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Key Points:

- Emissions of C₂-C₅ alkanes from oil and gas production maximize their contribution to O₃ enhancements over the central United States
- The Colorado Front Range is the O₃ non-attainment area that is most impacted by C₂-C₅ alkanes from the oil and gas sector
- Simulations indicate that oil and gas C₂-C₅ alkane emissions perturb remote O₃ production through increased NO_x export via PAN chemistry

Supporting Information:

Supporting Information S1

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Impacts of Emissions of C₂-C₅ Alkanes From the U.S. Oil and Gas Sector on Ozone and Other Secondary Species

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Abstract Inside many U.S. oil and gas-producing regions, the oil and gas sector dominates local anthropogenic emission fluxes of C_2 - C_5 alkanes. Here, we present a detailed analysis of the impact of these emissions on secondary species production over the continental United States using the GEOS-Chem model. Oil- and gas-producing areas in the central United States show the highest summertime surface ozone (O₃) enhancements due to oil and gas C_2 - C_5 alkane emissions. The Colorado Front Range is the most impacted 8-hr O₃ non-attainment area in the United States with 3-hr daytime instantaneous O₃ enhancements >4 ppb. From three selected non-attainment areas, the Colorado Front Range has (1) the lowest monthly mean VOC reactivity (1.5 s^{-1}); (2) the highest percent contribution of oil and gas sources (52%) to calculated VOC reactivity; and (3) the largest relative increases in PAN (peroxyacetyl nitrate), PPN (peroxypropionyl nitrate), and >C_4 alkyl nitrates. Enhanced abundances of PAN, PPN, and >C_4 alkyl nitrates have the potential to perturb remote O₃ production through increased NO_x export to remote regions via PAN chemistry. Globally, simulated C_2 - C_5 alkane emissions from the U.S. oil and gas sector contribute 0.5 Tg (~0.17%) to the tropospheric O₃ burden with a ~0.27% contribution in the Northern Hemisphere.

1. Introduction

Anthropogenic activity is a significant source of volatile organic compounds (VOC) in the United States. Although at a national level, anthropogenic VOC emissions decreased 11% from 2002 to 2011, VOC emissions from the U.S. oil and gas sector increased by 400% over the same period (Allen, 2016). Changes in isomeric ratios of C_4 - C_5 alkanes between 2001 and 2015 suggest an increasing influence of emissions from the oil and gas sector (Rossabi & Helmig, 2018). In a recent study by Fann et al. (2018), states in the central and eastern United States show the highest estimated health impacts associated to emissions from the oil and gas sector in the year 2025. Relative to methane (CH_4), C_2 - C_5 alkanes have the highest emission rates for non-methane VOCs emitted by oil and gas sources (Bourtsoukidis et al., 2019; Donoso et al., 1996; J. B. Gilman et al., 2010; Jessica B. Gilman et al., 2013; Goetz et al., 2017; Helmig et al., 2014; Katzenstein et al., 2003; Pétron et al., 2012; Thompson et al., 2014; Warneke et al., 2014). Emissions of C₂-C₅ alkanes from the oil and gas sector have resulted in enhanced abundances of these species throughout the Northern Hemisphere troposphere with particularly large enhancements over the central and eastern United States (Tzompa-Sosa et al., 2019). However, despite the high emission rates of C_2 - C_5 alkanes, relatively few studies have examined the contribution of these species to ozone (O_3) production at the surface (Edwards et al., 2013; Field et al., 2015; Helmig et al., 2016; Kort et al., 2016; McDuffie et al., 2016; Rappenglück et al., 2014; Tan, 2012). The C₂-C₅ alkanes have relatively low initial OH reactivity. However, Lindaas et al. (2019) show that in high abundances, these species can provide ample opportunities to recycle NO_x through RO_2 production at multiple stages of oxidation. The total VOC contribution to O_3 mixing ratios highly depends on meteorological, seasonal, and geographical conditions, as well as regional transport and local VOC and NO_x sources; thus, the estimates cannot be generalized or extrapolated across various oil and gas basins.

Although U.S. O_3 mixing ratios nationwide have been decreasing since 1980, from 2010 to 2017, the trend flattened out in many locations (U.S. EPA, 2018). Much of the research of the impacts of emissions from the oil and gas sector on O_3 has focused on the Colorado Front Range. Cheadle et al. (2017) estimated that oil and gas O_3 precursors contribute up to 30 ppb to summertime O_3 mixing ratios on individual days in the Northern Front Range of Colorado, where oil and gas development is the primary VOC source by mass (Eisele et al., 2009; *Jessica B.* Gilman et al., 2013). In this region, oil and gas alkane emissions contribute on average ~20% to regional photochemical O_3 production and ~50% to the regional VOC OH reactivity



during summer months (McDuffie et al., 2016). On high O_3 days, 30–40% of the O_3 production can be attributed to the oil and gas sector (Pfister et al., 2017). Lindaas et al. (2019) show that high O_3 days in the Colorado Front Range are also accompanied by high ratios of peroxypropionyl nitrate (PPN) to peroxyacetyl nitrate (PAN) and that propane (C_3H_8) and larger alkanes, primarily from the oil and gas industry, drive these high ratios. Despite their low O_3 production by mass (Russell et al., 1995), Helmig et al. (2016) estimated that a yearly increase of 4.2% (2009–2014) in U.S. C_2 - C_5 alkanes emissions could contribute to enhancements in summertime surface O_3 of up to 0.5 ppb yr⁻¹ inside U.S. oil and gas-producing regions.

This study uses U.S. emissions that include updates for C_2 - C_5 alkanes over oil and gas-producing regions within a chemical transport model (GESO-Chem). Using several simulations, we investigate the contribution of C_2 - C_5 alkane emissions from the U.S. oil and gas industry to regional VOC reactivity, oxidized nitrogen partitioning, and O_3 abundances at regional and global scales.

2. Model Configuration

Our simulations use GEOS-Chem model version 10-01 (Bey et al., 2001) driven by off-line GEOS-5 assimilated meteorological fields with 47 vertical levels. The U.S. anthropogenic emissions correspond to a model-ready version of the 2011 NEI (National Emission Inventory) that is part of the EPA 2011v6.3 emissions modeling platform (U.S. EPA, 2016; https://www.epa.gov/air-emissions-modeling/2011-version-63-technical-support-document), which was modified and implemented into GEOS-Chem by Tzompa-Sosa et al. (2019). NO_x (NO_x = NO + NO₂) emission fluxes correspond to a total of 3.7 Tg N (nitrogen) for the year 2011. This total is lower compared to modeled emissions of the 2011 NEIv1 of 4.3 Tg N and similar to an unadjusted 2013 estimate of 3.5 Tg N by Travis et al. (2016).

Relevant to this study, the implemented and modified 2011NEI include updated emission estimates from the oil and gas industry, adjustments to C_4 - C_5 alkane emissions, and considered C_3H_8 , benzene, and acetone as explicit species. From now on, this emission inventory will be referred as "updated 2011NEI." The updated 2011NEI in our 2011 baseline simulation has total emissions of ethane (C_2H_6), C_3H_8 , and C_4 - C_5 alkanes are 1.4 Tg, 1.0 Tg, and 7.0 TgC, respectively. Our C_2H_6 total is ~50% higher compared to modeled emissions of the 2011 NEIv1 and ~10% higher compared to an estimate made by Tzompa-Sosa et al. (2017). For C_3H_8 , the U.S. total here is much higher than what is included in the 2011 NEIv1 emissions (216% greater, supporting information [SI] Table S1). U.S. total emissions of C_4 - C_5 alkanes are estimated as 36% of the total paraffin emissions. A detailed description of this calculation can be found in Tzompa-Sosa et al. (2019). Figures S1–S4 show the changes in spatial distribution of NO and C_4 - C_5 alkanes emissions.

In this study, we investigate the contribution of C_2 - C_5 alkane emissions from the U.S. oil and gas industry to O_3 abundances at regional and global scales using two emission scenarios. The first emission scenario (baseline) uses a complete emission configuration, while in the second, we turn off all C_2 - C_5 alkane emissions from the U.S. oil and gas industry (OG-off). U.S. impacts to O_3 abundances were estimated using two nested simulations ($0.5^\circ \times 0.6^\circ$) over North America (40° to 140° W and 10° to 70° N) for the year 2011. Each nested simulation uses boundary conditions from a $2^\circ \times 2.5^\circ$ simulation with a spin-up of 18 months and the same emission inventory configuration as their corresponding nested runs. The time steps for the emissions are injected in the first (bottom) layer of the model. We use the $2^\circ \times 2.5^\circ$ simulations to calculate global impacts from the U.S. oil and gas industry to global and hemispheric O_3 abundances. Additionally, we include results from two emission scenarios with 60% and 30% reductions in U.S. anthropogenic NO_x emissions (section 3.2).

3. Results

3.1. Modeled U.S. Emissions of O₃ Precursors

3.1.1. Anthropogenic NO_x and Biogenic VOCs Emissions

The impact of the emissions of C_2 - C_5 alkanes on O_3 production over the United States can only be understood in the context of other O_3 precursors. There are large spatial gradients in the emissions of C_2 - C_5 alkanes, their relative contribution to overall OH reactivity is quite variable across the United States, and O_3 production is also dependent on NO_x abundance. Thus, we provide a description of the spatial





Figure 1. 2011 summertime (June, July and August) monthly average U.S. anthropogenic emission fluxes of NO_X (left panel) and biogenic emissions of isoprene (right panel).

distribution of other relevant emissions here. Our model simulation includes seven different anthropogenic and biogenic sources of NO_x (soil, biomass burning, biofuel, lightning, fertilizers, anthropogenic withoutairplanes-, and airplanes). Anthropogenic sources (including emissions from aircraft, biofuels, and fertilizer use) are responsible for 72% of the total U.S. emissions of NO_x. Emissions of NO_x are largest in urban areas. Consequently, NO_x emissions show a west-to-east gradient with higher emissions over the eastern United States, where more urban areas are located (Figure 1a). However, some regions with high NO_x emissions also correspond to semi-rural areas where oil and gas extraction is abundant. Even though NO_x emissions from the oil and gas sector represent <5% of total U.S. NO_x emissions, these emissions have increased by 94% between 2002 and 2011 compared to a 40% decrease of total anthropogenic emissions (Allen, 2016). Figure 1a shows summertime (June, July, and August) monthly average NO emissions for the year 2011. NO_x emission fluxes have low seasonality in terms of their spatial distribution and magnitude.

Biogenic VOCs are important O_3 precursors in some U.S. regions. The terrestrial biosphere is the largest source of VOCs over the United States; the highest emission fluxes occur over the southeastern United States, and they peak during summer months (Geron et al., 1997; Guenther et al., 2006; Sindelarova et al., 2014; Ying et al., 2015). To illustrate the typical spatial distribution of biogenic emissions, Figure 1b shows summertime isoprene emission fluxes.

3.1.2. Anthropogenic Emissions of C_2 - C_5 Alkanes and Contribution From the Oil and Gas Sector Anthropogenic emission fluxes of C_2 - C_5 alkanes have low seasonality and occur across the entire United States (Figure 2a). Emissions of C_2 - C_5 alkanes from the oil and gas sector are mainly clustered over the central United States (Figure 2b). At a national level, oil and gas sources dominate emissions of C_2 - H_6 and C_3 H₈, and urban sources (e.g., automobile combustion and fugitive emissions from gasoline and diesel distribution) dominate C_4 - C_5 alkane emissions. However, inside oil-and-gas-producing basins this sector is the primary source of C_2 H₆ and C_3 H₈ and C_4 - C_5 alkanes. Overall the oil and gas sector dominates local anthropogenic (urban and rural) emission fluxes of C_2 - C_5 alkanes with contributions >70% (Figure 2c). Our estimates of the oil and gas contribution to local total anthropogenic emissions of C_2 - C_5 alkanes inside individual U.S. oil and gas basins agree with prior studies [*Jessica B.* Gilman et al., 2013; Peischl et al., 2016; Warneke et al., 2014].

3.2. Monthly Mean Daytime O3 Mixing Ratios at the Surface

We compare monthly mean daytime O_3 mixing ratios at the surface from our baseline simulation to Air Quality System (AQS, https://www.epa.gov/aqs) data. For the baseline simulation, we estimate the monthly mean daytime O_3 mixing ratio using 3-hr instantaneous model output. To be consistent, we use corresponding AQS observations and calculate the model bias (Model—AQS). The emissions of O_3 precursors in our baseline simulation result in a consistent nation-wide overestimation of observed daytime O_3 mixing ratios at the surface. The bias occurs throughout the year and is highest during August 2011 (Figure 3). August is the month with not only the highest averaged daytime surface O_3 bias (18.8 ppb) but also with the highest tropospheric O_3 mixing ratios throughout the column. The calculated normalized mean bias (NMB) for





Figure 2. Annual average of emission fluxes of C_2 - C_5 (ngC m² s⁻¹, panels a and b) and percentage contribution of oil and gas emission sources to total anthropogenic fluxes of C_2 - C_5 (panel c).



Figure 3. Comparison between observed and modeled (baseline) monthly mean daytime surface O_3 mixing ratios for August 2011. Model results use daytime 3-hr instantaneous output. AQS observations correspond to the same daytime hours. In the left figure, the dash line represents 1:1 line, and the correlation coefficient (*r*) and normalized mean bias (NMB) are also shown. In the right panel, the filled circles represent the locations of AQS network sampling stations with 2011 O_3 data. The color of each filled circle represents the difference between modeled and observed (model—AQS) monthly mean surface O_3 mixing ratios.



each month ranges from 9.6% to 44.0% (Figure S1 in SI). Overall, lower NMB values and averaged biases occur in March, April, and May, while the highest correlation coefficient values occur in July, August, and September.

Travis et al. (2016) investigated O₃ mixing ratios in the southeast United States. They scaled the 2011NEIv1 to 2013 (multiplying NO_x emissions by 0.89) and found a NMB of 26–31% when comparing modeled versus observed O_3 vertical profiles. After reducing NO_x emissions of non-power-plant NEI emissions by 60%, their O_3 column bias was reduced to a NMB of 4.5%. They estimated that total U.S. anthropogenic fuel NO_x emissions were between 1.7 and 2.6 Tg N for the year 2013. We note that between the 2011NEIv1 used by Travis et al. (2016) and the updated 2011NEI used in this study, there are important changes in the emission totals and the spatial distribution of U.S. anthropogenic O_3 precursors (Table S1 and Figures S2–S5 in SI). We tested two emission scenarios with reductions of 60% and 30% in U.S. anthropogenic NO_x emissions. Similar to Travis et al. (2016), we reduced by 60 and 30% the non-power plant NO_x emissions (excluding commercial marine vessels and railroad emissions) in the updated 2011NEI and kept the rest of the emissions as in our baseline simulation. The resulting total U.S. anthropogenic NOx emissions from these iterations were 2.8 Tg N (30% reduction) and 2.1 Tg N (60% reduction). For both emission scenarios summertime O_3 mixing ratios were 1–3 ppb higher than our baseline simulation over most of the United States. It is unclear if our systematic overestimation of observed summertime surface O₃ mixing ratios stems from a misrepresentation of U.S. emissions of O₃ precursors or from other processes such as dry deposition to vegetation (Silva & Heald, 2018). Silva and Heald (2018) found that correcting dry deposition biases over both coniferous and deciduous forests (located in the Midwestern United States) led to a decrease in summer surface O_3 mixing ratios of approximately 2 ppb. We are not the first study to point out this issue. There are known unresolved GEOS-Chem surface biases of summertime O₃ mixing ratios (Hu et al., 2018; Sherwen et al., 2016; Travis et al., 2016). GEOS-Chem boundary layer appears to have excessive vertical mixing (Travis et al., 2016), possibly due to an overestimation of the sensible heat flux (Holtslag & Boville, 1993). Also, the combined implementation of recent improvements in GEOS-Chem chemistry for halogens (Sherwen et al., 2016), aromatic hydrocarbons (Yan et al., 2019), and short-chain alkyl nitrates (C_1 - C_3) RONO2; Fisher et al., 2018) is expected to better reproduce observed O_3 mixing ratios near the surface.

3.3. Impact of C₂-C₅ Alkane Emissions From Oil and Gas on U.S. O₃ Abundances

The difference in O₃ mixing ratios between the baseline simulation and the simulation without emissions of C_2 - C_5 alkanes from the oil and gas sector (OG-off) provides an estimate of the impact of these emissions on O_3 mixing ratios throughout the column. Figure 4 shows seasonal average O_3 enhancements in the boundary layer (defined here as the average of model levels below 2 km). Results show that while the emission rates have low seasonality, their impact on boundary layer O_3 mixing ratios varies by season and altitude due to seasonal variations in meteorological parameters and thus reaction rates. The "ozone season" is not consistent across the United States. For example, it spans March to September in Colorado, March to October in Northern Texas, January to December along the Texas Gulf Coast, and April to October in Pennsylvania (https://www3.epa.gov/ttnamti1/archive/files/ambient/criteria/reldocs/seasons.pdf, accessed on March 20, 2020). Higher O₃ enhancements occur during summertime over the central United States, and these enhancements are largest below 1 km. Maximum enhancements occur over major oil and gas-producing areas in eastern Colorado, Kansas, and the Texas-Oklahoma Panhandle. A first order of magnitude sensitivity study conducted by Helmig et al. (2016) estimated that the 4.2%/year increase of United States. C2-C5 alkane emissions over the period 2009-2014 increased summertime seasonal average surface O₃ by 0.07–0.50 ppb/year over the central part of the United States. Their simulations also indicated that other regions like California and the northeastern United States experience surface O₃ enhancements as a result of the dramatic rise in U.S. C_2 - C_5 alkane emissions. The results presented in Figure 4 are different from those presented in Helmig et al. (2016). Helmig et al. (2016) increased U.S. C₂-C₅ alkane emissions from all anthropogenic sectors (the increase was attributed to oil and gas sources) from the Hemispheric Transport of Air Pollutants, Phase II (HTAP2) emission inventory; thus, the spatial distribution of the emissions that were increased is different between the two approaches. Our study considers updated 2011NEI U.S. C_2 - C_5 alkane emissions from the oil and gas sector only; Figure 2c shows that these emissions are largely concentrated in the central part of the United States.



Journal of Geophysical Research: Atmospheres



Figure 4. 2011 seasonal mean O_3 enhancements driven by emissions of C_2 - C_5 alkanes from the U.S. oil and gas industry.

The highest surface O_3 enhancements due to oil and gas C_2 - C_5 alkane emissions occur in August. Figure 5 shows average daytime surface O_3 enhancements from 3-hr instantaneous mean model output for August 2011. The central part of the United States is the most impacted region with monthly mean daytime O_3 enhancements up to 3 ppb in some model grid cells. Among all the U.S. O_3 non-attainment areas (Figure S6 in SI), the Northern Colorado Front Range has the highest surface O_3 enhancements resulting from C_2 - C_5 alkane emissions from the oil and gas sector. Figure 6 compares August 2011 3-hr daytime instantaneous O_3 enhancements over three O_3 non-attainment areas located inside major oil and gas-producing basins. The Northern Colorado Front Range O_3 non-attainment area shows simulated daytime O_3 enhancements up to 4 ppb that are driven by C_2 - C_5 alkane emissions from the oil and gas sector. As discussed in the introduction, there have been a number of recent studies aiming to quantify surface O_3 enhancements due to oil and gas emissions in the Northern Colorado Front Range.



Figure 5. August 2011 daytime average O_3 enhancements (calculated from simulated 3-hr instantaneous output) due to C_2 - C_5 alkanes emitted by the U.S. oil and gas sector.





Figure 6. August 2011 3-hr daytime instantaneous O_3 enhancements over three O_3 non-attainment areas located inside important oil and gas-producing basins.

Figures 4 and 5 show that outside the central part of the United States, the O_3 enhancements resulting from oil and gas C_2 - C_5 alkane emissions are lower. For example, the 3-hr daytime instantaneous O_3 enhancements over Dallas, TX, and Pittsburgh, PA are largely less than 1 ppb, a factor of 3 smaller than the enhancements estimated for the Colorado Front Range (Figure 5). Previous studies have investigated the contribution of oil and gas emissions to regional O_3 enhancements inside the oil and gas-producing basins encompassing these two O_3 non-attainment areas (Kemball-Cook et al., 2010; Pacsi et al., 2015; Roohani et al., 2017). Depending on the scenario approach and emission inventory configuration (e.g., base year of U.S. emissions, emission factors assigned for future scenarios, etc.), prior estimates of surface O_3 enhancements due to local oil and gas emissions vary from 0.6–5 ppb in Texas and 0.1–0.5 ppb in Pennsylvania.

3.4. Contribution of U.S. C₂-C₅ Alkane Emissions From the Oil and Gas Industry to the Hemispheric O_3 Burden

We estimate the contribution of C_2 - C_5 alkane emissions from the oil and gas sector to the hemispheric O_3 burden using two $2^{\circ} \times 2.5^{\circ}$ global simulations (baseline and OG-off). Tzompa-Sosa et al. (2019) estimated that the oil and gas industry is the largest anthropogenic source of C_2H_6 (90%) and C_3H_8 (84%), and this sector is the third largest source for C_4 - C_5 alkanes (26%) in the United States. The global tropospheric contribution of C_2 - C_5 alkane emissions from the U.S. oil and gas sector to the O_3 burden is 0.5 Tg for the year 2011, which represents 0.17% of the global tropospheric O_3 burden. Due to the short lifetime of C_2 - C_5 alkanes compared to the interhemispheric transport time, the highest O₃ enhancements are located over the Northern Hemisphere, where their contribution to the tropospheric O₃ burden is 0.27%. The highest contribution to O₃ surface mixing ratios over land areas downwind the United States occurs during August over northern Africa, where the enhancement is up to 0.30 ppb (Figure 7). A 2009-2014 simulation by Helmig et al. (2016), which considered an annual increase of 4.2% in C2-C5 alkane emissions from U.S. sources with constant emissions of CH_4 , $>C_5$ alkanes, and NO_x emissions, showed a similar spatial distribution of surface O₃ enhancements outside the U.S. during summertime. The Helmig et al. (2016) enhancements are an order of magnitude smaller because their results reflect only the impact of the 4.2% increase of U.S. C2-C5 alkane emissions, while our results show the 2011 enhancements due to total updated U.S. oil and gas C2-C5 alkane emissions.



Figure 7. Averaged surface O_3 enhancements due to U.S. emissions of C_2 - C_5 alkanes from the oil and gas sector for August 2011.







3.5. Impact of C2-C5 Alkane Emissions From Oil and Gas on VOC Reactivity

The primary tropospheric sink of C_2 - C_5 alkanes is oxidation via reaction with hydroxyl radicals (OH). The VOC reactivity is calculated by multiplying the rate constant of the reaction of each individual VOC with OH ($k_{OH,VOC}$) times the concentration of that species; the sum of these products is the total VOC OH reactivity [Abeleira et al., 2017; *Jessica B*. Gilman et al., 2013; McDuffie et al., 2016]. Here, we use simulated monthly average mixing ratios at the surface during August 2011 to calculate $k_{OH,VOC}$. Figure 8 shows regional VOC reactivity in each of the three selected O₃ non-attainment areas (see section 3.3) for our baseline and OG-off simulations. Additionally, we calculated the percent contribution of oil and gas sources to the regional VOC reactivity in each non-attainment area.

Figure 8 shows that among the three selected O₃ non-attainment areas, the Colorado Front Range has the lowest monthly mean VOC reactivity (1.5 s^{-1}) for the baseline simulation but the highest percent contribution of oil and gas sources (52%). The model attributes 47% (0.7 s⁻¹) of the 1.5 s⁻¹ VOC reactivity in this region to oil and gas C_2 - C_5 alkanes. Similarly, a recent study by Pfannerstill et al. (2019) around the Arabian Peninsula found the highest contribution from alkanes to total OH reactivity (on average 1.2 s⁻¹ or 9% of total OH reactivity) in the Arabian Gulf (also known as Persian Gulf). Among the regions in that study, the Arabian Gulf is the region that encompasses the largest number of gas fields. Compared to Dallas and Pittsburg (Rutter et al., 2015; Swarthout et al., 2015), the lower VOC reactivity in the Front Range is due lower biogenic emissions combined with minimal traffic-related alkenes and aromatics emissions [Abeleira et al., 2017; Jessica B. Gilman et al., 2013; McDuffie et al., 2016]. The model simulated VOC reactivity in the Front Range is on the lower end of previous summertime studies (e.g., Abeleira et al., 2017 estimated VOC reactivity values of $1.3-2.4 \text{ s}^{-1}$). However, we note that reported VOC reactivity values vary depending on the number of VOCs considered. For example, Abeleira et al. (2017) considered 31 non-methane VOC (NMVOC) species (including C2-C8 alkanes) and reported VOC reactivity values of 1.3–2.4 s⁻¹. Swarthout et al. (2013) measured three times as many NMVOC species (considering up to C₁₀ alkanes) and obtained a larger VOC reactivity range (2.0-12.0 s⁻¹). The GEOS-Chem model lumps VOC species (e.g., alkenes with more than 2 carbons, alkyl nitrates with more than 3 carbons) according to the similarity on their chemical mechanisms. The low VOC reactivity in our simulations may indicate that the emissions in the model are too low for the existing categories or that there are additional categories that should be included to more accurately simulate these regions. Figure 8 also indicates that the simulation without emissions of C_2 - C_5 alkanes from the oil and gas sector (OG-off) substantially perturbed the VOC reactivity in the Colorado Front Range compared to the other regions. Given the nonlinearity of O₃ chemistry and the potential for interactions between species, this may have introduced additional uncertainty into our results for this region.





Figure 9. Percent changes in oxidized reactive nitrogen partitioning driven by U.S. C_2 - C_5 alkane emissions from the oil and gas sector for August 2011 for three different O_3 non-attainment areas.

Dallas is the selected region with the highest simulated VOC reactivity (2.6 s^{-1}). In the simulation, isoprene plus its oxidation products, methacrolein and methyl vinyl ketone, dominate VOC reactivity; together they account for 44% of the VOC reactivity in this region (34% from isoprene alone). Oxygenated VOCs (formal-dehyde, acetaldehyde, acetone, and methyl ethyl ketone) account for 34% of the VOC reactivity in the simulation, and formaldehyde is the largest single contributor (26%) in the simulation. C₂-C₅ alkanes are responsible for just 8% (0.2 s^{-1}), and oil and gas C₂-C₅ alkane sources comprise 3.5% (0.1 s^{-1}) of the regional VOC reactivity in the simulation. Rutter et al. (2015) estimated that natural gas and fugitive emissions are responsible on average of 13% of the total OH reactivity. However, they did not provide an estimate of the VOC reactivity associated only with C₂-C₅ alkanes from the oil and gas sector. Nevertheless, the low regional contribution of oil and gas sources compared to biogenic sources is consistent across both studies.

For the Pittsburgh non-attainment area, we estimate a VOC reactivity of 2.1 s⁻¹. In this region, isoprene and its oxidation products account for approximately half of the VOC reactivity $(1.0 \text{ s}^{-1}; 0.8 \text{ s}^{-1} \text{ from isoprene})$. Similar to Dallas, oxygenated VOCs are the second largest contributors to VOC reactivity $(0.6 \text{ s}^{-1}, 30\%)$ and C_2 - C_5 alkanes from the oil and gas sector comprise just a fraction of the VOC reactivity $(0.04 \text{ s}^{-1}, 1.7\%)$. The model output in this region is comparable to recent VOC reactivity measurements by Swarthout et al. (2015). They found that isoprene dominated the biogenic contribution to VOC reactivity on average by 47%. However, if biogenic VOCs were excluded, C_1 - C_{10} alkanes comprised ~50% of the regional VOC reactivity, with CH₄ alone contributing to 35% of the non-biogenic VOC reactivity. The latter contribution estimated by Swarthout et al. (2015) highlights the impact of long-lived compounds (such as CH₄) to regional VOC reactivity. Future modeling studies, especially over oil and gas regions, should consider both, short and long lived alkane species, in order to provide a more accurate estimate of the main contributors to regional VOC OH reactivity.

3.6. Impacts to NO_y Partitioning

The model also shows that enrichments in C_2 - C_5 alkanes, driven by emissions from the oil and gas sector, cause differences in oxidized reactive nitrogen partitioning (Figure 9). The model shows that C_2 - C_5 alkanes increase the production of acyl peroxy nitrates and alkyl nitrates; the largest relative changes occur in the Colorado Front Range, and thus, we focus our discussion on this location. Surface observations of many key NO_y species were collected during summer 2015 at the Boulder Atmospheric Observatory (BAO). The measurement site was impacted by plumes of aged wildfire smoke for several weeks during summer 2015, so we provide some summary statistics for both the smoke-free portion of the data set and for the full data set. For NO_x, PAN, PPN, and HNO₃ summer 2015 smoke-free mean mixing ratios of these species were 5.39 \pm 5.3 (\pm 1 σ) ppb, 185 \pm 131 (\pm 1 σ) ppt, 22 \pm 22 (\pm 1 σ) ppt, and 0.43 \pm 0.60 (\pm 1 σ) ppb, respectively. For

 NO_x , PAN, PPN, and HNO₃ mean mixing ratios of these species were $5.73 \pm 5.7 (\pm 1\sigma)$ ppb, $223 \pm 159 (\pm 1\sigma)$ ppt, $27 \pm 25 (\pm 1\sigma)$ ppt, and $0.45 \pm 0.60 (\pm 1\sigma)$ ppb, respectively, in the full dataset (Lindaas et al., 2017; Lindaas et al., 2019). For comparison, the mean mixing ratios of these species for August 2011 in the simulation are 6.1 ppb, 337.6 ppt, 49.6 ppt, and 1.8 ppb, respectively. Modeled PAN and PPN are consistent with observations. Much prior attention has been given to evaluating the GEOS-Chem PAN simulation (Fischer et al., 2014), and the model version used here is not substantively different with respect to PAN than the Fischer et al. (2014) version with the exception of the improved U.S. alkane emissions. The production chemistry for PPN in the model has not been carefully evaluated. For NO_x , the updated 2011NEI simulation produced NO_x mixing ratios higher compared to 2015 observations in the region. We note that in Colorado absolute NO_x emissions in 2011NEI are roughly 10% higher compared to 2014NEI estimates (Cheadle et al., 2017). Also, work in the oil and gas Ulintah Basin by Ahmadov et al. (2015) estimated that NO_x emissions from the oil and gas sector might be overestimated by a factor of 4 in the 2011NEI. Regarding HNO₃, there are known gas phase HNO₃ biases in GEOS-Chem. The model has been shown to significantly overestimate concentrations over the United States, and model developments in wet scavenging are underway (Luo et al., 2019).

Though the molar yield varies depending on NO_x levels, acetaldehyde is produced in GEOS-Chem from C_2H_6 , C_3H_8 , and C_4 - C_5 alkanes (Millet et al., 2010); acetaldehyde is an immediate precursor for PAN (peroxyacetyl nitrate; $CH_3C(O)O_2NO_2$). PPN (peroxypropionyl nitrate; $CH_3CH_2C(O)O_2NO_2$) is the other PAN homologue that is included in the GEOS-Chem chemical mechanism. Enhanced PPN in the model is produced during the oxidation of the emissions of C_3H_8 and C_4 - C_5 alkanes. Additional C_2 - C_5 alkanes from the oil and gas sector also increase the production of $>C_4$ alkyl nitrates (model species R4N2; shown in Figure S7). The model version used here does not include C_1 - C_3 alkyl nitrates (Fisher et al., 2018). While the relative increases for PAN, PPN, and R4N2 are large, the relative decreases in NO and HNO₃ in the model are small. These species are much larger reservoirs.

Though direct comparisons are not possible given the model configuration and timing used here, changes in the model are qualitatively consistent with limited observations of secondary reactive nitrogen species in regions impacted by the oil and gas sector. For example, Lindaas et al. (2019) found elevated PPN to PAN ratios on elevated O_3 days observed during summer 2015 in the Colorado Front Range; idealized box model simulations initialized with simultaneous NMVOC measurements from that summer indicate that C_3H_8 and n-pentane are likely the dominant PPN precursors in this region. The simulations in Lindaas et al. (2019) support the hypothesis that alkane emissions from the oil and gas sector are major NMVOC precursors of PPN and PAN in Colorado Front Range. Similar high ratios were also observed during summer 2014 by Zaragoza et al. (2017), and they concluded that the PPN to PAN ratio was higher than other U.S. urban areas because of the higher abundance of alkanes from the oil and gas sector. Elevated mixing ratios of C_3 - C_4 alkyl nitrates have also been observed in rural Kansas, a region with major industrial activities associated with oil and natural gas extraction (Katzenstein et al., 2003).

4. Conclusions

We present the first detailed analysis of the impact of C_2 - C_5 alkane emissions from the oil and gas sector on secondary species production over the continental United States using the GEOS-Chem chemical transport model. The simulations imply that C_2 - C_5 alkane emissions from the oil and gas sector contribute to summertime O_3 over several U.S. regions, including 8-hr O_3 non-attainment areas. Our specific findings are summarized as follows:

(1) The highest surface O_3 enhancements due to oil and gas C_2 - C_5 alkane emissions occur in August below 1 km, and the maximum O_3 enhancements occur over major oil and gas-producing areas in eastern Colorado, Kansas, and the Texas-Oklahoma Panhandle. Emissions of C_2 - C_5 alkanes are mainly clustered over this central region of the United States, and these regions are characterized by lower anthropogenic emission fluxes of NO and biogenic VOC fluxes than the eastern United States.

(2) We calculate August 2011 3-hr daytime instantaneous O_3 enhancements over three O_3 non-attainment areas located inside important oil and gas-producing basins. This analysis shows that the Colorado Front



Range is the most impacted O_3 non-attainment area in the United States with 3-hr daytime instantaneous O_3 enhancements from C_2 - C_5 alkanes >4 ppb.

(3) To further investigate the impact of C_2 - C_5 alkanes on the photochemistry leading to O_3 production, we examine monthly mean VOC reactivity for three O_3 non-attainment areas. The Colorado Front Range has the lowest monthly mean VOC reactivity (1.5 s⁻¹) for the baseline simulation but the highest percent contribution of oil and gas sources (52%).

(4) The model simulation also shows that C_2 - C_5 alkane emissions from the oil and gas sector impact the relative abundances of oxidized reactive nitrogen species. In particular, C_2 - C_5 alkane emissions from the oil and gas sector increase the production of PAN, PPN, and > C_4 alkyl nitrates. Thus, the emissions from the oil and gas sector have the potential to also perturb remote O_3 production through increased NO_x export to remote regions via PAN chemistry.

(5) We also calculate the contribution of C_2 - C_5 alkane emissions from the U.S. oil and gas sector to the global tropospheric O_3 burden. We estimate the contribution to be 0.5 Tg for the year 2011, representing ~0.17% of the global tropospheric O_3 burden. These emissions contribute ~0.27% to the Northern Hemisphere tropospheric O_3 burden.

In conclusion, the emissions from oil and gas extraction appear to contribute to a new VOC mixture with a spatial distribution that is different from national patterns in VOCs, otherwise primarily from urban and biogenic sources. Our analysis only considered the impact of C_2 - C_5 alkane emissions from the oil and gas sector on secondary species production. In reality, the oil and gas sector also contributes to the emissions of other hydrocarbon precursors, such as small unsaturated hydrocarbons and aromatic species. The present work builds on efforts to better represent the emissions of C_2 - C_5 alkanes from the U.S. oil and gas industry in global models. To quantify the full impact of the U.S. oil and gas sector on O_3 production on regional-to-local scales, further work is needed to evaluate and improve the way other species are represented.

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References

- Abeleira, A., Pollack, I. B., Sive, B., Zhou, Y., Fischer, E. V., & Farmer, D. K. (2017). Source characterization of volatile organic compounds in the Colorado northern front range metropolitan area during spring and summer 2015. *Journal of Geophysical Research: Atmospheres,* 122, 3595–3613. https://doi.org/10.1002/2016jd026227
- Ahmadov, R., McKeen, S., Trainer, M., Banta, R., Brewer, A., Brown, S., et al. (2015). Understanding high wintertime ozone pollution events in an oil- and natural gas-producing region of the western US. Atmospheric Chemistry and Physics, 15(1), 411–429. https://doi.org/ 10.5194/acp-15-411-2015
- Allen, D. T. (2016). Emissions from oil and gas operations in the United States and their air quality implications. Journal of the Air & Waste Management Association (1995), 66(6), 549–575. https://doi.org/10.1080/10962247.2016.1171263
- Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., et al. (2001). Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. *Journal of Geophysical Research*, 106(D19), 23,073–23,095. https://doi.org/ 10.1029/2001jd000807
- Bourtsoukidis, E., Ernle, L., Crowley, J. N., Lelieveld, J., Paris, J.-D., Pozzer, A., et al. (2019). Non-methane hydrocarbon (C2–C8) sources and sinks around the Arabian peninsula. *Atmospheric Chemistry and Physics*, 19(10), 7209–7232. https://doi.org/10.5194/acp-19-7209-2019
- Cheadle, L. C., Oltmans, S. J., Petron, G., Schnell, R. C., Mattson, E. J., Herndon, S. C., et al. (2017). Surface ozone in the Colorado northern front range and the influence of oil and gas development during FRAPPE/DISCOVER-AQ in summer 2014. *Elementa Science of the Anthropocene*, 5(0), 61. https://doi.org/10.1525/elementa.254
- Donoso, L., Romero, R., Rondón, A., Fernandez, E., Oyola, P., & Sanhueza, E. (1996). Natural and anthropogenic C2 to C6 hydrocarbons in the central-eastern Venezuelan atmosphere during the rainy season. *Journal of Atmospheric Chemistry*, 25(2), 201–214. https://doi.org/ 10.1007/bf00053791
- Edwards, P. M., Young, C. J., Aikin, K., deGouw, J., Dubé, W. P., Geiger, F., et al. (2013). Ozone photochemistry in an oil and natural gas extraction region during winter: Simulations of a snow-free season in the Uintah Basin, Utah. *Atmospheric Chemistry and Physics*, *13* (17), 8955–8971. https://doi.org/10.5194/acp-13-8955-2013
- Eisele, A. P., Hannigan, M., Milford, J., Helmig, D., Milmoe, P., Thomas, G., et al. (2009). Understanding air toxics and carbonyl pollutant sources in Boulder County, Colorado, Final Report, U.S. Environmental Protection Agency, Region 8. Retrieved from https://www3.epa. gov/ttnamti1/files/20052006csatam/BCPHAirToxicsReportEPA.pdf
- Fann, N., Baker, K. R., Chan, E. A. W., Eyth, A., Macpherson, A., Miller, E., & Snyder, J. (2018). Assessing human health PM2.5 and ozone impacts from U.S. Oil and Natural Gas Sector Emissions in 2025. *Environmental Science & Technology*, 52(15), 8095–8103. https://doi. org/10.1021/acs.est.8b02050
- Field, R. A., Soltis, J., McCarthy, M. C., Murphy, S., & Montague, D. C. (2015). Influence of oil and gas field operations on spatial and temporal distributions of atmospheric non-methane hydrocarbons and their effect on ozone formation in winter. *Atmospheric Chemistry* and Physics, 15(6), 3527–3542. https://doi.org/10.5194/acp-15-3527-2015
- Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., et al. (2014). Atmospheric peroxyacetyl nitrate (PAN): A global budget and source attribution. Atmospheric Chemistry and Physics, 14(5), 2679–2698. https://doi.org/10.5194/acp-14-2679-2014



- Fisher, J. A., Atlas, E. L., Barletta, B., Meinardi, S., Blake, D. R., Thompson, C. R., et al. (2018). Methyl, ethyl, and propyl nitrates: Global distribution and impacts on reactive nitrogen in remote marine environments. *Journal of Geophysical Research: Atmospheres*, 123(21), 12,429–412,451. https://doi.org/10.1029/2018jd029046
- Geron, C. D., Nie, D., Arnts, R. R., Sharkey, T. D., Singsaas, E. L., Vanderveer, P. J., et al. (1997). Biogenic isoprene emission: Model evaluation in a southeastern United States bottomland deciduous forest. *Journal of Geophysical Research*, 102(D15), 18,889–18,901. https:// doi.org/10.1029/97jd00968
- Gilman, J. B., Burkhart, J. F., Lerner, B. M., Williams, E. J., Kuster, W. C., Goldan, P. D., et al. (2010). Ozone variability and halogen oxidation within the Arctic and sub-Arctic springtime boundary layer. Atmospheric Chemistry and Physics, 10(21), 10,223–10,236. https:// doi.org/10.5194/acp-10-10223-2010
- Gilman, J. B., Lerner, B. M., Kuster, W. C., & de Gouw, J. A. (2013). Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado. *Environmental Science & Technology*, 47(3), 1297–1305. https://doi.org/10.1021/es304119a
- Goetz, J. D., Avery, A., Werden, B., Floerchinger, C., Fortner, E. C., Wormhoudt, J., et al. (2017). Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale. *Elementa Science of the Anthropocene*, 5(0), 1. https://doi.org/ 10.1525/journal.elementa.182
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., & Geron, C. D. (2006). Estimates of global terrestrial isoprene emissions using MEGAN (model of emissions of gases and aerosols from nature). Atmospheric Chemistry and Physics, 6(11), 3181–3210. https://doi. org/10.5194/acp-6-3181-2006
- Helmig, D., Rossabi, S., Hueber, J., Tans, P., Montzka, S. A., Masarie, K., et al. (2016). Reversal of global atmospheric ethane and propane trends largely due to US oil and natural gas production. *Nature Geoscience*, 9(7), 490–495. https://doi.org/10.1038/ngeo2721
- Helmig, D., Thompson, C. R., Evans, J., Boylan, P., Hueber, J., & Park, J. H. (2014). Highly elevated atmospheric levels of volatile organic compounds in the Uintah Basin, Utah. *Environmental Science & Technology*, 48(9), 4707–4715. https://doi.org/10.1021/ es405046r
- Holtslag, A. A. M., & Boville, B. A. (1993). Local versus nonlocal boundary-layer difusion in a global climate model. Journal of Climate, 6, 1825–1842. https://doi.org/10.1175/1520-0442(1993)006<1825:lvnbld>2.0.co;2
- Hu, L., Keller, C. A., Long, M. S., Sherwen, T., Auer, B., Da Silva, A., et al. (2018). Global simulation of tropospheric chemistry at 12.5 km resolution: Performance and evaluation of the GEOS-Chem chemical module (v10–1) within the NASA GEOS Earth system model (GEOS-5 ESM). *Geoscientific Model Development*, 11(11), 4603–4620. https://doi.org/10.5194/gmd-11-4603-2018
- Katzenstein, A. S., Doezema, L. A., Simpson, I. J., Blake, D. R., & Rowland, F. S. (2003). Extensive regional atmospheric hydrocarbon pollution in the southwestern United States. *Proceedings of the National Academy of Sciences of the United States of America*, 100(21), 11,975–11,979. https://doi.org/10.1073/pnas.1635258100
- Kemball-Cook, S., Bar-Ilan, A., Grant, J., Parker, L., Jung, J., Santamaria, W., et al. (2010). Ozone impacts of natural gas development in the Haynesville shale. *Environmental Science & Technology*, 44(24), 9357–9363. https://doi.org/10.1021/es1021137
- Kort, E. A., Smith, M. L., Murray, L. T., Gvakharia, A., Brandt, A. R., Peischl, J., et al. (2016). Fugitive emissions from the Bakken shale illustrate role of shale production in global ethane shift. *Geophysical Research Letters*, 43(9), 4617–4623. https://doi.org/10.1002/ 2016gl068703
- Lindaas, J., Farmer, D. K., Pollack, I. B., Abeleira, A., Flocke, F., & Fischer, E. V. (2019). Acyl Peroxy nitrates link oil and Natural gas emissions to high ozone abundances in the Colorado front range during summer 2015. *Journal of Geophysical Research: Atmospheres*, 124), 2336–2350. https://doi.org/10.1029/2018jd028825
- Lindaas, J., Farmer, D. K., Pollack, I. B., Abeleira, A., Flocke, F., Roscioli, R., et al. (2017). Changes in ozone and precursors during two aged wildfire smoke events in the Colorado front range in summer 2015. Atmospheric Chemistry and Physics, 17(17), 10,691–10,707. https:// doi.org/10.5194/acp-17-10691-2017
- Luo, G., Yu, F., & Schwab, J. (2019). Revised treatment of wet scavenging processes dramatically improves GEOS-Chem 12.0.0 simulations of surface nitric acid, nitrate, and ammonium over the United States. *Geoscientific Model Development*, 12(8), 3439–3447. https://doi.org/ 10.5194/gmd-12-3439-2019
- McDuffie, E. E., Edwards, P. M., Gilman, J. B., Lerner, B. M., Dubé, W. P., Trainer, M., et al. (2016). Influence of oil and gas emissions on summertime ozone in the Colorado northern front range. *Journal of Geophysical Research: Atmospheres*, 121, 8712–8729. https://doi.org/ 10.1002/2016jd025265
- Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., et al. (2010). Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations. *Atmospheric Chemistry and Physics*, 10(7), 3405–3425. https://doi.org/10.5194/acp-10-3405-2010
- Pacsi, A. P., Kimura, Y., McGaughey, G., McDonald-Buller, E. C., & Allen, D. T. (2015). Regional ozone impacts of increased natural gas use in the Texas power sector and development in the eagle ford shale. *Environmental Science & Technology*, 49(6), 3966–3973. https://doi. org/10.1021/es5055012
- Peischl, J., Karion, A., Sweeney, C., Kort, E. A., Smith, M. L., Brandt, A. R., et al. (2016). Quantifying atmospheric methane emissions from oil and natural gas production in the Bakken shale region of North Dakota. *Journal of Geophysical Research: Atmospheres*, 121, 6101–6111. https://doi.org/10.1002/2015jd024631
- Pétron, G., Frost, G., Miller, B. R., Hirsch, A. I., Montzka, S. A., Karion, A., et al. (2012). Hydrocarbon emissions characterization in the Colorado front range: A pilot study. *Journal of Geophysical Research*, 117(D4), n/a. https://doi.org/10.1029/2011jd016360
- Pfannerstill, E. Y., Wang, N., Edtbauer, A., Bourtsoukidis, E., Crowley, J. N., Dienhart, D., et al. (2019). Shipborne measurements of total OH reactivity around the Arabian peninsula and its role in ozone chemistry. *Atmospheric Chemistry and Physics*, *19*(17), 11,501–11,523. https://doi.org/10.5194/acp-19-11501-2019
- Pfister, G., Flocke, F., Hornbrook, R. S., Orlando, J. J., Lee, S., & Schroeder, J. (2017). Process-Based and Regional Source Impact Analysis for FRAPPÉ and DISCOVER-AQ 2014 Rep. In National Center for Atmospheric Research and Atmospheric Chemistry Observations and Modeling Laboratory. Boulder, CO:National Center for Atmospheric Research (NCAR). Retrieved from https://pdfs.semanticscholar. org/f398/ee19043fc43e1f1398c51228de208c0d7b1d.pdf
- Rappenglück, B., Ackermann, L., Alvarez, S., Golovko, J., Buhr, M., Field, R. A., et al. (2014). Strong wintertime ozone events in the upper Green River basin, Wyoming. Atmospheric Chemistry and Physics, 14(10), 4909–4934. https://doi.org/10.5194/acp-14-4909-2014
- Roohani, Y. H., Roy, A. A., Heo, J., Robinson, A. L., & Adams, P. J. (2017). Impact of natural gas development in the Marcellus and Utica shales on regional ozone and fine particulate matter levels. *Atmospheric Environment*, 155, 11–20. https://doi.org/10.1016/j. atmosenv.2017.01.001
- Rossabi, S., & Helmig, D. (2018). Changes in atmospheric butanes and pentanes and their isomeric ratios in the continental United States. Journal of Geophysical Research: Atmospheres, 123, 3772–3790. https://doi.org/10.1002/2017jd027709





- Russell, A., Milford, J., Bergin, M. S., McBride, S., McNair, L., Yang, Y., et al. (1995). Urban ozone control and atmospheric reactivity of organic gases. *Science*, 269(28 July 1995(5223), 491–495. https://doi.org/10.1126/science.269.5223.491
- Rutter, A. P., Griffin, R. J., Cevik, B. K., Shakya, K. M., Gong, L. W., Kim, S., et al. (2015). Sources of air pollution in a region of oil and gas exploration downwind of a large city. *Atmospheric Environment*, *120*, 89–99. https://doi.org/10.1016/j.atmosenv.2015.08.073
- Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., et al. (2016). Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem. Atmospheric Chemistry and Physics, 16(18), 12,239–12,271. https://doi. org/10.5194/acp-16-12239-2016
- Silva, S. J., & Heald, C. L. (2018). Investigating dry deposition of ozone to vegetation. Journal of Geophysical Research: Atmospheres, 123, 559–573. https://doi.org/10.1002/2017jd027278
- Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., et al. (2014). Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. *Atmospheric Chemistry and Physics*, 14(17), 9317–9341. https://doi.org/10.5194/acp-14-9317-2014
- Swarthout, R. F., Russo, R. S., Zhou, Y., Hart, A. H., & Sive, B. C. (2013). Volatile organic compound distributions during the NACHTT campaign at the Boulder atmospheric observatory: Influence of urban and natural gas sources. *Journal of Geophysical Research*, 118(18), 10,614–10,637. https://doi.org/10.1002/jgrd.50722
- Swarthout, R. F., Russo, R. S., Zhou, Y., Miller, B. M., Mitchell, B., Horsman, E., et al. (2015). Impact of Marcellus shale natural gas development in Southwest Pennsylvania on volatile organic compound emissions and regional air quality. *Environmental Science & Technology*, 49(5), 3175–3184. https://doi.org/10.1021/es504315f

Tan, J.-H. (2012). Non-methane hydrocarbons and their ozone formation potentials in Foshan, China. Aerosol and Air Quality Research, 12(3), 387–398. https://doi.org/10.4209/aaqr.2011.08.0127

- Thompson, C. R., Hueber, J., & Helmig, D. (2014). Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado. *Elementa: Science of the Anthropocene, 2*, 000035. https://doi.org/10.12952/journal. elementa.000035
- Travis, K. R., Jacob, D. J., Fisher, J. A., Kim, P. S., Marais, E. A., Zhu, L., et al. (2016). Why do models overestimate surface ozone in the Southeast United States? *Atmospheric Chemistry and Physics*, *16*(21), 13,561–13,577. https://doi.org/10.5194/acp-16-13561-2016
- Tzompa-Sosa, Z. A., Henderson, B. H., Keller, C. A., Travis, K., Mahieu, E., Franco, B., et al. (2019). Atmospheric implications of large C2-C5 alkane emissions from the U.S. Oil and Gas Industry. *Journal of Geophysical Research: Atmospheres*, 124, 1148–1169. https://doi. org/10.1029/2018jd028955
- Tzompa-Sosa, Z. A., Mahieu, E., Franco, B., Keller, C. A., Turner, A. J., Helmig, D., et al. (2017). Revisiting global fossil fuel and biofuel emissions of ethane. Journal of Geophysical Research: Atmospheres, 122, 2493–2512. https://doi.org/10.1002/2016JD025767
- U.S. Environmental Protection Agency (2016). Technical support document: Preparation of emissions inventories for the version 6.3, 2011 emissions modeling platform, Edited by Environmental Protection Agency.
- U.S. Environmental Protection Agency (2018). Ozone Trends. Edited by Environmental Protection Agency. Accessed June 10, 2019. Retrieved from https://www.epa.gov/air-trends/ozone-trends
- Warneke, C., Geiger, F., Edwards, P. M., Dube, W., Pétron, G., Kofler, J., et al. (2014). Volatile organic compound emissions from the oil and natural gas industry in the Uintah Basin, Utah: Oil and gas well pad emissions compared to ambient air composition. Atmospheric Chemistry and Physics, 14(20), 10,977–10,988. https://doi.org/10.5194/acp-14-10977-2014
- Yan, Y., Cabrera-Perez, D., Lin, J., Pozzer, A., Hu, L., Millet, D. B., et al. (2019). Global tropospheric effects of aromatic chemistry with the SAPRC-11 mechanism implemented in GEOS-Chem version 9-02. *Geoscientific Model Development*, 12(1), 111–130. https://doi.org/ 10.5194/gmd-12-111-2019
- Ying, Q., Li, J., & Kota, S. H. (2015). Significant contributions of isoprene to summertime secondary organic aerosol in eastern United States. Environmental Science & Technology, 49(13), 7834–7842. https://doi.org/10.1021/acs.est.5b02514
- Zaragoza, J., Callahan, S., McDuffie, E. E., Kirkland, J., Brophy, P., Durrett, L., et al. (2017). Observations of acyl Peroxy nitrates during the front range air pollution and photochemistry Experiment (FRAPPÉ). Journal of Geophysical Research: Atmospheres, 122), 12,416–12,432. https://doi.org/10.1002/2017JD027337