text{NO}_2 \rightarrow \text{HOC}_6\text{H}_4\text{NO}_2$), which terminate radical chains and sequester NO_x , thereby suppressing the $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$ recycling pathway. These combined effects reduce OH availability for isoprene oxidation, resulting in decreased methacrolein production.

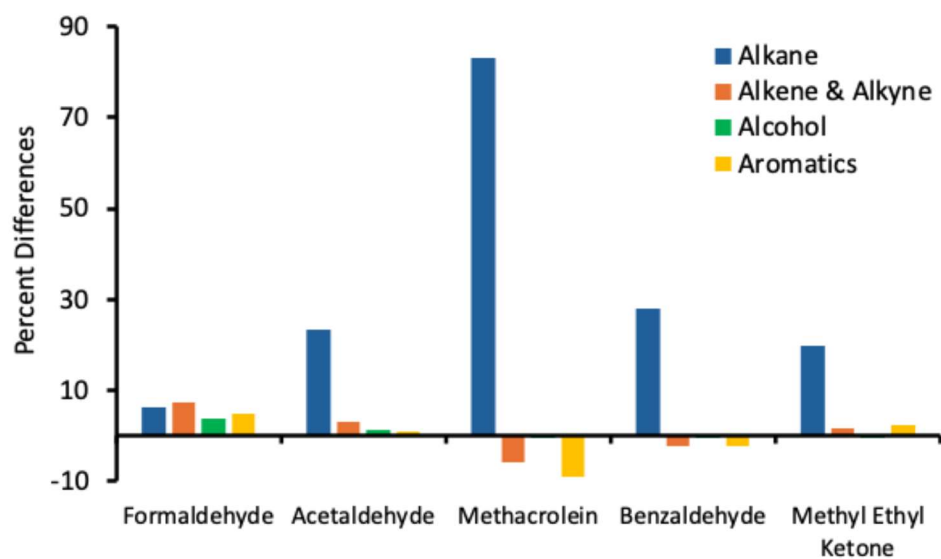


Figure 5: Sensitivity of carbonyl compounds to changes in NMO precursor groups (MCMv331 output). The bars represent the changes in carbonyl mixing ratios due to an increase in the NMO mixing ratio of 50%.

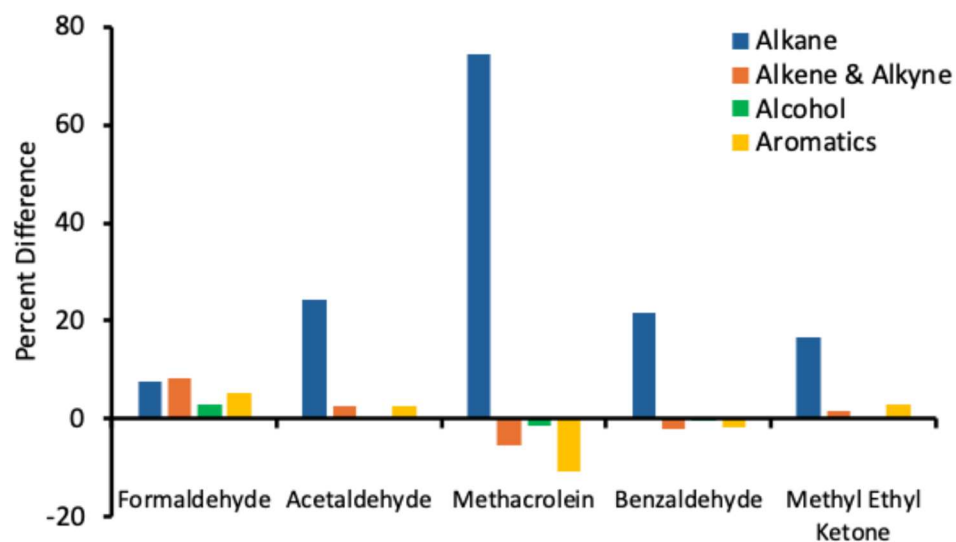


Figure 6: Sensitivity of hydrocarbons to carbonyl compounds (SAPRC07 Output). The bars represent the changes in carbonyl mixing ratios due to the increase in the hydrocarbon initial mixing ratio by 50%.

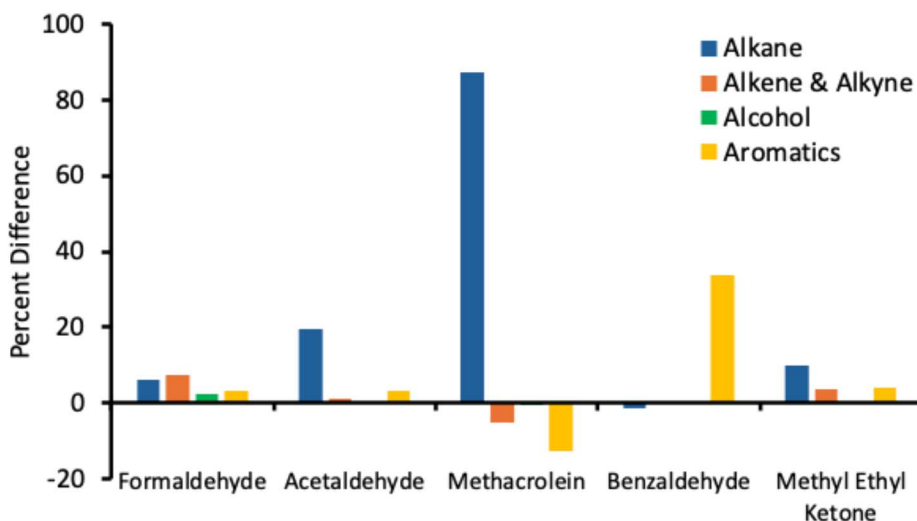
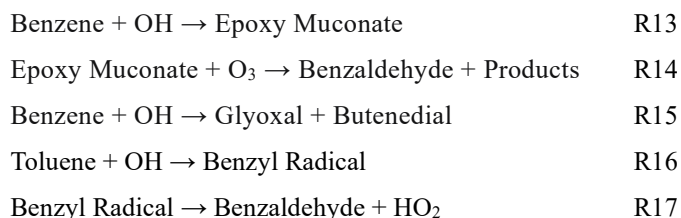


Figure 7: Sensitivity of hydrocarbons to carbonyl compounds (RACM2 Output). The bars represent the changes in carbonyl mixing ratios due to the increase in the hydrocarbon initial mixing ratio by 50%.

Sensitivity analyses following the same method with the SAPRC07 and RACM2 (Figures 6 and 7) chemical mechanisms showed similar trends as MCMv331, except aromatics had a more substantial positive effect on benzaldehyde formation than alkanes, according to RACM2. R13 and R14 represent the formation of benzaldehyde from benzene in RACM2. Here, benzene reacts with OH to produce an epoxy muconate intermediate, which reacts with O₃ to directly produce benzaldehyde (R14, accounting for 72.1% of benzaldehyde production). In contrast, in MCMv331, ring-opening chemistry produces dicarbonyls (glyoxal, butenedial) that cannot form benzaldehyde because the aromatic ring is destroyed (R15). In MCMv331, benzaldehyde production requires the intact benzene ring and occurs only through the minor side-chain oxidation pathway (R16-R17, 0.7% of production), with 99.3% coming from direct emissions. This mechanistic difference explains why increasing aromatics has a stronger positive effect on benzaldehyde in RACM2 than in MCMv331.



The CB6 mechanism is based on carbon bond types rather than explicit chemical species, resulting in fundamentally different formaldehyde sensitivity compared to MCMv331 (Figure 8). In MCMv331, alkane oxidation produces

methoxy radicals (CH_3O) through sequential fragmentation, which decompose directly to formaldehyde (R6). In contrast, CB6 represents alkanes as paraffinic carbon bonds (PAR), and their oxidation produces a lumped alkoxy intermediate (ROR) that decomposes exclusively to ketones (KET), acetaldehyde, acetone, and higher aldehydes but not formaldehyde. Meanwhile, alkenes in CB6 directly produce formaldehyde with high yields ($\text{Ethene} + \text{OH} \rightarrow 1.56 \text{ Formaldehyde}$). Since alkane oxidation consumes 34% of OH without producing formaldehyde, increasing alkanes reduces OH availability for alkene oxidation, resulting in decreased formaldehyde production. Acetaldehyde and ketone formation remain alkane-dominated in CB6, consistent with other mechanisms. This carbon-bond lumping approach fundamentally alters formaldehyde's NMOC sensitivity in CB6 compared to more explicit mechanisms like MCMv331 & SAPRC07.

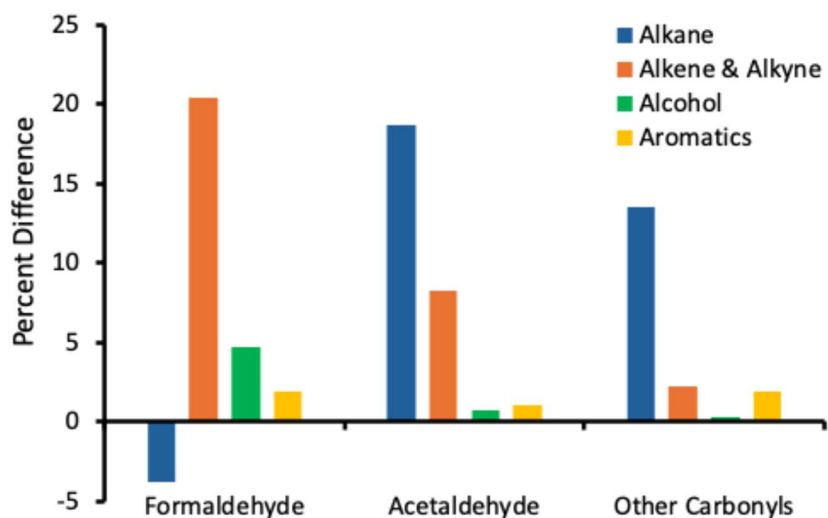


Figure 8: Sensitivity of hydrocarbons to carbonyl compounds (CB6 Output). The bars represent the changes in carbonyl mixing ratios due to the increase in the hydrocarbon initial mixing ratio by 50%.

3.4 Contribution of Hydrocarbons to Winter O_3 Formation

To elucidate the impact of various hydrocarbons on winter O_3 formation and gain deeper insights into the underlying chemistry, we conducted a sensitivity analysis using the same chemical mechanisms as before. Figure 9 reveals that both MCMv331 and SAPRC07 chemical mechanisms exhibit similar chemical behavior, with alkanes having the most significant influence on winter O_3 formation. A 50% increase in the mixing ratio of alkanes resulted in approximately a 0.29 ppb/h and 0.35 ppb/h increase in O_3 production rate on the fourth day of the simulation with the MCMv331 and SAPRC07 mechanisms, respectively. The dominant role of alkanes in winter O_3 formation can be attributed to their high ambient mixing ratio and efficient radical propagation chemistry. Although alkane reactions with OH radicals have moderate rate constants, their elevated mixing ratios enable efficient production of alkyl peroxy radicals.

These peroxy radicals subsequently propagate the $\text{NO} \rightarrow \text{NO}_2$ conversion cycle, ultimately contributing to O_3 production (R1–R5). While this fundamental chemistry is represented in all mechanisms, RACM2 underestimates the full impact of alkane degradation due to over-simplification through species lumping. Compared to MCMv331, RACM2 shows a 76% reduction in parent alkane species and an 86% reduction in peroxy radical species after lumping. This simplification results in a 34% reduction in HO_2 radical yields from alkane oxidation, which consequently reduces the apparent contribution of alkanes to O_3 production relative to MCMv331.

In MCMv331 and SAPRC07, aromatics emerge as the second most important precursor for winter O_3 formation due to their efficient sequential multi-step oxidation chemistry. The initial OH-addition to the aromatic ring produces bicyclic peroxy radicals, which subsequently undergo ring-opening to form highly reactive dicarbonyl compounds such as glyoxal and methylglyoxal. These dicarbonyls photolyze to produce additional HOx radicals, creating a radical amplification chain that significantly enhances O_3 production per aromatic molecule oxidized. Simulations using RACM2 showed a similar magnitude of aromatic-induced O_3 production change compared to MCMv331 and SAPRC07. The CB6 mechanism identified alkanes as the major contributor, similar to MCMv331 and SAPRC07. However, it ranked alkenes and alkynes, rather than aromatics, as the second-highest contributors to winter O_3 production, diverging from the trends observed in the other chemical mechanisms.

Although alkanes show the largest contribution to O_3 production, a 50% increase in alkane mixing ratios results in only a modest change of about 0.2 to 0.4 ppb h^{-1} in the O_3 production rate on day four of the model run across the chemical mechanisms. This limited response likely occurs because both physical and chemical constraints begin to develop by the fourth day of the simulation (Figure S1). As the inversion persists, the accumulation of precursors approaches a balance between emissions into the basin and loss through air exchange at the top of the inversion, which limits further increases in O_3 forming compounds (Edwards et al., 2014). At the same time, highly reactive NMOCs are consumed during the early days of the episode, and the remaining NMOC mixture is dominated by slower reacting species that are less efficient at producing O_3 (Koss et al., 2015; Lyman et al., 2018). Further, more NO_x is consumed as photochemical activity is enhanced day upon day, leading to less NO_x available to produce O_3 (Lyman et al., 2018). Thus, precursor mixing ratios by 50% has a much smaller effect on O_3 production on day four than during the earlier days.

Previous box model and observational studies indicate that alkanes can play a critical role in wintertime O_3 production in oil and gas–influenced regions (Chen et al., 2020; Koss et al., 2015). In Utah’s Uintah Basin, light alkanes are the most abundant in NMOC (Table S2). Although light alkanes react more slowly with OH radicals than aromatics, their high ambient mixing ratios cause them to dominate the NMOC mixture by volume and account for approximately 70% of OH-initiated hydrocarbon oxidation (Koss et al., 2015). Studies in other oil and gas producing regions similarly report that light alkanes contribute about 60% of total OH reactivity and play an important role in the formation of carbonyl compounds, which serve as major radical sources for O_3 production (Gillman et al., 2013; Edwards et al., 2014; Field et al., 2015).

The contribution of different NMOC groups to the O₃ production rate remained largely unchanged after incorporating heterogeneous chemistry in the box model simulation using MCMv331, consistent with the explanation provided in Section 3.2 (Figure S5). Figure S5 shows that a 50% increase in the mixing ratio of each NMOC group with heterogeneous chemistry resulted in nearly similar magnitudes of change in O₃ production rate as without heterogeneous chemistry.

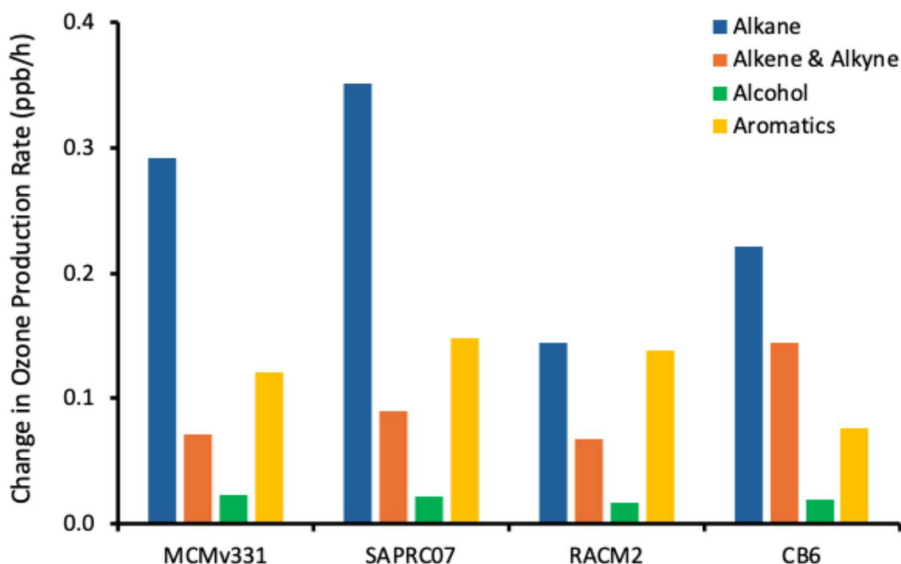


Figure 9: Sensitivity of hydrocarbons to O₃ production rate. The bars represent the changes in O₃ production rate from the base model due to the increase in hydrocarbon initial mixing ratio by 50%.

4. Conclusion

This box model study provides a comprehensive understanding of the chemical processes governing winter O₃ formation in the Uinta Basin, along with an evaluation of the performance of different chemical mechanisms. Our analysis identified formaldehyde as the most critical carbonyl species driving wintertime O₃ production, followed by acetaldehyde, a finding consistently observed across MCMv331, RACM2, and SAPRC07 mechanisms. Formaldehyde photolysis serves as a primary source of HO₂ radicals, which subsequently convert NO to NO₂ and ultimately produce O₃. Among the NMOC groups, alkanes emerged as the dominant contributors to O₃ formation across all mechanisms, primarily due to their high ambient mixing ratios from oil and gas operations and their efficient production of alkyl peroxy radicals that propagate NO_x cycling. Aromatics ranked as the second most important precursor in MCMv331 and SAPRC07 simulations, attributed to their multi-step oxidation chemistry that produces reactive dicarbonyl

intermediates and amplifies radical production. The inclusion of heterogeneous chemistry had minimal impact on NMOC and carbonyl contributions to winter O₃ formation, indicating that the primary chemical pathways remain unaffected (Figures S4 and S5).

Significant differences were observed among the chemical mechanisms in representing NMOC contributions to carbonyls and winter O₃ production. RACM2 showed lower contributions from alkanes due to its heavy lumping of alkane species, which resulted in approximately 34% lower HO₂ yields from alkane oxidation compared to MCMv331. It also identified aromatics as the major contributor to benzaldehyde rather than alkanes. In CB6, ketones showed the highest carbonyl contribution to O₃ formation because CB6 lumps higher ketones into a single species. This lumping concentrated the contributions of multiple ketone compounds that would be tracked individually in MCMv331, and reduced the importance of formaldehyde as an O₃ precursor in CB6. Among the lumped mechanisms evaluated, SAPRC07 best reproduced the chemical behavior of the explicit MCMv331, making it the recommended choice for regulatory modeling of winter O₃ episodes. CB6 may be suitable for pollutant concentration estimation but lacks the detail needed to understand the underlying chemical processes.

The findings of this study can help regulatory agencies develop effective O₃ mitigation strategies in the Uinta Basin and similar oil and gas producing regions experiencing wintertime O₃ pollution. Alkanes and aromatics from oil and gas operations are the primary emission targets for reducing winter O₃. Alkanes dominate O₃ formation and serve as the main precursors for most carbonyl production, while aromatics contribute through their efficient multi-step oxidation chemistry. Identifying and controlling the sources of these two NMOC groups would effectively mitigate wintertime O₃ episodes. The primary uncertainty related to this study is that the sensitivity analysis output across chemical mechanisms may vary in different regions due to differences in emission source profiles, meteorological conditions, and topographical characteristics, all of which influence NMOC composition, radical cycling, and pollutant accumulation.

Code availability: The F0AM Box model script can be provided by the corresponding author upon request.

Data availability: Measurement data used in this study are available at <https://www.usu.edu/binghamresearch/data-access>.

Author contribution: SL and LD planned the overall research framework and study objectives. LD conducted all atmospheric chemistry simulations and data processing. LD prepared the initial manuscript draft, including figures and interpretation of model results. SL provided critical revisions, contributed to the interpretation of findings, and supervised the entire project.

Competing interests: The authors declare that they have no conflict of interest.

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