VIA EMAIL

June 8, 2020

Colorado Air Quality Control Commission
Colorado Department of Public Health and Environment
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RE: Marginal Nonattainment Area requirements for the 2015 Ozone National Ambient Air Quality Standard

Dear Commissioners:

On behalf of the thousands of our members and supporters who are harmed by ozone pollution in the Denver Metro / North Front Range area, the Center for Biological Diversity, WildEarth Guardians, Public Employees for Environmental Responsibility (PEER), and Sierra Club are writing to submit comments on the Colorado Air Quality Control Commission's (Commission) consideration of approving the emissions statement, 2017 baseline year emissions inventory and SIP compliance certifications to be submitted to the EPA, satisfying Marginal Nonattainment Area requirements for the 2015 Ozone National Ambient Air Quality Standard. These comments focus on the 2017 baseline year emission inventory underreporting emissions, especially with regard to the oil and gas sector. While these comments cover the emissions inventory for the 2015 ozone national ambient air quality standard (NAAQS) marginal nonattainment area, the problem of undercounting emissions is also very relevant to the serious nonattainment SIP for the 2008 ozone NAAQS, which the Commission will be addressing in the future.

I. INTRODUCTION

In evaluating these comments, it is important to understand the context of the Commission's and the Air Pollution Control Division's (Division) repeated failure to bring the Denver-Boulder-Greeley-Ft. Collins-Loveland, CO area ("Metro-Denver") into attainment with the ozone NAAQS. This failure has resulted in death, disease and lost of fundamental freedoms for Coloradans, damage to our majestic natural areas like Rocky Mountain National Park, and millions of dollars in costs to the state economy in the form of lost wages and worker productivity, medical bills, decreased agriculture production, and tourism. These failures were due in part to emission inventories which undercounted emissions.

EPA designated the Metro-Denver area as nonattainment for the 1997 ozone NAAQS. 69 Fed. Reg. 23,858, 23,868 (Apr. 30, 2004). The nonattainment area included Boulder, Denver, Jefferson, Douglas, Broomfield, Adams, and Arapahoe Counties and parts of Larimer and Weld Counties. *Id.*

EPA deferred the effective date of Metro-Denver's nonattainment designation for the 1997 ozone NAAQS under a program, later deemed illegal, called the Early Action Compact. The Early Action Compact required areas to not violate the ozone NAAQS. Metro-Denver failed to comply with the Early Action Compact because it continued to violate the 1997 ozone NAAQS and thus EPA allowed the nonattainment designation to become effective. 74 Fed. Reg. 2,936, 2,944, ftnt. b (Jan. 16, 2009).

EPA designated Metro-Denver as a marginal nonattainment area for the 2008 ozone NAAQS. 77 Fed. Reg. 30,088, 30,110 (May 21, 2012). The area failed to attain the 2008 ozone NAAQS by its marginal attainment date. It was thus "bumped up" to a moderate nonattainment area. 81 Fed. Reg. 26,697, 26,699 (May 4, 2016).

The area then failed to attain the 2008 ozone NAAQS by its moderate attainment date. 83 Fed. Reg. 56,781, 56,784 (Nov. 14, 2018). The area was thus bumped up again, this time to a serious nonattainment area. 84 Fed. Reg. 70,789 (Dec. 26, 2019).

It is very likely that the Metro-Denver area will fail to attain the 2008 ozone NAAQS by its serious attainment date. To avoid this failure, the Chatfield Park ozone monitor would have to have a fourth highest value this year of 67 parts per billion. This is lower than the values in past years. The only reason this failure would be avoid is because of the global COVID-19 pandemic and oil pricing, which is forcing much of the Denver Julesburg oil out of the market.

EPA designated Metro-Denver as a marginal nonattainment area for the 2015 ozone NAAQS. 83 Fed. Reg. 25,776, 25,792 (June 4, 2018). It only took until February 27, 2020 for ozone levels to be high enough so that we knew, once again, that the Metro-Denver area failed to attain the ozone NAAQS. Thus, Metro-Denver will be bumped up to a moderate nonattainment area for the 2015 ozone NAAQS.

The path to reversing this deplorable string of failures is not to keep doing the same thing over and over. Rather, to succeed, the Commission must take a new approach. This new approach should include creating an emission inventory that accurately depicts air pollution.

II. TOP DOWN "INVENTORIES," OR FLUX ESTIMATES DEMONSTRATE THAT THE DIVISION'S BOTTOM UP EMISSION INVENTORY UNDERCOUNTS EMISSIONS. THUS, THE COMMISSION SHOULD ADJUST THE EMISSION INVENTORY BASED ON THE TOP DOWN EMISSION INVENTORY.

The scientific literature shows that bottom up emission inventories, like the one before the Commission, underestimate oil and gas emissions. Helmig, D. 2020. Air Quality Impacts from Oil and Natural Gas Development in Colorado, Elem Sci Anth, 8: 4, Attached as Ex. 1 at 20. This literature is based on actually measuring pollution by "aircraft profiling upwind and downwind of production regions, determination of horizontal winds and boundary layer depth [Karion et al., 2013; Karion et al., 2015; Peischl et al., 2015; Peischl et al., 2018]." *Id.*

Problems with the bottom up inventories include "extrapolation of limited

information of facility-scale emissions from venting, flashing, and leakage, and the neglect of differences in practices of operators." *Id.* Also, the bottom up inventories are annual averages with little to no temporal information. *Id.* In fact, the Final Technical Support Document for the current emission inventory states: "Emissions data that were on an annual basis were apportioned to a daily rate by dividing by 365." Final TSD at 4.

The underestimation is significantly. *Petron et al.*, [2012] found that "uncertainties attached [to bottom up regulatory] estimates can be as high as a factor of two." *Id.* Benzene, a known human carcinogen, "were too low by at least a factor of five." *Id.*

Tzompa-Sosa et al., [2017] found that even increasing the fossil fuel emission inventory by 40% in the Central U.S., including Colorado, was not enough to yield agreement with observations. *Id.* "Pfister et al. [2017a], in their modeling of FRAPPE and DISCOVER-AQ data, found that they had to increase O&NG non-ethane emissions by a factor of four over their best inventory estimate for the best match between observations and model output." *Id.* The most recent study mentioned in the Helmig paper, *Peischl et al.*, 2018, found that Regional Air Quality Council VOC estimate undercounted by a factor of approximately three when compared to data from NOAA aircraft surveying.

In light of the above, the Commission should not approve the emissions inventory. Rather, the Commission should charge the Division to work with the outstanding research community we have in Colorado and elsewhere to come up with an adjustment factor for the Division to have its emission inventory more closely match actual observed levels of pollution, or another defensible approach. Again, this is critical not only for this emission inventory but also for future emission inventories that create consequential regulatory actions like setting values for reasonable further progress reductions and motor vehicle emission budgets.

III. NUMEROUS FLAWS EXIST IN THE DIVISION'S BOTTOM UP INVENTORY WHICH NEED TO BE CORRECTED.

As explained above, considering the long history of failure to attain the ozone standards by the required date, and the fact that bottom up emission inventories are not supported by actual measurements of pollution, the Commission cannot rationally approve the emission inventory before it. Furthermore, as explained below, there are numerous specific shortcomings with this emission inventory.

Clean Air Act §182(a)(1) mandates that the emission inventory be a comprehensive, accurate, current inventory of actual emissions from all sources. Unfortunately, the current emission inventory does not meet this mandate.

It appears that the emission inventory does not comprehensively include all sources of emissions. The technical support document appears to include some pre-production emissions, but some is not all. *See* Final TSD at 9, Table 4.

The emission inventory includes zero NOx emissions from agricultural area sources. Emission Inventory at 7. But agricultural soils, including those which have fossil fuel derived fertilizers, are a huge source of NOx emissions. One study on this topic is by Maya Almaraz, who is at University of California at Davis, a school noted for its work on agriculture. *See Almaraz, M. et al*, Agriculture is a major source of NOx pollution in California, Sci. Adv. 2018, attached as Exhibit 2. In this study, two methods were used: a bottom-up spatial model of soil NOx emissions and a top-down approach from airborne observations. *Id.* at 1. This study found that cropland soil increased the NOx budget by 20 to 51%. *Id.*

In additional residential fuel combustion is excluded from the emission inventory. Emission Inventory at 2. The Emission Inventory claims this is "because emissions from this category are negligible in the summer." *Id.* But residential fuel combustion occurs in hot water heaters and cooking stoves, as well as furnaces. While people may not use their furnaces in the summer, they certainly use their hot water heaters and cooking stoves. There is no evidence in the record that emissions from hot water heaters and cooking stoves are negligible. So it is arbitrary to exclude this source of NOx and VOC emissions.

It is worth noting that natural gas and propane burning cook stoves are a source of serious indoor air pollution.[1] The Commission could obtain significant co-benefits for public health by regulating these sources. But the first step in regulating them should be including them in the emissions inventory.

Furthermore, all of the information in the inventory for point sources, oil and gas industry included, come from the APENs. However, by exclusively using the APENs as the only source of information, the inventory is excluding the emissions from sources that are APEN-exempt. These APEN-exempt sources maybe small or of short duration, but they are numerous and many of them are routine part of oil and gas activities.

Colorado Regulation 3 Part A.II.D includes a list of all the APEN-exempt sources. The most notable are sources with less than 1 ton/year of emissions inside the ozone nonattainment area (or less than 2 ton/year outside the nonattainment area), internal combustion engines rated below 5 MMBTU/hr, construction activities with less than 6 months of duration, and oil and gas operations (well site and associated equipment) during the exploration and/or production drilling, workovers, completions and testing.

Most, if not all the above are part of any oil and gas site both in their initial stage and/or later during their production phase; from clearing and grading the terrain, building roads, transporting material, drilling, using small power generators engines, small heaters, and small flares. Because APENs are not submitted per facility but per individual piece of equipment, many of these units are small enough to be exempt and therefore are not accounted for in the inventory.

One of these individual sources may be insignificant, but when counted by the hundreds or the thousands, their emissions are relevant enough to warrant including them in the inventory.

[1] *See for example* https://rmi.org/insight/gas-stoves-pollution-health

Notably, APEN-exempt sources are required to be reported to the Division even if no permit is issued to them, so the Division could and should calculate those emissions and include them in the inventory.

As for mobile sources, there is no indication that the emission inventory includes "cheating" diesel engines like Volkswagens. The Division is well-aware of the widespread diesel engines which use defeat devices to pass tailpipe tests, as the state got significant money from the settlement. But in this emission inventory, the Divisions appears to have ignored this issue.

Also, it does not appear that the mobile source inventory considered "collector cars" which are exempt from emission testing, or cars which have obtained a repair waiver. These old cars can have emissions which are an order of magnitude, or more, higher than modern cars. And the current regulations do not in any way prohibit people from using these cars as their primary means of transportation on a daily basis.

As to non-road sources, which include heavy duty equipment used in mining, construction, and oil & gas exploration and production, they are underestimated because the Division does not regulate them, these types of vehicles do not require license plates, and only some of them require registration at a county office. As a result, the Division does not know with certainty how many of them are there operating at a given time inside the ozone nonattainment area. Yet many of these units have very large engines that generate significant amounts of NOx and other pollutants. To accurately account for these emissions the Commission should require a general APEN and permit for the emissions of all equipment, non-road vehicles included, associated with the exploration phase of oil and gas activities inside the ozone nonattainment area.

Similarly, the mobile source emission inventory does not appear to address Colorado's unusually high "cut points" for its emission testing for vehicles. Using generic emission factors rather than one's specific to Colorado is not accurate.

As to the requirement that the emission inventory be accurate and reflect actual emissions, this emission inventory fails in this regard also. For point sources, the emission inventory uses APENs. Emission Inventory at 5. Especially for power plants, which tend to operate and thus emit more in the summer, the emission inventory should use emission data from continuous emissions monitoring systems (CEMS). This would be accurate information about actual emissions and is readily available.

In fact, it does not appear that there is any actual emissions data in the inventory at all. Rather, the emissions inventory is based on the use of generic emission factors. There is no evidence to support a claim that these generic emission factors reflect actual emissions.

For example, the emission inventory says that condensate tanks are the largest source of VOC emissions. Many of these condensate tanks are controlled by an enclosed flare. Although the transparency is so lacking that we are forced to assume, we assume that the emission

inventory assumes that all of these enclosed flares reduce VOCs by 95 or even 98%. But the Division, and thus the Commission, has no evidence that actual emissions reflect 95% or higher removal efficiency. This is because there are no requirements for testing or monitoring emissions from enclosed flares. The Emission Inventory's assumption that regardless of how old the flare is, what condition it is, and what operating conditions it faces, it will always achieve at least 95% removal efficiency without any data to support this is arbitrary.

For area sources, the emissions inventory states it used data from the 2014 NEI and adjusted to 2017. Colorado saw a 39% growth in oil production between 2014 and 2017. *See* EIA Data, attached as Exhibit 3. The documents provided do not provide enough transparency to determine if the emission inventory reflects this substantial increase in actual production, and thus emissions. The Commission cannot approve the emission inventory unless it knows that the emission inventory does reflect this 39% increase in oil production.

Finally, the TSD explains that the "values for CE and RE were selected to account for changes observed in the 6 am to 9 am precursor levels at the CDPHE VOC monitoring site in Platteville, Colorado from 2012 to 2018. Final TSD at 8.

> However, inconsistencies in the sampling, uncertainties in the analysis protocols [Hood, 2019], siting of the sampling location, and the proximity of the sampling location to abundant nearby well sites make trend determinations and their interpretation for the wider region from these data uncertain.

Ex 1 at 21.

In contrast to the Platteville data, the Boulder reservoir VOC monitoring does not have these problems. Thus, the emission inventory should use the Boulder reservoir data which is much more reliable.

In conclusion, for the reasons explained above, the Commission should not approve the emission inventory.

Sincerely,

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POLICY BRIDGE

Air quality impacts from oil and natural gas development in Colorado

Detlev Helmig*,†

The rise of hydraulic fracturing techniques has fostered rapid growth of oil and natural gas (O&NG) extraction in areas across the United States. In the Denver-Julesburg Basin (DJB), which mostly overlaps with Weld County in the Northern Colorado Front Range (NCFR) north of the City of Denver Metropolitan Area (DMA), the well drilling has increasingly approached, and in many instances moved into urban residential areas. During the same time, the region has also experienced steady population growth. The DMA – NCFR has been in exceedance of the ozone U.S. National Ambient Air Quality Standard (NAAQS) and was designated a non-attainment area of the standard in 2007. Despite State efforts to curb precursors, ozone has consistently remained above the standard. A growing number of atmospheric studies has provided an ever increasing body of literature for assessing influences from O&NG industry emissions on air quality in the DMA-NCFR. This paper provides 1. An overview of available literature on O&NG influences on the regional air quality, 2. A summary of the pertinent findings presented in these works, 3. An assessment of the most important pollutants and air quality impacts, 4. Identification of knowledge and monitoring gaps, and 5. Recommendations for future research and policy.

Keywords: Air quality; Oil; Natural gas

Introduction

The development of hydraulic fracturing techniques has made it profitable to extract petroleum hydrocarbons from geologic shale formations. The application of this technology has caused a surge in new oil and natural gas (O&NG) drilling in shale basins across the United States, including in Colorado, where most of the activity has been in the Denver Julesburg Basin (DJB). In 2017, there were over 53,000 active O&NG wells in Colorado (**Figure 1**). The O&NG development is concentrated in a number of lower elevation basins, with ≈24,000 wells (January 2018) located in Weld County in the DJB, which in 2017 produced ≈90% of the oil in Colorado [*Swain*, 2018]. From 2010–2018, annual natural gas production in Weld County increased by a factor of 3.5, and annual oil production by a factor of ≈6.5 [*Drilling-Edge*, 2019].

Some of the growth of the O&NG industry has occurred within the periphery of urban and residential areas, raising concerns within communities. Proximity to O&NG operations has been associated with human health effects, with atmospheric emissions being a primary pathway of exposure. Types and causes of emissions are dependent on multiple variables and stages of the well development, and can arise, for instance, from heavy equipment use at the site and vehicle traffic, power generation, drilling operation, spillage and evaporation of fracking fluid, flowback of the extracted petroleum products, flaring, and fugitive or controlled hydrocarbon emissions during loading and transportation [*Adgate et al.*, 2014]. Fracking fluid is a mixture of a multitude of synthetic chemicals, with the composition typically kept proprietary by operators. Silica, added to the fracking fluid, dust, and soot/particles from diesel engines contribute to particulate exposure. Gaseous emissions arise from fracking fluid additives, controlled venting, flaring, and leakage of equipment, storage tanks, and pipelines. Directly emitted gaseous pollutants of concern for human health are hydrogen sulfide and petroleum constituents, including aromatic and polycyclic aromatic hydrocarbons. Combustion processes cause emissions of carbon monoxide, nitrogen oxides, volatile organic compounds (VOCs), and soot/particulates [*Adgate et al.*, 2014].

O&NG VOC emissions are a complex mixture of hydrocarbons. Some of the VOCs identified have the potential to affect the human endocrine system [*Colborn et al.*, 2014]. Enhanced levels of VOCs have been observed in air near O&NG wells, including the known human carcinogen benzene [*Verma et al.*, 2000; *Macey et al.*, 2014; *Sovacool*, 2014; *Halliday et al.*, 2016]. Human health risk assessments based on measured and modeled VOC concentrations near O&NG sites indicate increased risks for respiratory, neurological, and hematological health effects, as well as excess lifetime cancer risk above the U.S. Environmental Protection Agency (EPA) de minimis risk

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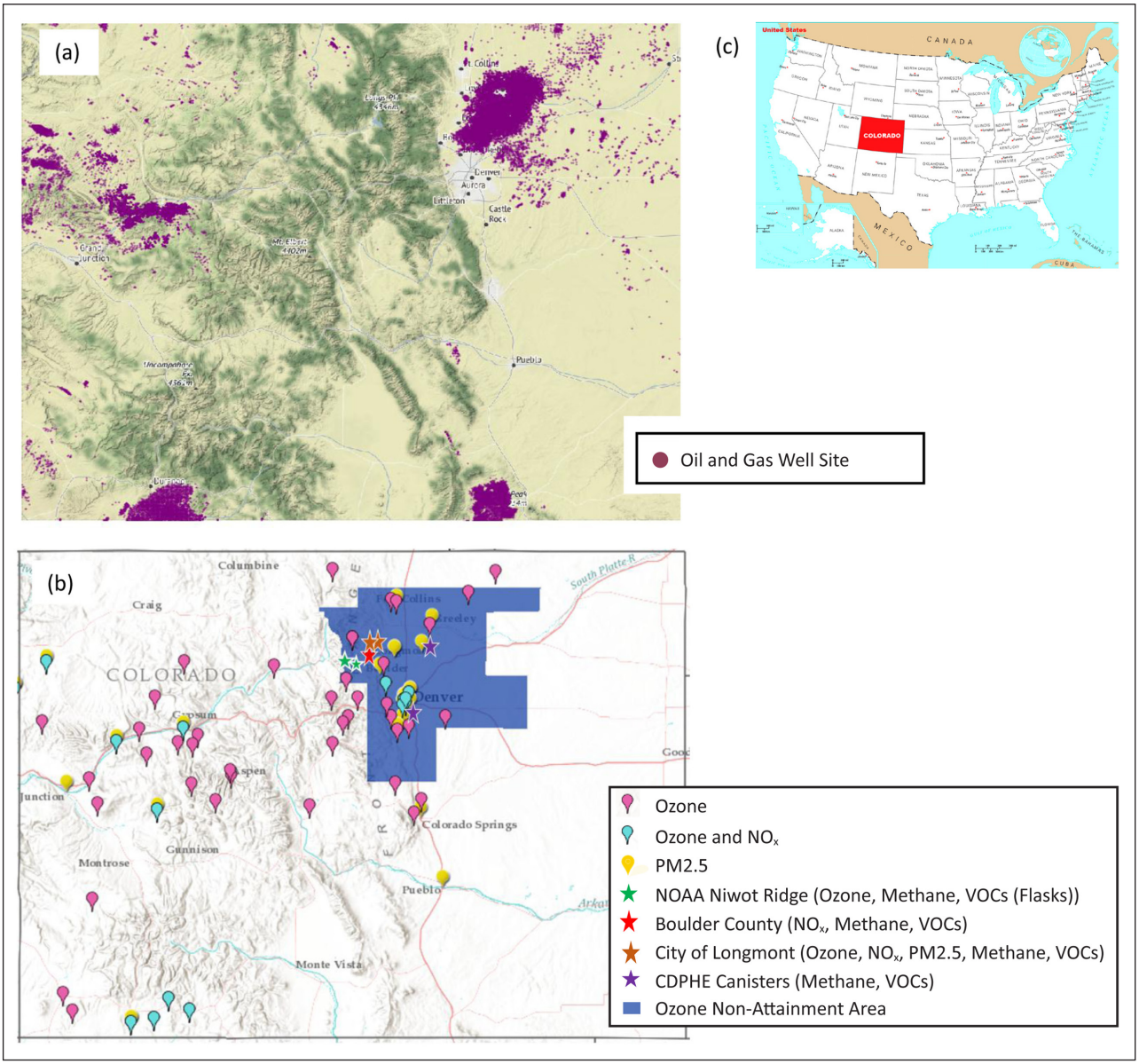

Figure 1: (a) Distribution of oil and gas well sites (purple dots) within the State of Colorado {COGCC, 2017 #1478}. **(b)** Air monitoring sites in Colorado that report ozone, nitrogen oxides, and PM2.5 data to the EPA Air Quality System archive (map downloaded from https://www.epa.gov/outdoor-air-quality-data/interactive-map-air-quality-monitors). Additional sites operated by NOAA and regional municipalities, and sites where methane and volatile organic compounds (VOCs) are measured were also added to the map. The blue area indicates the Northern Colorado Front Range (NCFR) ozone nonattainment area (NAA) east of the Rocky Mountains, encompassing the counties of Adams, Arapahoe, Boulder, Broomfield, Douglas, and Denver, as well as portions of Weld and Larimer counties. **(c)** Location of the State of Colorado. DOI: https://doi.org/10.1525/elementa.398.f1

of one in a million for people living nearest to O&NG sites [*McKenzie et al.*, 2012; *McKenzie et al.*, 2018; *McMullin et al.*, 2018; *Holder et al.*, 2019]. Associations between proximity to O&NG sites and health effects, including congenital heart defects, childhood leukemia, asthma, low birth weight, and preterm births have been reported [*HEI*, 2019]. In Colorado, children with congenital heart defects and leukemia are more likely to be born or living in the areas with the densest O&NG activity [*McKenzie et al.*, 2014; *McKenzie et al.*, 2017; *McKenzie et al.*, 2019]. While these studies indicate that VOC emissions from O&NG activities have the potential to and may be affecting the health of nearby residents, further study will be necessary to elucidate causality [*HEI*, 2019].

Furthermore, atmospheric oxidation of O&NG VOC emissions contribute to the photochemical formation of ozone and secondary aerosols, which pose additional health concerns. A recent EPA study estimated 1000 and 970 added premature deaths from particulates (PM2.5) and ozone exposure caused by O&NG pollutants in the U.S. by 2025, with 37 (from PM2.5) and 34 (from ozone) of those predicted to occur in Colorado [*Fann et al.*, 2018]. Polluted air from the Northern Colorado Front Range (NCFR) can be lofted during upslope flow conditions on the eastern Rocky Mountain slopes to high elevation where it can impact alpine ecosystems, including Rocky Mountain National Park [*Brodin et al.*, 2010; *Thompson et al.*, 2015; *Benedict et al.*, 2018]. Up to ≈20 ppb of additional ozone

in air transport associated with O&NG emission has been measured at the Rocky Mountain National Park Longs Peak monitoring station [*Benedict et al.*, 2019]. For southwestern Colorado, including Mesa Verde National Park, an maximum ozone enhancement of 9.6 ppb was estimated for the maximum daytime average 8-hour ozone (MDA8) from O&NG influences [*Rodriguez et al.*, 2009].

Increased surface ozone, at times exceeding health safety standards, have been observed in the NCFR for some 20 years. After 10 years of repeated exceedances of the 75 ppb U.S. ozone National Ambient Air Quality Standard (NAAQS), the Denver Metro Area (DMA) and NCFR, including the seven counties of Adams, Arapahoe, Boulder, Broomfield, Douglas, and Denver, as well as portions of Weld and Larimer counties, were designated as a 'Marginal' ozone nonattainment area (NAA) for the 2008 NAAQS. Because of a lack of progress in lowering ambient ozone, the area was bumped up from a "Marginal" to a "Moderate" NAA for the 2008 ozone standard in early 2016 [*CDPHE*, 2019a], and in December 2019, the EPA reclassified the area to a "Serious" NAA for the 2008 standard [*EPA*, 2019]. In consideration of new health exposure findings, the NAAQS was lowered from 75 to 70 ppb in 2015 to provide a stronger protection to communities. This lower threshold will make it even more challenging for the NCFR to reach compliance with the standard. Note, that even the 70 ppb standard is higher, and less protective than the ozone standard in many other nations, including Canada and the European Union, as well as the recommended guideline value by the World Health Organization (WHO, [*WHO*, 2019a]).

In December 2018, the Colorado Department of Public Health and Environment (CDPHE) petitioned to the EPA for deferral of the re-designation (Supplemental Materials). In their letter, the agency stated that "Colorado has seen a dramatic decline in ambient levels of oil and gas related VOCs" and that the "majority of ozone concentrations in the DMNFR (Denver Metro Northern Front Range) are the result of emissions outside of the State's control, including naturally occurring emissions and emissions transported from other states and countries". The arguments presented in the letter did not consider most of the considerable body of peer-reviewed literature on the impacts from O&NG industry operations on Colorado's air quality that has emerged during the past 10 years. Shortly after the new Colorado governor Jared Polis took office in 2019, he withdrew this petition, stating "There's too much smog in our air, and instead of hiding behind bureaucracy and paperwork that delay action, we are moving forward to make our air cleaner now" [*Nicholson*, 2019]. For directing this policy there is urgency to consider the current understanding of ozone precursor sources, atmospheric transport, and chemistry, from published literature. This article examines predominantly this peer-reviewed literature with the goal to provide the State agencies, boards, legislators, and policymakers a summary document for better assessing the role of O&NG industry emissions on NCFR-DMA air quality, with a particular emphasis on surface ozone.

Resources utilized and published work

This review and policy bridge provides an overview of the evolution of the understanding of atmospheric impacts and the current state of knowledge of O&NG emissions in Colorado. A comprehensive review and evaluation of health effects of atmospheric O&NG emissions in Colorado is intentionally not included. This review primarily builds on peer-reviewed journal articles. Included were all articles that were identified using various search strategies, regardless of the reputation of the journal or recognition of the published work by the community. There has been remarkable growth of literature over the past ten years (**Figure 2**). A good fraction of publications have arisen from the FRAPPE (Front Range Air Pollution and Photochemistry Experiment [*FRAPPE*, 2013]) and DISCOVER-AQ (Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality [*DISCOVER-AQ*, 2013]) campaigns that, in the summer of 2014, brought researchers from a wide array of disciplines and institutes to Colorado to study air pollution sources and chemistry in the NCFR. Outcomes of these studies are evident in the increase in published papers in subsequent years (**Figure 2**). Most research on O&NG impacts on air quality has centered in the NCFR, except a few studies that investigated methane emissions in the Four Corners region (region of the U.S. consisting of the southwestern corner of Colorado, southeastern corner of Utah, northeastern corner of Arizona, and northwestern corner of New Mexico). This review will focus on the NCFR research. A summary of published work arranged by publication year is provided in **Table 1**.

It is noteworthy that the majority of this work has been published in well recognized/high impact factor

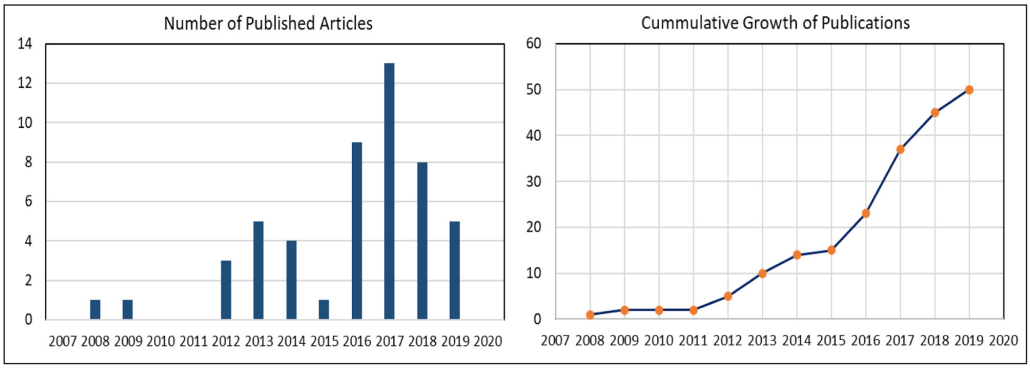

Figure 2: Growth of number of publications addressing air quality effects from O&NG development in Colorado. The 2019 number is the count to September 30, 2019. DOI: https://doi.org/10.1525/elementa.398.f2

Table 1: Summary of published literature addressing O&NG influences on air quality in Colorado. DOI: https://doi.org/10.1525/elementa.398.t1

Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2008	Not specified	CDPHE	Denver Metropolitan Area and North Front Range 8-Hour Ozone State Implementation Plan	State of Colorado Ozone Implementation Plan				X		Transport from cool pool area of the Platte Valley in Weld County results in a mean daily maximum 8-hour ozone of 71 ppb at the four Front Range monitors considered.
2009	Rodriguez et al.	Colorado State Univ.	Regional impacts of oil and gas development on ozone formation in the western United States	JAWMA	X			X	Chemical and transport modeling	A maximum MDA8 ozone enhancement of 9.6 ppb was estimated from O&NG emissions in southwestern Colorado.
2012	McKenzie et al.	Colorado School of Public Health	Human health risk assessment of air emissions from development of unconventional natural gas resources	Sci. Tot. Environ.	X		X		Health risk assessment	Median concentrations of benzene, ethylbenzene, toluene, and m-xylene/p-xlyene were 2.7, 4.5, 4.3, and 9 times higher in the well completion samples than in other natural gas development samples, respectively.
2012	Petron et al.	NOAA/CIRES	Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study	J. Geophys. Res.	X	X	X			Emissions of methane and light NMHC VOC are most likely underestimated in current inventories.
2012	Levi	Council on Foreign Relations	Comment on "Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study" by Pétron et al.	J. Geophys. Res.	X	X				Consideration of previously unconsidered observations results in a new methane flux estimates that are consistent with current inventories, but inconsistent with the estimates in Petron et al. (2012).
2013	Petron et al.	NOAA/CIRES	Reply to comment on "Hydrocarbon emissions characterization in the Colorado Front Range—A pilot study" by M.A. Levi	J. Geophys. Res.	X	X	X			Flashing emission and regulatory modeled composition profiles for a limited number of condensate tanks probably do not represent the true range of these parameters for the thousands of such sources across the DJB in 2008.

(Contd.)

Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2013	Gilman et al.	NOAA/CIRES	Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado	Environ. Sci. Technol.	X		X	X		On average, 55 ± 18% of the VOC-OH reactivity was attributable to emissions from O&NG operations, indicating that these emissions are a significant source of ozone precursors.
2013	Swarthout et al.	Univ. of New Hampshire	Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources	J. Geophys. Res.	X		X	X		Natural gas associated emissions have the potential to impact downwind air quality as natural gas NMHCs comprised ≈24% of the calculated OH reactivity.
2013	Brown et al.	NOAA/CIRES	Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT): Overview of a wintertime air chemistry field study in the front range urban corridor of Colorado	J. Geophys. Res.	X		X		Halogens, NO_x, NO_y, aerosol	Large observed mixing ratios of light alkanes, both in near-surface air and aloft, were attributable to local emissions from oil and gas activities.
2013	LaFranchi et al.	Lawrence Livermore National Laboratory	Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}CO_2$	Atmos. Chem. Phys.	X	X	X		CO, $^{14}CO_2$	Enhanced concentrations of CH_4 and C_3-C_5 alkanes were found in air influenced by emissions to the north and east of the Boulder Atmospheric Observatory (BAO) and were suggested to have been sourced from oil and gas fields located to the northeast.
2014	Petron et al.	NOAA/CIRES	A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin	J. Geophys. Res.	X	X	X			Emission of methane, VOC, and benzene in the DJB were estimated to be 3 times, at least a factor of 2, and 7 times, respectively, larger than EPA and State inventories.
2014	Kort et al.	Univ. of Michigan	Four corners: The largest US methane anomaly viewed from space	Geophys. Res. Let.	X	X				Spaceborne remote sensing indicated large CH_4 levels over the Four Corners region. Estimted emissions largely exceeded inventory estimates.

(Contd.)

Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2014	Thompson et al.	Univ. of Colorado	Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado	Elementa	X		X			At residences near oil and gas operations, mean mole fractions of the C_2-C_5 alkanes were enhanced by a factor of 18–77 relative to the regional background, and present at higher levels than typically found in large urban centers.
2014	Colburn et al.	The Endocrine Disruption Exchange	An exploratory study of air quality near natural gas operations	Human & Ecol. Risk Assess.	X		X		Health risk assessment	The number of NMHCs and their concentrations were highest during the initial drilling phase and did not increase during hydraulic fracturing in a closed-loop system.
2015	Richter et al.	Univ. of Colorado	Compact highly sensitive multi-species airborne mid-IR spectrometer	Applied Physics	X		X		Formaldehyde	Ethane was enhanced at least ten times above background levels in the DJB boundary layer. Regions with elevated ethane overlapped with elevated formaldehyde.
2016	Townsend-Small et al.	Univ. of Cincinnati	Using stable isotopes of hydrogen to quantify biogenicand thermogenic atmospheric methane sources: A case study from the Colorado Front Range	Geophys. Res. Lett.	X	X			Methane hydrogen and carbon stable isotopes analyses	Biogenic CH_4 comprised about 50% of total CH_4 observed in the active oil and gas extraction region.
2016	Franco et al.	Univ. of Liege, Belgium	Evaluating ethane and methane emissions associated with the development of oil and natural gas extraction in North America	Environ. Res. Lett.	X		X			Between 2009–2015, Fourier Transform Infrared (FTIR) ethane column observations over Boulder show a 5.0% per year rate of increase.
2016	Sullivan et al.	NASA Goddart	Quantifying the contribution of thermally driven recirculation to a high-ozone event along the Colorado Front Range using lidar	J. Geophys. Res.	X			X	Air recirculation	Complex meteorology in this region can significantly exacerbate pollution levels. A high summer 2014 surface ozone pollution event was associated with thermally driven upslope flow.

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Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2016	Reddy and Pfister	NCAR	Meteorological factors contributing to the interannual variability of midsummer surface ozone in Colorado, Utah, and other western U.S. states	J. Geophys. Res.	X			X	Reanalysis of meteorology and regional chemistry modeling	Significant correlations were found between July MDA8 O_3 and meteorological variables. Increased 500 hPa heights lead to high July O_3, particularly in areas of elevated terrain near urban sources of NO_2 and other O_3 precursors.
2016	Vu et al.	Univ. of California Riverside	Impacts of the Denver Cyclone on regional air quality and aerosol formation in the Colorado Front Range during FRAPPE 2014	Atmos. Chem. Phys.	X		X	X	Peroxyacetyl Nitrate (PAN), CO, NH_3, aerosol properties	Meteorological patterns associated with the Denver Cyclone increased pollutant levels, including aerosol loadings in the Denver metropolitan area. Cyclone conditions promote transport of aerosol constituents from the NCFR into the Denver metropolitan area, increasing aerosol mass loadings and reducing visibility.
2016	Halliday et al.	Pennsylvania State Univ.	Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014	J. Geophys. Res.	X		X			Unexpectedly high benzene mixing ratios were observed at a site near Platteville (maximum of 29.3 ppb), primarily at night, and assoicated to emissions from nearby O&NG operations.
2016	Frankenberg et al.	California Institute of Technology	Airborne methane remote measurements reveal heavytail flux distribution in Four Corners region	PNAS	X	X				In the Four Corners Region, methane sources include gas processing facilities, storage tanks, pipeline leaks, and well pads, and a coal mine; emissions ranged from 2 kg h^{-1} through ~5,000 kg h^{-1}.
2016	Dingle et al.	Univ. of California Riverside	Aerosol optical extinction during the Front Range Air Pollution and Photochemistry Éxperiment (FRAPPÉ) 2014 summertime field campaign, Colorado, USA	Atmos. Chem. Phys.	X		X		Aerosol	The light extinction coefficient best correlated with organic aerosols in O&NG emissions and with nitrate aerosols under O&NG and agriculture influences.

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Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2016	McDuffie et al.	NOAA/CIRES	Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range	J. Geophys. Res.	X		X	X		O&NG alkanes contribute over 80% to the observed carbon mixing ratio, roughly 50% to the regional VOC OH reactivity, and approximately 20% to regional photochemical O_3 production.
2017	Tzompa-Sosa et al.	Colorado State Univ.	Revisiting global fossil fuel and biofuel emissions of ethane	J. Geophys. Res.	X		X	X		Over northeastern Colorado, year 2001 ethane inventory emissions had to be increased by more than 40% for modeled atmospheric mixing ratios to match observations.
2017	Evans and Helmig	Univ. of Colorado	Investigation of the influence of transport from oil and natural gas regions on elevated ozone levels in the northern Colorado Front Range	JAWMA	X			X		Transport from areas with O&NG operations accounted for on the order of 65% of 1-hr averaged elevated ozone levels at BAO and South Boulder, while the Denver urban corridor accounted for 9%.
2017	Abeleira et al.	Colorado State Univ.	Source characterization of volatile organic compounds in the Colorado Northern Front Range metropolitan area during spring and summer 2015	J. Geophys. Res.	X		X	X		The NCFR is more strongly influenced by O&NG sources of VOCs than other urban and suburban regions in the U.S.
2017	Cheadle et al.	CIRES/NOAA	Surface ozone in the Colorado northern Front Range and the influence of oil and gas development during FRAPPE/DISCOVER-AQ in summer 2014	Elementa	X		X	X	NO_x	Correlation analyses in case studies showed that oil and gas related activities are a NO_x and O_3 precursor source.
2017	Pfister et al.	NCAR	Process-Based and Regional Source Impact Analysis for FRAPPÉ and DISCOVER-AQ 2014	Final Report to CDPHE			X	X	NO_x	Mobile sources and oil and gas related emissions are the largest contributors to local ozone production in the Northern Front Range Metro Area (NFRMA).
2017	Baier et al.	Pennsylvania State Univ.	Higher measured than modeled ozone production at increased NO_x levels in the Colorado Front Range	Atmos. Chem. Phys.	X		X	X	Ozone production rate	Ozone production rates peak during late morning. Rates predicted by three models were lower than direct observations.

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Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2017	Abeleira and Farmer	Colorado State Univ.	Summer ozone in the northern Front Range metropolitan area: weekend–weekday effects, temperature dependences, and the impact of drought	Atmos. Chem. Phys.	X		X	X	NO_x	Ozone in the NCFR area was either stagnant or increasing between 2000 and 2015, likely because of decreasing NO_x emissions in a NO_x -saturated environment and increased anthropogenic VOC emissions.
2017	Robertson et al.	Univ. of Wyoming	Variation in methane emission rates from well pads in four oil and gas basins with contrasting production volumes and compositions	Environ. Sci. Technol.	X	X				In the DJB, ~70% of total methane emissions were from 20% of the well pads The total mass of methane emitted as a percent of gross methane produced was 2.1% (1.1–3.9%).
2017	Kaser et al.	NCAR	The effect of entrainment through atmospheric boundary layer growth on observed and modeled surface ozone in the Colorado Front Range	J. Geophys. Res.	X			X	Boundary layer growth, contribution of entrainment and synoptic transport to O_3	A large day-to-day variability of ozone above the atmospheric boundaray layer was attributed to differing air mass origins. On average, morning boundary layer growth contributed 4.8 ppb hr^{-1} to the morning hour ozone increase.
2017	Pfister et al.	NCAR	Using observations and source specific model tracers to characterize pollutant transport during FRAPPÉ and DISCOVER-AQ	J. Geophys. Res.	X				Air flow characterization	During upslope events, frequently, there is a separation of air masses that are heavily influenced by oil and gas emissions to the north and dominated by urban emissions to the south. NCFR pollution can "spillover" into the valleys to the west of the Continental Divide.
2017	Yacovitch et al.	Aerodyne Research Inc.	Natural gas facility methane emissions: Measurements by tracer flux ratio in two US natural gas producing basins	Elementa	X	X				Methane emission rates from DJB gathering stations (kg CH_4 hr^{-1}) were lower compared to results from other basins.
2017	Zaragoza et al.	Colorado State Univ.	Observations of acyl peroxy nitrates during the Front Range Air Pollution and Photochemistry Experiment (FRAPPE)	J. Geophys. Res.	X		X	X	PAN, Peroxyproply nitrate (PPN)	Anthropogenic VOCs played a dominant role in PAN production during periods with high O_3. The contribution of biogenic VOCs to local O_3 production was relatively small.

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Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2017	Smith et al.	Univ. of Michigan	Airborne quantification of methane emissions over the Four Corners Region	Environ. Sci. Technol.	X	X				Using five independent days of measurements, an average regional CH_4 flux of 0.54 ± 0.20 Tg yr^{-1} was calulated, in close agreement with a space-based estimate for 2003–2009.
2018	Bien and Helmig	Univ. of Colorado	Changes in summertime ozone in Colorado during 2000–2015	Elementa	X			X		Median and upper percentile surface O_3 in the DMA has not declined at the rates seen in other western U.S. regions.
2018	McKenzie et al.	Univ. of Colorado	Ambient nonmethane hydrocarbon levels along Colorado's Northern Front Range: Acute and chronic health risks	Environ. Sci. Technol.	X		X			O&NG air pollutant concentrations increased with proximity to an O&NG facility, as did health risks.
2018	Peischl et al.	NOAA/CIRES	Quantifying methane and ethane emissions to the atmosphere from Central and Western U.S. oil and natural gas production regions	J. Geophys. Res.	X	X	X			Total CH_4 and C_2H_6 emissions attributed to O&NG operations in the Denver Basin region remained statistically unchanged between 2008 and March 2015.
2018	Fann et al.	US EPA Research Triangle Park	Assessing human health PM2.5 and ozone impacts from U.S. oil and natural gas sector emissions in 2025	Environ. Sci. Technol.	X		X	X	PM2.5	Under current growth projections O&NG emissions are predicted to cause 37 and 34 annual premature deaths from the added PM2.5 and ozone production, respectively, in Colorado by 2025.
2018	McMullin et al.	CDPHE	Exposures and health risks from volatile organic compounds in communities located near oil and gas exploration and production activities in Colorado (U.S.A.)	Int. J. Environ. Res. & Public Health	X		X		Health effects	56 VOCs emitted from O&NG operations in Colorado were identified. Further characterization of primary and secondary VOCs emitted from O&NG sites during different phases of operations is needed to address the community health relevance.
2018	Benedict et al.	Colorado State Univ.	Impact of Front Range sources on reactive nitrogen concentrations and deposition in Rocky Mountain National Park	PeerJ	X		X		NO_x, NO_y, ammonia	Elevated concentrations of reactive nitrogen were associated with emissions from oil and gas operations, which are frequently co-located with agricultural production and livestock feeding areas in the region, and from urban areas.

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Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2018	Abdi-Oskouei et al.	Univ. of Iowa	Impacts of physical parameterization on prediction of ethane concentrations for oil and gas emissions in WRF-Chem	Atmos. Chem. Phys.	X		X		EPA emission inventory	Comparison between airborne measurements and WRF-Chem model simulations indicated a low bias of ethane in the NFRMA close to O&NG activities, suggesting underestimation of O&NG emissions in the 2011 National Emissions Inventory (NEI).
2018	Bahreini et al.	Univ. of California Riverside	Sources and characteristics of summertime organic aerosol in the Colorado Front Range: Perspective from measurements and WRF-Chem modeling	Atmos. Chem. Phys.	X				Aerosol characterization	It was estimated that the O&NG sector contributed to <5% of total organic aerosol, but up to 38% of anthropogenic secondary organic aerosol in the NCFR.
2019	Oltmans et al.	NOAA	Boundary layer ozone in the Northern Colorado Front Range in July-August 2014 during FRAPPE and DISCOVER-AQ from vertical profile measurements	Elementa	X			X		The association of high O_3 days at BAO with transport from O&NG sectors suggested that O&NG emissions were an important source of O_3 precursors and are crucial in producing peak O_3 events. Exposure of populations in the Foothills area is not captured by the current regulatory network, and likely underestimated.
2019	Tsompa-Soza et al.	Colorado State Univ.	Atmospheric implications of large C_2-C_5 alkane emissions from the U.S. oil and gas industry	J. Geophys. Res.	X		X			Of four regions analyzed, Boulder showed the highest percentage contribution from the oil and gas sector to total abundances of C_2-C_5 alkanes throughout the troposphere.
2019	Lindaas et al.	Colorado State Univ.	Acyl peroxy nitrates link oil and natural gas emissions to high ozone abundances in the Colorado Front Range during summer 2015	J. Geophys. Res.	X	X	X	X	Acyl peroxy nitrates (APNs), photochemical modeling	Anthropogenic VOC precursors dominated APNs production when O_3 was most elevated in the NCFR in summer 2015. Propane and n-pentane, primarily from O&NG emissions, drive elevated PPN/PAN ratios during high O_3 events. Emissions from the O&NG sector contribute to O_3 production on high O_3 days.

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Year	Authors	Lead Author Affiliation	Title	Journal	Peer Review	Methane	VOCs	Ozone	Other	Main Findings*
2019	Kille et al.	Univ. of Colorado	Separation of methane emissions from agricultural and natural gas sources in the Colorado Front Range	Geophys. Res. Let.	X	X	X		Ammonia	Natural gas methane sources dominate over agricultural and other sources, but the latter are relatively more important when excess CH_4 is smaller than 5 ppb.
2019	Benedict et al.	Colorado State Univ.	Volatile organic compounds and ozone in Rocky Mountain National Park during FRAPPÉ	Atmos. Chem. Phys.	X		X	X		The study estimated that for that high ozone events associated with O&NG signatures, NCFR sources contributed ≈20 ppb of additional ozone.

* Text in this column contains cited or partially shortened text from the listed articles.

Table references: [*CDPHE*, 2008; *Rodriguez et al.*, 2009; *Levi*, 2012; *McKenzie et al.*, 2012; *Pétron et al.*, 2012; *Brown et al.*, 2013; *Gilman et al.*, 2013; *LaFranchi et al.*, 2013; *Pétron et al.*, 2013; *Swarthout et al.*, 2013; *Colborn et al.*, 2014; *Kort et al.*, 2014; *Petron et al.*, 2014; *Thompson et al.*, 2014; *Richter et al.*, 2015; *Dingle et al.*, 2016; *Franco et al.*, 2016; *Frankenberg et al.*, 2016; *Halliday et al.*, 2016; *McDuffie et al.*, 2016; *Reddy and Pfister*, 2016; *Sullivan et al.*, 2016; *Townsend-Small et al.*, 2016; *Vu et al.*, 2016; *Abeleira et al.*, 2017; *Abeleira and Farmer*, 2017; *Cheadle et al.*, 2017; *Evans and Helmig*, 2017; *Kaser et al.*, 2017; *Pfister et al.*, 2017a; *Pfister et al.*, 2017b; *Robertson et al.*, 2017; *Smith et al.*, 2017; *Tzompa-Sosa et al.*, 2017; *Yacovitch et al.*, 2017; *Zaragoza et al.*, 2017; *Abdi-Oskouei et al.*, 2018; *Bahreini et al.*, 2018; *Benedict et al.*, 2018; *Bien and Helmig*, 2018; *Fann et al.*, 2018; *McKenzie et al.*, 2018; *McMullin et al.*, 2018; *Peischl et al.*, 2018; *Yacovitch et al.*, 2018; *Benedict et al.*, 2019; *Kille et al.*, 2019; *Lindaas et al.*, 2019; *Oltmans et al.*, 2019; *Tzompa-Sosa et al.*, 2019].

peer-reviewed science journals. Lead and contributing authors are from federal laboratories (i.e. NCAR, NOAA) and Colorado and out-of-state universities. The journal count is led by the Journal of Geophysical Research (18), followed by seven publications in Atmospheric Chemistry and Physics, and five articles each in Environmental Science and Technology and Elementa. This publication record can be deemed as a testimony of the recognized importance of this research, having attracted leading scientists from top U.S. research institutions.

Monitoring networks

Air quality monitoring and air sampling is conducted by the CDPHE, NOAA, the National Park Service, Boulder County, and the City of Longmont. A map showing the distribution of monitoring sites and measured species is shown in **Figure 1**. Ozone is monitored at the highest number of sites, followed by PM2.5, and nitrogen oxides. There currently is only one location with continuous VOCs monitoring (Boulder Reservoir [*Helmig et al.*, 2020], Boulder County site in **Figure 1**); however, two more sites are anticipated to begin VOCs monitoring within the next year (Longmont Union Reservoir (the eastern of the City of Longmont sites in **Figure 1**) and Rocky Flats North (CDPHE site south of Boulder, **Figure 1**)). Continuous methane monitoring is currently conducted at the Boulder Reservoir and Longmont airport (the western of the City of Longmont sites in **Figure 1**); continuous methane monitoring at the Longmont Union Reservoir is planned to start in early 2020. Besides this real-time monitoring, methane and VOCs are also quantified in flasks and canisters samples collected at Niwot Ridge (NOAA) and at Platteville and downtown Denver (CAMPS) by CDPHE. There is a relatively high density of sites in the DMA, but a relatively sparse network within and along the periphery of the DJB O&NG area.

Nitrogen oxides

Nitrogen oxide (NO and NO_2 = NO_x) emissions associated with O&NG development arise from a number of sources, including flaring, on-site electrical power generation, heavy equipment operation at fracking sites, and the heavy truck traffic for moving equipment and fluids in and out of O&NG well sites. Other sources are compressor stations, and heavy tanker truck traffic for transporting produced oil and gas products from the site. NO_x emissions arising from these sources have been studied in a number of O&NG basins [*Bogacki and Macuda*, 2014; *Field et al.*, 2014; *Majid et al.*, 2017; *Archibald et al.*, 2018]. However, this literature review did not identify any studies from the DJB, leaving the contribution from the DJB O&NG sector to the regional NO_x emissions uncertain. The Regional Air Quality Council emissions inventory lists the year 2017 total O&NG NO_x sources at 65.8 tons per day, which is a 59% increase over the year 2011 emissions [*Brimmer*, 2019].

Methane

Methane is emitted by a variety of sources, with wetlands, landfills, feedlots, seepage from geological reservoirs, and O&NG extraction, distribution, and industries being the most significant ones on a global scale. Methane is a potent greenhouse gas. The methane background in the global atmosphere has more than doubled since preindustrial [*Kirschke et al.*, 2013]. The increase of methane from anthropogenic sources is the second ranked contribution (after CO_2) to radiative forcing from anthropogenic greenhouse gases. The oxidation of methane in the atmosphere is also a pathway for ozone production, which constitutes another climate forcing pathway. Ozone exerts stress on the natural and agricultural ecosystems and human and animal life (see below). It has been estimated that a reduction of global methane emission by 20% would reduce the ozone MDA8 by ≈1 ppb in the background atmosphere [*West and Fiore*, 2005; *West et al.*, 2006]. The benefits of methane reductions are shared internationally. The 20% emissions reduction was estimated to avoid ≈30,000 premature deaths by 2030 globally [*West et al.*, 2006].

The O&NG industry is the single most significant source of methane in Colorado [*Pétron et al.*, 2012]. Quantifying the methane flux from the O&NG industry has been challenging as the geographic area of the O&NG activities overlaps with agricultural, beef, and dairy production, which all constitute significant methane sources. Methane to non-methane hydrocarbon (NMHC) relationships, in particular those with ethane and propane, and the stable isotopic signature of methane, have been used to decipher the O&NG contribution to the total methane flux. Point source measurements near emission sources, mobile lab ground surveying, and aircraft observations, in combination with inventory information, have been used to derive basin-wide O&NG methane flux estimates. Three NOAA studies, covering observations during three short time windows within the 2008–2015 period, are summarized in **Table 2**. Data in this table are scaled to annual flux estimates. As all these experiments relied on relatively short observation periods, there is an inherent uncertainty from the lack of knowledge if, and how representative these shorter observations were for year-round conditions. Further, variability in parameterizations and uncertainties in assumptions that go into these flux estimates cause relatively large uncertainty ranges in the results (column 3). The best estimate values of the three studies are relatively consistent, nonetheless, spanning 130–169 Gg yr^{-1}. According to the U.S. Energy Information Administration, Colorado households consume an average of 103 million BTU of natural gas per year [*EIA*, 2009], which converts to ≈2 tons of household natural gas consumption per year. Therefore, the *Peischl et al.* [2018] O&NG methane

Table 2: Basin-wide O&NG methane flux estimates for the DJB. DOI: https://doi.org/10.1525/elementa.398.t2

Time Period	Methane Flux Gg yr^{-1}		Reference
	mean	range	
Summer 2008	130	72–252	Petron et al., 2012
May 29, 2012; May 31, 2012	169	109–229	Petron et al., 2014
March 2015	158	88–228	Peischl et al., 2018

emissions estimate corresponds to the natural gas consumed by ≈84,000 Colorado households.

These data points are too few, and uncertainties are too large, to make statements about potential trends in the methane flux over this time window with statistical certainty. Considering the increase in natural gas production during this time period, the relatively flat total emissions would indicate a reduction in the relative fugitive emissions rate. *Peischl et al.* [2018] present a statistical analysis that results in an 83% likelihood of a reduced methane leakage rate during 2008–2015.

Methane emissions result in atmospheric concentration increases in the source regions and downwind. Due to the relatively long atmospheric lifetime of methane (≈9 years) in comparison to NMHCs, at ≈1900 ppb the methane background is 3–4 orders of magnitudes higher, and methane enhancements are moderate (≈10%) on a relative scale. The slow atmospheric oxidation of methane causes relatively little of the regionally emitted methane to be oxidized locally. Modelling work [*Lindaas et al.*, 2019] estimated a 2% contribution from DJB-wide emitted methane oxidation to the regional ozone production.

The Four Corners area is another Colorado region that has received attention because of its recognized methane emissions. Based on satellite data analyses, *Kort et al.* [2014] reported "... the largest anomalous CH_4 levels viewable from space over the conterminous U.S. are located at the Four Corners region in the Southwest U.S." Their work primarily pointed out discrepancies between inventory and these satellite data derived methane flux estimates. Follow-up studies have confirmed an abundance of fossil methane sources in the Four Corners regions, with contribution from coal shaft venting, natural seepage, and O&NG well and distribution sites [*Frankenberg et al.*, 2016]. The methane flux estimate for the Four Corners region of 540 ± 200 Gg yr^{-1} (1σ) [*Smith et al.*, 2017] exceeds the methane O&NG flux estimates for the DJB by a factor of ≈3.

Volatile organic compounds

Petroleum NMHC are the dominant constituents of VOC emissions from O&NG sources. Atmospheric VOCs in the DJB are highly elevated, largely due to O&NG emissions. NMHC and the combined atmospheric carbon from all species exceeds those in major urban areas [*Swarthout et al.*, 2013]. Relative abundances of VOC species scale inversely with molecular size; ethane is typically the NMHC emitted at the highest flux, followed by propane, then the butanes, and so forth. There are dozens of individual VOCs that have been listed in O&NG emissions. However, the bulk of the mass is contributed by a narrower count. For instance, in O&NG plumes identified in continuous monitoring at the Boulder Reservoir, the 16 most abundant VOC species account for approximately 90% of the total O&NG emitted VOC mass [*Helmig et al.*, 2020]. O&NG VOC emissions also contain aromatic constituents, such as the BTEX species (benzene, toluene, ethylbenzene, xylenes) [*Pétron et al.*, 2012; *Gilman et al.*, 2013; *Swarthout et al.*, 2013; *Koss et al.*, 2017]. While these are relatively low, sub-1% constituents, they have received notable attention because of their recognized health impacts on humans.

Over the past five years, ethane has become an increasingly utilized tracer for natural gas VOC emissions. This increased attention to ethane has also been fostered by new instrumentation that has recently become available for sensitive and fast response ethane detection [*Richter et al.*, 2015; *Yacovitch et al.*, 2015; *Yacovitch et al.*, 2017; *Barkley et al.*, 2019; *Kostinek et al.*, 2019]. Ethane has relatively weak non-O&NG source emissions, which makes it a sensitive tracer for identifying O&NG plumes and influences. The ethane to methane enhancement ratio has been used to characterize emissions from particular basins, and for scaling the VOCs flux to methane. In the DJB, natural gas on average has an ethane/methane molar ratio of 12–16% (ppb/ppb), equivalent to a 23–30% mass ratio [*Peischl et al.*, 2018; *Kille et al.*, 2019; *Helmig et al.*, 2020], which is close to the estimated mean of all U.S. O&NG basin emissions [*Helmig et al.*, 2016].

Atmospheric monitoring data show highly variable VOC concentrations. Large VOC enhancements can occur in air plumes originating from O&NG source regions [*Swarthout et al.*, 2013; *Rossabi et al.*, 2017; *Helmig et al.*, 2018]. This effect is also evident in the large relative standard deviation of statistical analyses of the region's VOCs data [*Rossabi et al.*, 2000]. At the Boulder Atmospheric Observatory (BAO, **Figure 3a**), located in Erie at the transition between the more densely populated and industrialized DMA to the south, and the DJB O&NG and agricultural areas to the north, air composition was found to have variable urban and O&NG signatures from significant mixing and recirculation of air influenced by these different sources [*McDuffie et al.*, 2016]. As with any surface-emitted source, VOC concentrations also vary significantly between day and night, with typically higher nighttime concentrations due to the nighttime absence of dilution of surface air from convective mixing [*Swarthout et al.*, 2013; *Halliday et al.*, 2016]. Concentrations drop with height [*Swarthout et al.*, 2013], indicating that releases occur at the surface.

Several studies have demonstrated spatial gradients with increasing mean VOC concentrations and increasing variability with decreasing distance to O&NG wells and operations. Total alkanes concentrations increased by a factor of 10 from distances >1600 m to distances of <152 m [*McKenzie et al.*, 2018]. Even higher gradients (up to a factor of ≈30) were found for BTEX species. The significance of O&NG sources to ambient BTEX was demonstrated in continuous surface measurements conducted at a site near Platteville (**Figure 3a**) during FRAPPE [*Halliday et al.*, 2016]. Benzene values exceeding 10 ppb, with a maximum of 29.3 ppb, were observed on multiple occasions, particularly at night when emissions were trapped near the surface. The mean nighttime value (0.73 ppb) for August 2014 was above the 1:100,000 increased lifetime cancer risk threshold (0.5 ppb) listed by the World Health Organization [*WHO*, 2019b]. Benzene values above 10 ppb were also reported in nine canister samples collected from a mobile surface platform downwind of different O&NG facilities, including operations labelled as "waste water disposal well" and "oil waste dumping facility" [*Pfister et al.*, 2017a]. Newer observations from mobile platforms presented by

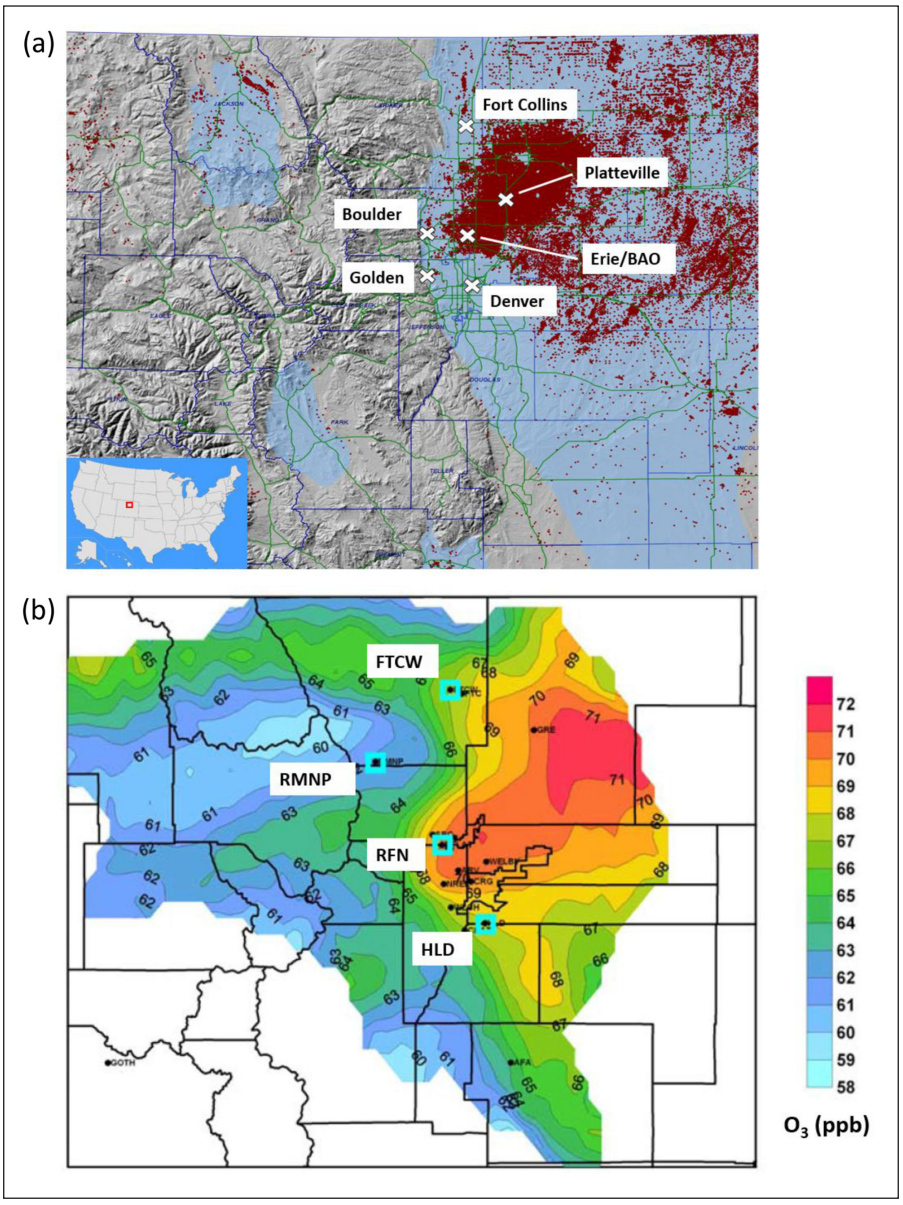

Figure 3: Comparison of geographical distribution of O&NG well locations with elevated ozone source region. **(a)** The Colorado Northern Front Range with major urban cities Fort Collins, Boulder, and Denver, as well as the study sites Boulder Atmospheric Observatory (BAO) in Erie and Platteville that are mentioned in the text. Active oil and gas wells are indicated by red dots (map from by Colorado Oil and Gas Conservation Commission website, https://cogcc.state.co.us/#/home). The map area matches the geographical area depicted in (b). The inset in the bottom left corner shows as a red rectangular the approximate location of the map area within the State of Colorado. **(b)** Source footprint analysis for elevated ozone measured at the four indicated monitoring sites. This figure is a reproduction of Figure 3–13 from the DMA and North Front Range 8-Hour Ozone State Implementation Plan [*CDPHE*, 2008]. The color contours are the results of a correlation analysis of ozone measured at the four surface size with HYSPLIT back trajectories. The contours display "... the mean May 17–August 15, 2006, Front Range daily maximum 8-hour ozone concentrations resulting from transport from given source areas. These are the average concentrations that result at these four monitors when an air mass originates in a given area." [*CDPHE*, 2008]. The four ozone monitoring locations (squares) are Fort Collins West (FTCW), Rocky Mountain National Park (RMNP), Rocky Flats North (RFN), and Highland (HLD). DOI: https://doi.org/10.1525/elementa.398.f3

NOAA and University of Wyoming scientists point to even larger BTEX enhancements downwind of drilling operations and produced wastewater facilities: *Madronich et al.* [2019] found an abundance of benzene mixing ratios in the 10–50 ppb range near Greeley in the center of Weld County. *Mielke-Maday et al.* [2019], in their analysis of correlating wind with benzene data, found the highest benzene enhancements when winds originated from the direction of a nearby multi-well pad. Thus far, the highest concentrations were recorded in proximity of oil and gas wastewater disposal facilities in eastern Weld County, with maximum BTEX plume values approaching 500 ppb downwind of these facilities [*Edie et al.*, 2019].

Horizontal gradients in VOCs have also been demonstrated on a larger regional scale along transects from the periphery towards the center of the DJB. This behavior

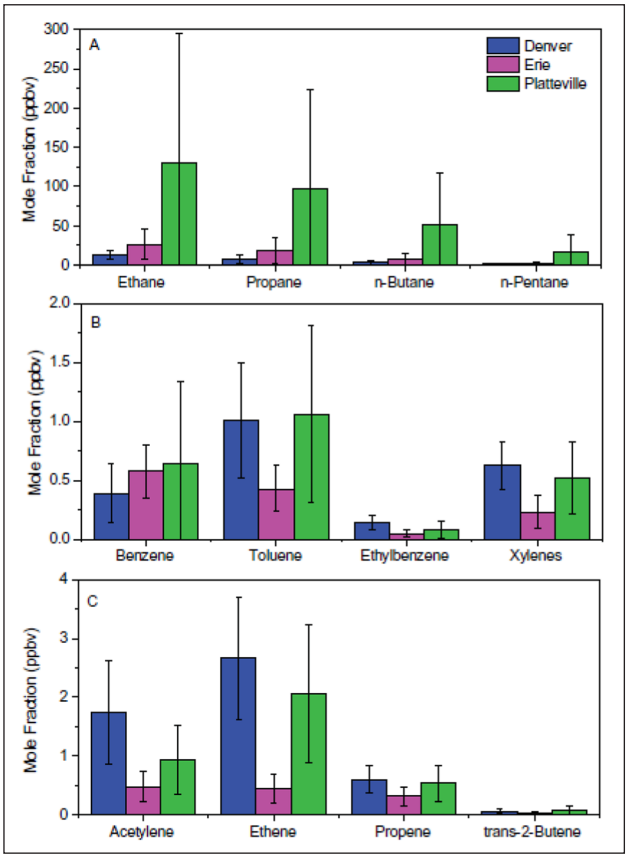

Figure 4: Statistical comparison of 2013 atmospheric monitoring data for twelve VOCs from downtown Denver, Erie, and Platteville [*Thompson et al.*, 2014]. DOI: https://doi.org/10.1525/elementa.398.f4

has been seen in surface [*Thompson et al.*, 2014; *Helmig et al.*, 2015; *Rossabi et al.*, 2017; *Rossabi et al.*, 2019] and aircraft data [*Richter et al.*, 2015]. A representative example is illustrated in **Figure 4**, comparing data from a site in downtown Denver, data from Erie (southern border of the DJB), and from Platteville (**Figure 3a**). Mean mole fractions for the alkane NMHC are a factor of 10–50 higher at Platteville than in Denver, with Erie values falling in between. The Platteville ethane and propane values are among the highest ambient concentration values for these species ever published in the literature. For higher molecular weight NMHC and aromatic compounds, spatial gradients are less pronounced, indicating that emission sources for these compounds have a more even geographical distribution. Besides health concerns from direct exposure, these emissions are a major culprit for the regional photochemical ozone production that will be discussed in the next section.

Ozone

Ozone has long been recognized as an important air pollutant. Breathing air with elevated ozone irritates the respiratory system and can cause acute and chronic respiratory cardiovascular health effects. People with asthma, children, and the elderly are particularly at increased risk. There is a rich literature on ozone health effects (i.e. [*Fleming et al.*, 2018; *Lefohn et al.*, 2018]). The risk increases with ozone concentration and length of exposure. Health effects have been noted in numerous studies below the current 70 ppb NAAQS [*Fleming et al.*, 2018]. Exposure of communities to elevated ozone has been proven to increase mortality rates during and shortly after increased ozone events [*Gryparis et al.*, 2004; *Bell et al.*, 2005]. In an extensive study across 90 U.S. urban communities, a 0.5% increase in daily mortality was found for a 10 ppb increase in daily mean ozone [*Bell et al.*, 2005].

Through plant respiration and surface uptake, ozone is also damaging to vegetation [*Mills et al.*, 2018]. The stress on vegetation from ozone reduces plant growth and productivity, causing significant loss to U.S. and global farming industries and food supply [*Van Dingenen et al.*, 2009; *Lapina et al.*, 2016].

Ozone is not a directly emitted pollutant, but is formed in the atmosphere through a series of photochemical reactions that are fueled by emission of VOCs and NO_x in the presence of sunlight. The efficiency of this chemistry is rather complex, depending on other variables, including the ratio of VOC/NO_x, VOC speciation and reactivity, solar radiation, temperature, wind speed and dispersion conditions. This causes rates of ozone production to vary substantially, from single digits to tens of ppb h^{-1} during mid-day hours.

Background ozone is generally higher in the western U.S. overall than in the eastern U.S. [*Zhang et al.*, 2011; *Cooper et al.*, 2012; *Jaffe et al.*, 2018], causing air moving into the NCFR being on average higher in ozone than in many other parts of the country. An analysis by the U.S. EPA estimates the non-U.S. background contribution on days when ozone is relatively high (>60 ppb) at 38 ppb, which is the highest among 12 included comparison sites [*EPA*, 2008], and more than half of the current ozone NAAQS. The contribution of ozone from long-range transport is on average contributing more to the background in spring than during the primary summer ozone season [*Cooper et al.*, 2012; *Lin et al.*, 2017]. During 2000–2015, the resulting summer ozone background (range of median ozone during summer at Colorado rural, non-mountain monitoring stations) was 32–49 ppb, with mean and median values of 41 ppb ([*Bien and Helmig*, 2018]; Supplemental Materials). Downward folding of high troposphere/lower stratosphere air has been observed on a few occasions to bring elevated ozone to the surface. These conditions depend on the strength and location of the polar jet, are irregular, and have been reported exclusively for the spring [*Langford et al.*, 2009; *Lin et al.*, 2015]. Emissions from wildfires can contribute to ozone production, with the rate and total amount of ozone produced being sensitive to the fire and plume conditions [*Jaffe and Wigder*, 2012; *Jaffe et al.*, 2013]. Overall, fire emissions are a minor contribution compared to the role of anthropogenic emissions to the larger geographic scale ozone buildup [*Lin et al.*, 2017]. This influence is highly variable, and estimated to enhance the Intermountain West regional summer MDA8 by 0.3–1.5 ppb [*Lu et al.*, 2016]. Regional ozone production is further promoted by the dry and sunny climate. Combined, these conditions make it more challenging for regions in the western U.S., including the NCFR, to control ozone,

as it leaves less room than in other regions for local ozone production to exceed the standard [*Cooper et al.*, 2015]. Notably, background ozone at remote high elevations sites across the western U.S. during summer has been declining during the most recent decade [*Bien and Helmig*, 2018; *Jaffe et al.*, 2018], which should constitute favorable conditions for the NCFR on its path towards lowering surface ozone.

A compelling case demonstrating the influence of O&NG emissions on surface ozone in the NCFR was first published in the *Denver Metropolitan Area and North Front Range 8-Hour Ozone State Implementation Plan* in 2008 [*CDPHE*, 2008]. Combining summer ozone data from four sites along the NCFR with air transport back trajectory analyses showed that for elevated ozone events during mid-May to mid-August 2006, air transport from the center of the DJB was associated with the highest ozone values, whereas transport from surrounding areas, including the DMA, brought in air with lower ozone levels (**Figure 3b**). The geographical overlap of the source footprint with highest ozone with the area of highest O&NG well density (**Figure 3a**), provided credence to the argument that O&NG industry emissions played an important role in ozone production and high ozone occurrences. Daytime summer ozone production rates of 7–8 ppb hr^{-1} have been seen in ambient diurnal ozone data [*CDPHE*, 2008; *Cheadle et al.*, 2017]. Direct measurements of the ozone production capacity in Golden during FRAPPE found maximum late morning ozone production rates about two times that high [*Baier et al.*, 2017]. Assessing the relative benefit of VOCs versus NO_x controls is extremely challenging in the NCFR. VOC/NO_x ratios vary widely across the region, with lower ratios present in the DMA, and higher ratios in the VOC-rich DJB. These different air masses can mix during transport and recirculation, causing a wide range of spatial and temporal differing conditions and ozone production regimes.

Two studies estimated the contribution of O&NG VOCs to the total reactivity with the OH radical using VOC speciation and atmospheric concentrations at the BAO. This variable can serve as a metric for the chemical reactivity of air and its potential for producing ozone. A NOAA study estimated that 55 +/– 18% of the reactivity was attributable to O&NG emissions [*Gilman et al.*, 2013]. *Swarthout et al.* [2013], using a similar approach but with independently collected data, determined a value of 57%. While OH reactivity does not directly translate to ozone production, based on these results, both groups predicted that O&NG VOC emissions would enhance and play a significant role in the regional ozone budget. It should be noted that these measurements were conducted in the late winter, when ozone production is relatively moderate in the NCFR. Therefore, these findings represent, for example, lower influence from biogenic VOCs.

A NOAA study, i.e. *McDuffie et al.* [2016], went a step further and incorporated VOC speciation and VOCs reactivity in a photochemical model. Their findings showed "that O&NG alkanes contribute over 80% to the observed carbon mixing ratio, roughly 50% to the regional VOC OH reactivity, and approximately 20% to regional photochemical ozone production." Using observations from BAO for correlation analyses and modeling of oxidation chemistry, *Lindaas et al.* [2019] stipulated that O&NG emissions contribute to ozone production on high ozone days; however, that study fell short of providing a quantitative estimate. Another modeling study by NCAR scientists [*Pfister et al.*, 2017b], building on FRAPPE data for the wider NCFR area, concluded that on average, O&NG emissions contribute 30–40% to the local ozone production on high ozone days. It needs to be emphasized that all of these studies derived estimates for the ozone produced regionally, not the total ozone, which is also determined by the background that is transported into the region (see above).

These predictions from reactivity consideration and modeling are backed by a series of observational studies: *Evans and Helmig* [2017], using a correlation analysis of ambient ozone and wind data from BAO and the South Boulder Creek regulatory monitor, found that during 2009–2012, 65% (average between both sites) of elevated ozone events were associated with transport from O&NG production regions. *Cheadle et al.* [2017], analyzing selected cases of observations near Greeley during FRAPPE, estimated that O&NG emissions contributed up to ≈20 ppb to ozone production on high ozone days. *Oltmans et al.* [2019] conducted an in depth analysis of the conditions on high ozone days at BAO. Their analysis showed an association of high ozone days with transport from sectors with intense O&NG production towards the northeast. The authors concluded that O&NG emissions were an important source of ozone precursors and are crucial in producing peak ozone events in the NCFR. The ozone production chemistry is primarily driven by VOCs of anthropogenic origin; biogenic emissions appear to have a minor contribution to the NCFR ozone production chemistry [*Cheadle et al.*, 2017; *Lindaas et al.*, 2019].

Ozone enhancements in air enriched with O&NG emissions have been measured all the way up the Rocky Mountain National Park in upslope flow along the eastern slopes of the Rocky Mountains. *Benedict et al.* [2019] estimated that high ozone events associated with O&NG emissions contributed ≈20 ppb of additional ozone at the Rocky Mountain National Park Longs Peak air monitoring station. This poses the question of ecosystem impacts of the elevated ozone on the natural environment, including Rocky Mountain National Park. Ozone has long been known to damage crops, and reduce yields in agriculture [*Heck et al.*, 1982; *Van Dingenen et al.*, 2009; *Avnery et al.*, 2011]. For sensitive crops, those losses can be well more than 10%, accounting to a significant revenue loss to the farming industry [*Morgan et al.*, 2003; *Avnery et al.*, 2011]. The DJB O&NG production overlaps with a region that is also considered the agricultural heartland of Colorado. Colorado's agricultural industry provides over $40 billion to the state economy [*USDA*, 2018]. There have been no assessments to date on the revenue loss to this industry from the elevated ozone caused by O&NG emissions within the State.

Particulates

The DMA has a history of air quality problems from particulates pollution that goes back to the 1970s and 80s [*Waggoner et al.*, 1983]. The episodic wintertime occurrences of reduced visibility from accumulation of gaseous and particulate matter near the surface have been named the 'Denver Brown Cloud' [*Neff*, 1997]. They are tied to the peculiar topographical and meteorological conditions in the NCFR, where during the winter, shallow (<500 m) boundary layer heights, low convective mixing, also promoted by snow cover and cold soils, can promote accumulation and buildup of particular emissions over several days. A series of studies revealed a mix of sources, with traffic, urban, and agricultural emissions [*Wolff et al.*, 1981]. Most of the visibility reduction was found to be associated to particulates smaller than 2.5 μm [*Groblicki et al.*, 1981]. Secondary aerosol production, particularly growth of organic aerosol, as air recirculates over areas with different source signatures, was identified as a major contributing mechanism for aerosol buildup [*Sloane et al.*, 1991]. This secondary production of aerosol and ozone occurred on winter days, with temperatures as low as 6°C [*Ferman et al.*, 1981].

Despite the population growth of the DMA/NCFR, occurrences of Denver Brown Cloud episodes and the aerosol loading (*CDPHE*, 2019, unpublished results) have seen a gradual decline during the past two decades, most likely thanks to stricter air pollution control measures.

O&NG operations are sources of atmospheric aerosol in several ways. Heavy equipment operation, soot emissions from diesel engines and power generation, unloading and handling of silica that can be added as a fracking fluid constituent, and soot from oil and gas flaring, are some of the important primary emissions sources. There is also potential of secondary aerosol formation from the atmospheric oxidation of gaseous emissions, such as H_2S, SO_2, NO_x, and VOCs. These gases are known to produce less volatile chemicals during their atmospheric oxidation, which can serve as aerosol nuclei or add to existing aerosol. Comparatively few published studies have addressed aerosol from O&NG operations in Colorado. The reason may lie in the difficulty of attribution, which is more difficult for PM2.5 relative to ozone, whose formation mechanism is better defined.

Continuous vertical profiles of aerosol and gaseous components were measured during the NACHTT (Nitrogen, Aerosol Composition, and Halogens on a Tall Tower) campaign at the BAO [*Brown et al.*, 2013]. The aerosol mass was dominated by nitrate, which was mostly from sources within the region. Other significant contributions were from organics and sulfate, with sulfate primarily being transported long-range. While the composition of organic gas phase compounds was noted to have a strong O&NG influence, the study conclusions do not specify O&NG influences on the aerosol composition. An investigation on aerosol dependency on circulation patterns in the NCFR found that cyclone conditions promoted the transport of aerosol constituents from the northern Front Range into the DMA, increasing aerosol mass loadings and reducing visibility [*Vu et al.*, 2016]. The circulation pattern would be expected to cause air to become enriched in O&NG emissions while passing over the DJB, before circling back into the DMA. The organic fraction made the largest component of total aerosol. The study, however, did not specify if the high organic aerosol loading was associated to O&NG precursor emissions.

Two publications report on the O&NG contribution to the NCFR aerosol loading in the context of FRAPPE. *Dingle et al.* [2016] determined extinction enhancements relative to the amount of the combustion tracer carbon monoxide. They found an increase in the extinction coefficient with the aging of air masses that was accompanied by formation of secondary organic aerosol; the extinction was strongest correlated with organic aerosol in O&NG-influenced air, and with nitrate aerosol in O&NG and agriculture emissions. *Bahreini et al.* [2018] reported a significant contribution of non-combustion organic aerosol. Organic aerosol was on average 40% higher in plumes with a high O&NG influence, and the organic aerosol was dominated by secondary constituents, suggesting that they may be products of O&NG VOCs oxidation. The study concluded that O&NG sector emissions contribute up to 38% to the secondary organic aerosol in the region.

Atmospheric circulation influences in the NCFR

The impact of O&NG emissions on NCFR air quality is exacerbated by very peculiar atmospheric circulation patterns. *Johnson and Toth* [1982] were the first ones to present an in depth characterization of the daily cycle of mountain-valley winds. At night, cooler air flows from the mountains and down the Platte River valley over the plains (west to east transport). During the day, the air flow reverses, bringing air from over the plains (and O&NG source regions; east to west transport) back to the foothills. Such recycling can continue over several days. During daytime, upslope flow is a prominent flow regime. This circulation is driven by the warming of the easterly slopes of the Rocky Mountains range, causing convective uplifting that is pulling in air from the east. The flow reverses during the night, with cooler air from higher elevations descending the mountains and forcing west to east air transport.

Figure 5 is a partial reproduction of a figure from *Evans and Helmig* [2017]. These windroses, generated from summer data at BAO, show the very distinct diurnal flow behavior, with flows from north to southeasterly directions dominating during the daytime hours, and south to westerly winds predominant at night. The study analyzed wind data from eight locations along the NCFR. The average diurnal winds were remarkably consistent, demonstrating the importance of this flow regime for the wider NCFR. The transition time between these two flow regimes changes with distance from the mountain slopes, with locations further east experiencing an on average later onset of upslope flow conditions. The diurnal flow regimes are most pronounced during the summer because of the larger solar irradiance that is providing the thermal forcing.

The upslope flow paths are somewhat segregated, such that there is a separation of air masses that are more

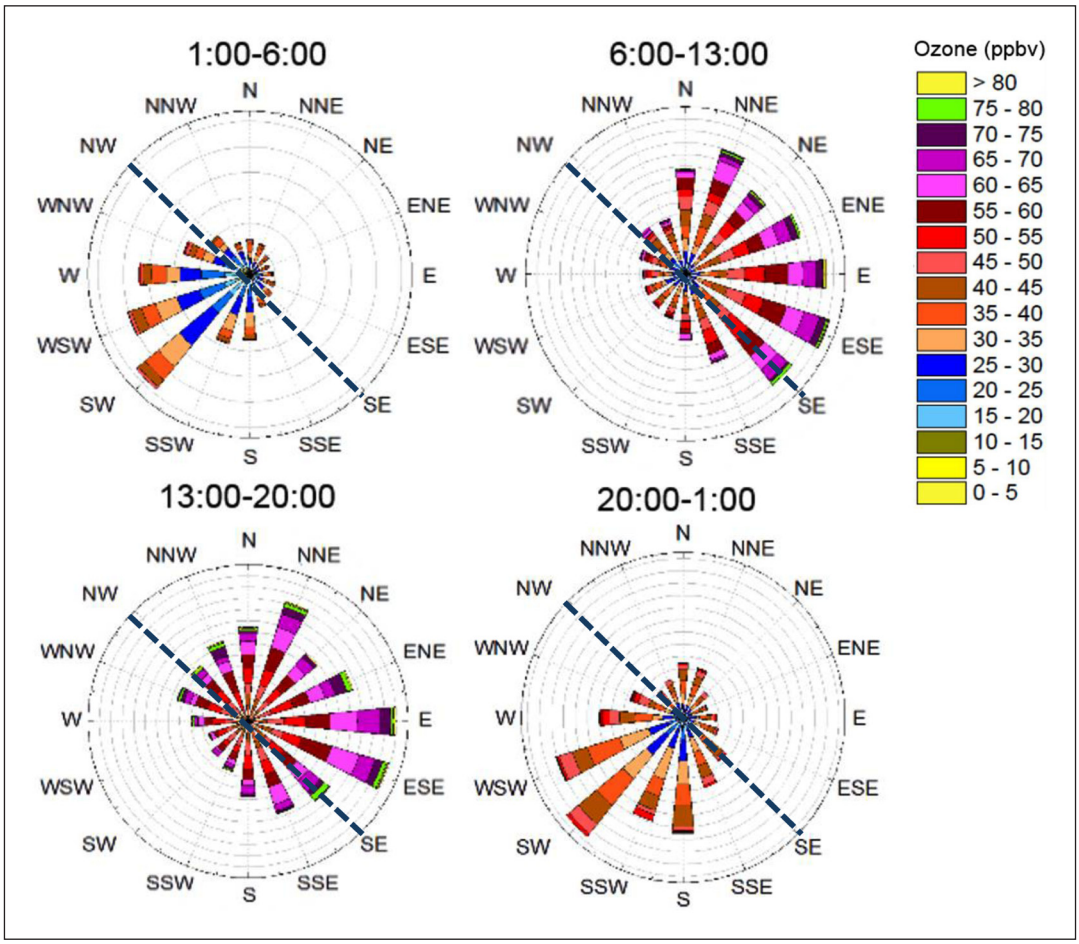

Figure 5: Polar histograms showing wind direction at BAO for the summer months (June 1–August 31, 2009–2012), broken up into four diurnal time windows (times are in Mountain Standard Time (MST)) [*Evans and Helmig*, 2017]. Colors represent the ozone distribution within each sector according to the scale provided in the legend. The dotted line is an approximate illustration of the sectors with O&NG activities (NW to SE), with the O&NG sectors the ones located in the NNW – ESE portion of the wind roses. DOI: https://doi.org/10.1525/elementa.398.f5

heavily influenced by O&NG emissions to the north of the DMA, whereas air masses south of North Denver are more strongly influenced by urban emissions [*Pfister et al.*, 2017a]. Air enriched with emissions from urban, traffic, O&NG, and other regional sources can get 'trapped' along the mountain slopes during late afternoon. This is reflected by highest ozone levels being observed at monitoring sites nearest to the mountain slopes [*Bien and Helmig*, 2018] and at the lower elevations in the foothills [*Brodin et al.*, 2010]. In upslope flow, polluted air from the NCFR regularly reaches high elevation zones on the eastern side of the Rocky Mountain Continental Divide [*Brodin et al.*, 2010; *Benedict et al.*, 2019]. On days with particularly strong flow conditions, NCFR pollution can "spillover" into the valleys to the west of the Continental Divide [*Pfister et al.*, 2017b].

Although a classical view of high pollution episodes invokes a stagnant high pressure region, usually over flat terrain, the meteorology of the NCFR leads to more complex circulation regimes. A common regime in the winter occurs with downslope westerly warm winds from the Rocky Mountains flowing over colder air drawn from the east toward a low pressure trough along the foothills, or due to lee-cyclogenesis located over southeast Colorado [*Neff*, 1997]. During the summer, the 'Denver Cyclone' is often observed. These conditions provide a similar opportunity for trapping pollutants near the surface [*Wilczak and Glendening*, 1988; *Wilczak and Christian*, 1990; *Szoke*, 1991]. In this case, the Denver Cyclone occurs nearer the surface with warmer air aloft from the south that originated over the Palmer Divide, a ridge extending to the east and south of Denver. As the air from the east (underlying the warmer air aloft) carries pollutants and precursors from the eastern plains, the air can stagnate as it encounters the topographic barrier to the west. This circulation pattern can cause pollution to circulate and accumulate for several days, leading to increases of secondary pollutants. *Vu et al.* [2016] demonstrate an up to an 80% increase in aerosol constituents during a cyclone episode during FRAPPE.

The frequency and prominence of high ozone occurrences is correlated with high pressure systems that promote sunny weather, high temperatures, stagnant air circulation, which are conditions that are favorable for photochemical ozone production. *Reddy and Pfister* [2016] investigated this relationship and proposed a method in which monthly 500-mbar pressure heights were used for correcting the year-to-year variability in the

fourth highest MDA8 ozone. Further, these conditions promote cyclic terrain-driven circulations that reduce pollution transport away from sources. The authors recommend correcting annual MDA8 data using monthly 500-mbar pressure heights for reducing weather influences on ozone trends.

Inventories

Emission inventories have been developed by state and national regulatory agencies in support of air quality modeling and for directing policy development. These bottom-up inventories are based on emissions estimates of facility types and operations with regional/basin-wide scaling using best available facility counts. Evaluation of the bottom-up inventory estimates has mostly been accomplished by university and NOAA scientists through comparing with top-down flux estimates that were developed from aircraft and surface data. Experimental capabilities for basin-wide, top-down flux determinations have improved remarkably over recent years. Emissions have been estimated by determining the enhancement in the basin outflow by aircraft profiling upwind and downwind of production regions, determination of horizontal winds and boundary layer depth [*Karion et al.*, 2013; *Karion et al.*, 2015; *Peischl et al.*, 2015; *Peischl et al.*, 2018].

Most of these studies have pointed out inconsistencies in inventories and a likely underestimation of O&NG inventory surface emissions. Uncertainties of bottom-up inventories can arise from the extrapolation of limited information of facility-scale emissions from venting, flashing, and leakage, and the neglect of differences in practices of operators. Inventories are annual averages with little to no temporal information. *Vaughn et al.*, [2018] demonstrated that this may be part of inventory uncertainties and discrepancy between bottom-up and top-down emission estimates. Further, the lack of temporal information makes source apportionment and model performance evaluation more difficult.

In an extensive evaluation of methane and VOC emissions representation in the Western Regional Air WRAP Phase III inventory [*WRAP*, 2009], *Pétron et al.*, [2012] concluded that "there are notable inconsistencies between our results and state and national regulatory inventories". They further stated "Our analysis suggests that the emissions of the species we measured are most likely underestimated in current inventories and that the uncertainties attached to these estimates can be as high as a factor of two". Results also showed that methane sources from natural gas industries in Colorado were most likely underestimated by at least a factor of two. Besides methane and total VOC, the study also assessed benzene, and concluded that for this species State inventory estimates were too low by at least a factor of five. *Levi* [2012] commented on the difficulties and high sensitivity of the top-down emissions estimation based on emission ratios of VOC species.

In their assessment of the National Emissions Inventory (NEI) for 2010, *Tzompa-Sosa et al.* [2017] found that inventory fossil fuel emissions had to be increased by 40% for the Northern Hemisphere to yield agreement with observations, except for the central U.S., including Colorado, where even the 40% increase under-predicted observed mixing ratios in the lower troposphere.

Pfister et al. [2017a], in their modeling of FRAPPE and DISCOVER-AQ data, found that they had to increase O&NG non-ethane emissions by a factor of four over their best inventory estimate for the best match between observations and model output.

The most recent evaluation, based on NOAA aircraft surveying [*Peischl et al.*, 2018], illustrates relatively little improvement in agreement between inventories and top-down emission estimates. The NOAA study determined a DJB-wide ethane flux of 7.0 +/− 1.1 × 10^3 kg hr^{-1}, which translates to 61 +/− 10 × 10^6 kg (kilotonnes) yr^{-1}. This ethane flux alone is higher than then current Regional Air Quality Council O&NG non-ethane total VOC bottom-up inventory flux of 56 × 10^6 kg yr^{-1} [*Brimmer*, 2019]. With ethane constituting approximately 30% of the total O&NG VOC flux in the regional oil and gas emissions [*Gilman et al.*, 2013; *Swarthout et al.*, 2013], the *Peischl et al.* [2018] ethane flux equates to a total O&NG VOC flux of ≈230 × 10^6 kg yr^{-1} (**Table 3**). Excluding ethane yields ≈170 × 10^6 kg yr^{-1}, which exceeds the non-ethane Regional Air Quality Council (RAQC) total VOC estimate by a factor of ≈three.

Taken together, these available comparison studies highlight the deviations between the bottom-up and top-down emissions estimates. Unfortunately, there is a scarcity of top-down estimates available for this evaluation, and each of these have relatively large uncertainty windows themselves. Nonetheless, these disagreements diminish the confidence in the bottom-up inventories, and air quality modeling that is building on these most likely under-predicted emissions.

Changes in O&NG emissions and atmospheric concentrations

Since 2008, Colorado has implemented regulations to reduce VOC emissions from O&NG sources, and methane-specific regulations came into place in 2014 [*Ogburn*, 2014; *CDPHE*, 2019c]. State inventories largely build on projected emissions reductions from these measures. However, there are very few data records that allow an evaluation of the important questions, if and how actual O&NG emissions in the DJB have changed over time. There is no published peer-review literature at this time that has addressed this question and presented trend results that would allow assessing basin-wide emission changes with statistically significant certainty. Data from after the methane emissions rule adoption in 2014 would be most helpful in understanding the benefits of that regulation and current emission levels.

Comparing historic with modern observations of VOC data from Boulder, *Thompson et al.* [2014] stated "An initial look at comparisons with data sets from previous years reveals that ambient levels for oil and gas-related NMHC in Erie, as well as further downwind in Boulder, have not decreased, but appear to have been increasing, despite tightening of emissions standards for the oil and gas industries in 2008."

CDPHE has been conducting canister air sampling at Platteville since 2011 [*CDPHE*, 2019b]. However, inconsistencies in the sampling, uncertainties in the analysis protocols [*Hood, 2019*], siting of the sampling location, and the proximity of the sampling location to abundant nearby well sites make trend determinations and their interpretation for the wider region from these data uncertain.

Ethane column observations conducted from 2010–2015 at the NCAR Foothills Laboratory in Boulder are presented in *Franco et al.* [2016]. Their best estimate is a rate of increase of 5.0% per year. This rate is above estimated rates for the increase of ethane in the Northern Hemisphere background atmosphere during this time window [*Helmig et al.*, 2016], which implies increasing ethane emissions in the region. However, the uncertainty interval in this result is rather large. Including newer data, extending the record to 2010–2018, did not yield a trend in the atmospheric ethane abundance (J. Hannigan, NCAR, personal communication, April 2019).

NOAA conducted sampling of VOCs, with up to daily resolution, from 2007–2016 at 300 m height from the BAO tower. Data for the O&NG VOC tracer propane collected during midday to afternoon hours, when boundary layer mixing is most progressed, do not show statistically significant changes, indicating stable total emissions of O&NG VOCs during this 9-year time window [*Oltmans et al.*, 2020].

Lastly, the methane flux estimates listed in **Table 2**, covering observations between 2008–2015, do not show any changes in the total methane flux that are outside of the uncertainty windows of the individual observations. Assuming that the VOC/methane ratio has remained constant, these methane flux determinations do not suggest changes in basin-wide VOC emissions. Considering the large increase in natural gas production during this time period, a reduction in the fraction of emitted methane (relative to the produced quantity of natural gas) and VOCs appears probable [*Peischl et al.*, 2018].

Available VOC emissions estimates, differentiated by ethane, benzene, and total VOC, are provided in **Table 3**. The latest estimate in each category is based on relative observations of VOC/methane at the Boulder Reservoir during 2017–2018, scaled to the *Peischl et al.* [2018] year 2015 methane flux estimate. Therefore, these two data sets are linked to each other.

In summary, at this time, there do not appear to be observational records that allow deducing, with statistical significant certainty, if and how methane and/or VOC emissions may have changed in the DJB over the past 15 years. There is no convincing evidence for an overall decrease in VOC emissions at this time. Certainly, none of these data show increases that scale with the DJB O&NG production increase (e.g. 3.5–6.5 times for natural gas and oil, respectively, for 2010–2018). Therefore, it appears likely that relative emissions rates have declined, likely due to the implementation of stricter emission controls. However, the growth of the number of operations has probably counteracted those relative emissions reductions, resulting in overall basin-wide stable total emissions.

Table 3: Comparison of DJB ethane, benzene, and total VOC flux estimates. DOI: https://doi.org/10.1525/elementa.398.t3

***VOC*/Year**	**VOC Best Flux Estimate tons yr^{-1}**	**Reference**
Ethane		
2011	29,000	Swarthout et al., 2013
2015	61,000	Peischl et al., 2018
2017/2018	36,000*	Helmig et al., 2020
Benzene		
2011	570	Swarthout et al., 2013
2012	1500	Petron et al., 2014
2017/2018	620*	Helmig et al., 2020
Total VOC		
2006	64,000	Bar-Ilan et al., 2008
2011	79,000	Swarthout et al., 2013
2015/2017/2018	134,000*	Helmig et al., 2020
2015/2017/2018	231,000**	Helmig et al., 2020

* Derived by scaling 2017/2018 relative VOC/methane ratios observed in O&NG plumes at the Boulder Reservoir to the *Peischl et al.* [2018] year 2015 DJB methane flux estimate.

** Same as above, but applying the 2017/2018 relative VOC/ethane ratios observed in O&NG plumes at the Boulder Reservoir to the *Peischl et al.* [2018] year 2015 DJB ethane flux estimate.

Oil and natural gas emissions and air quality

Air quality impacts from O&NG emissions arise from acute, chronic, and carcinogenic effects of primary emissions, particularly of BTEX VOC in close proximity to operations, and emissions of NO_x and particulates from equipment and on-site power generation. These exposures are of concern for residents living within a few hundred meters to kilometers of O&NG operations. According to the survey of *McKenzie et al.* [2016], in 2012, ≈56,000 citizens lived within a radius of 1000 feet of O&NG operations in Colorado. These populations are at greatest risks for these exposures. Secondary products that are formed via photochemical processing of emissions during transport are another concern. Here, the pollutants of importance are ozone and PM2.5. These species are transported across a wide spatial scale in the NCFR, thereby affecting a much larger population. In excess of 3.5 million people live in the NCFR ozone NAA. Approximately half of the NAA (mostly the northern part) is moderately to heavily influenced by O&NG emissions. This part of the NCFR is where O&NG emissions have the greatest impact on ozone and exceedances of the NAAQS. Atmospheric levels of particulates are relatively modest in the NCFR, with particulate air quality thresholds being exceeded only occasionally, for instance during wildfire plume transport events and wintertime inversion conditions. Nonetheless, health impacts from particulates originating from O&NG sources are estimated to be similar as for ozone [*Fann et al.*, 2018]. However, ozone is currently the much more recognized regional pollutant.

Emissions of most primary air pollutants continue downwards trends in most of the United States. This also applies to surface ozone; implementation of pollution control measures has resulted in declining surface ozone across wide geographical scales in developed North American and European countries [*Fleming et al.*, 2018]. For instance, the compilation of ozone trends shown in **Figure 6** provides a nice testimony for decreases in surface ozone across the U.S. These downward trends are particularly remarkable in light of the population growth, increase in energy demand and production, and climate change, which is driving higher ozone production rates from the increase of ozone precursors and faster reaction rates in a warmer climate. Assessments in the magnitude of this effect vary by study. This ozone 'climate penalty' potentially can be rather significant, with some estimates predicting an up to 3–6 ppb increase in surface ozone per degree of temperature increase [*Rasmussen et al.*, 2012].

Several studies have pointed out a decline of ozone precursor emissions from other source categories (non-O&NG) in the NCFR. Several publications have noted reductions in DMA NO_x, based on CDPHE NO_x surface monitoring data [*Bishop and Stedman*, 2008; *Cooper et al.*, 2012; *Abeleira and Farmer*, 2017; *Bien and Helmig*, 2018]. DMA and NCFR declining NO_x trends are further confirmed by satellite imaging [*Witman et al.*, 2014; *Lamsal et al.*, 2015], and indirectly inferred from the diurnal ozone behavior [*Bien and Helmig*, 2018]. Because of the distribution of measurement sites, these analyses mostly reflect NO_x emissions in the DMA and not the entire NCFR, and emission reductions that have been achieved from automobiles and power generation plants.

Trends in VOCs are more difficult to assess. In downtown Denver, there is clear evidence that automobile-associated

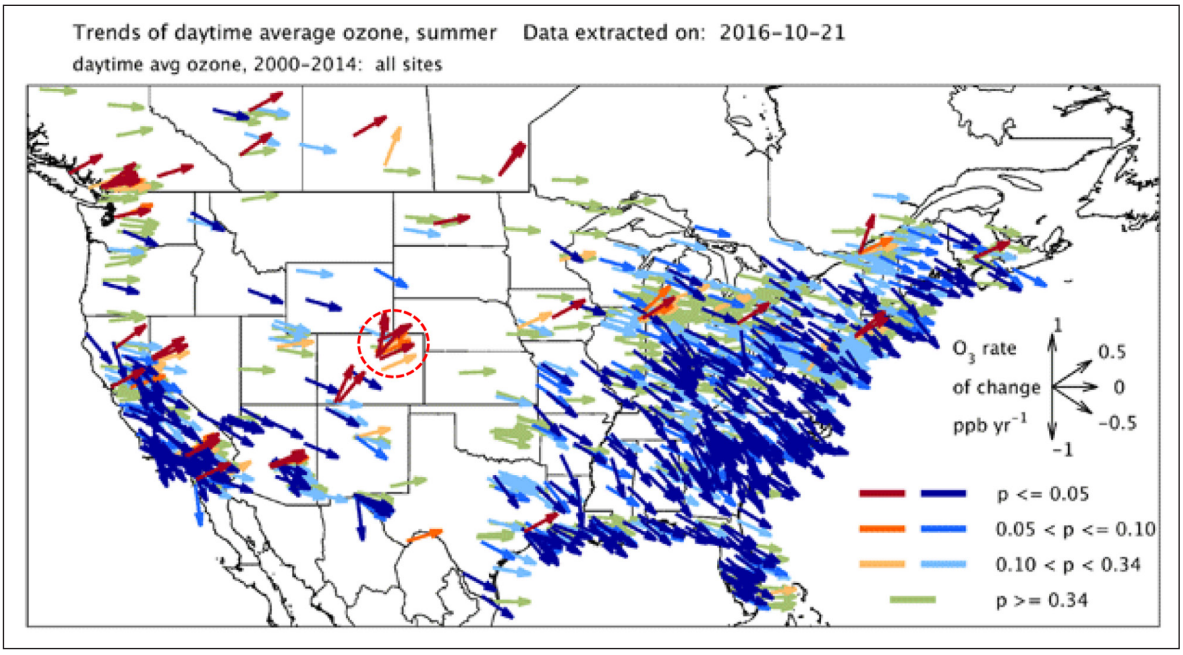

Figure 6: Regional trend analysis of surface ozone observations from monitoring in the U.S. and Canada. These results reflect the 2000–2014 changes in summer ozone [*Chang et al.*, 2017]. The arrow direction indicates the sign and magnitude of the ozone trend according to the scale given in the inset (i.e. downward arrows are indicative of declining ozone), and the color coding shows the statistical significance of the ozone change, with statistical significant changes (at P > 95%) indicated by the bold colors. The DMA/NCFR is indicated by the red circle. This figure is a partial reproduction of Figure 1 in *Chang et al.* (2017). DOI: https://doi.org/10.1525/elementa.398.f6

VOC emissions have been declining [*Bishop and Stedman*, 2008]. Currently, there are no other publications that have reported DMA or NCFR VOC trend analyses, and there is no peer-reviewed research that supports the State agency's conclusion of "a dramatic decline in ambient levels of oil and gas related VOCs" (Supplemental Materials). Taken together, findings from these Colorado NO_x and VOC studies from non-O&NG sources mirror the national trend.

Large year-to-year variations in surface ozone causes trend analyses to be sensitive to the chosen time window. Trend behavior can differ substantially for different ozone metrics, i.e. summer versus annual ozone, different percentile values in the ozone distribution, and the MDA8 or the Design Value (the 3-year running mean of the 4th highest annual MDA8).

Reddy and Pfister [2016] corrected the dependence of high summer ozone occurrences on the predominance of high pressure weather conditions in their investigation of the 1995–2013 NCFR ozone record. They report that these corrected, deemed more robust time series analyses, showed "...a general increase for the Front Range [MDA8] since 2004, broken only by the recession of late 2008".

Lower ozone percentile values, reflecting mostly nighttime ozone, have clearly increased since 2000, most likely due to a weakening nighttime ozone sink from reaction with NO [*Bien and Helmig*, 2018]. The increasing low percentile/nighttime ozone values are possibly contributing to the observed increases in mean and median ozone. During 2000–2015, 10 out of 11 DMA/NCRF sites displayed a positive rate of change, with four out of those being statistically significant trends (p-value < 0.05) [*Bien and Helmig*, 2018]. Trends in the high percentile ozone values that are most relevant for health effects and regulatory considerations are more inconsistent. 2000–2014 Design Value time series plots for the DMA/NCFR sites Chatfield, Rock Flats North, South Boulder Creek, Fort Collins West, and the National Renewable Energy Lab in Golden [*Bien and Helmig*, 2018], suggest a behavior of gradually decreasing values; however, linear regression analyses do not result in statistically significant trends. For the 2000–2015 window, considering a total of 11 DMA/NCFR sites, and 28 linear regressions for summer ozone 95th percentile values, MDA8, and Design Value trend analyses, 9 slope results were positive and 18 were negative. The two times higher negative values count may suggest a predominance of declining ozone behavior. However, the only statistically significant trend results (three) were all positive, indicating increasing ozone. Inclusion of 2016–2018 data in the ozone trend analysis indicates a steadily declining regional Design Value in the last seven years (Supplemental Materials).

The DMA/NCFR ozone behavior deviates from that of most other regions in the U.S. This is most evident in the summer daytime average ozone trends (**Figure 6**). While this ozone metric has clearly (at many sites with statistical significance) been heading downwards across the U.S., increasing values were determined for most sites in the DMA/NCFR. Persisting elevated ozone conditions were evident during 2018; ozone data collected by CDPHE in the NCRF were higher than in any of the previous five years, with a season maximum of 89 ppb and 32 exceedance days of the 8-hour 70 ppb NAAQS at the Boulder Reservoir site alone (see **Figure 7** for the Boulder Reservoir July 2018 ozone record; additional exceedance days for the ozone NAAQS were recorded in all other months from May–September).

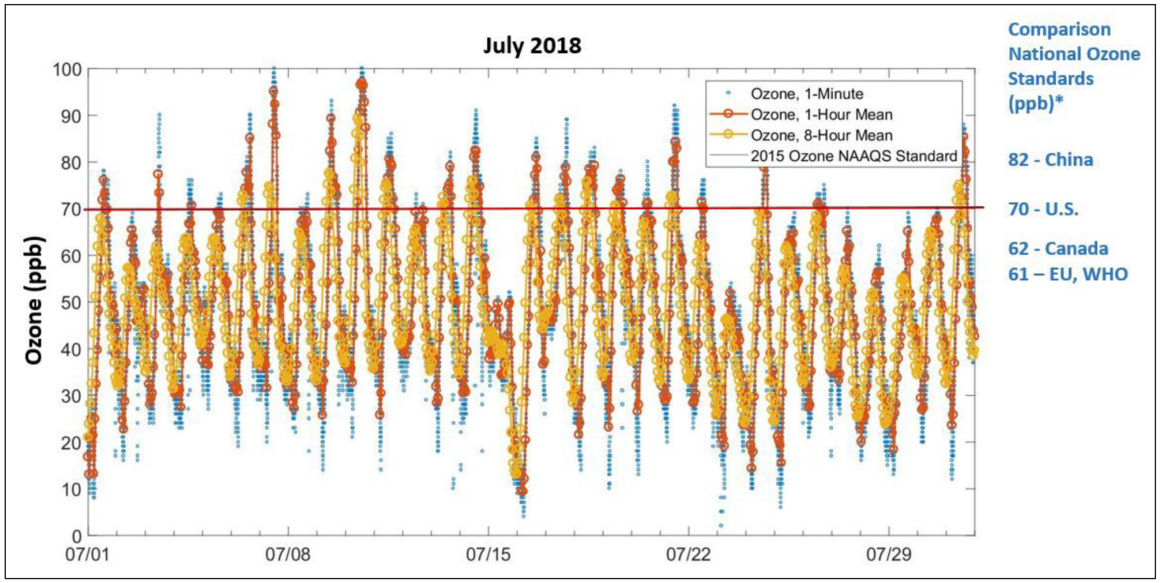

Figure 7: Record of the ozone monitoring by CDPHE at the Boulder Reservoir for July 2018. Data are plotted at the 1-min resolution of the data acquisition, as hourly values, and as 8-hour running mean, which is the regulatory metric. Also shown is the current U.S. ozone NAAQS and, for comparison, 8-hour ozone air quality standards in other selected nations. Shown values are the maximum permitted values to be in compliance. The U.S. and Canada standard applies to the 3-year running mean of the MDA8. *China, the European Union (EU), and the World Health Organization (WHO) list their ozone standards in concentration units. Those were converted to mole fraction values for conditions of 1 atm and 25°C. The WHO value is a guideline. DOI: https://doi.org/10.1525/elementa.398.f7

There are convincing arguments that support the conclusion that the deviation in the Colorado ozone behavior with the national trend is caused by emissions from the O&NG sector, both from O&NG signatures seen in elevated ozone episodes [*Cheadle et al.*, 2017; *Oltmans et al.*, 2019] and from photochemical modeling [*Pfister et al.*, 2017a]. As already pointed out above, biogenic VOC emissions have a relatively minor contribution to regional ozone production; elevated ozone episodes are primarily associated with elevated anthropogenic VOCs [*Cheadle et al.*, 2017; *Zaragoza et al.*, 2017; *Lindaas et al.*, 2019]. The effect of O&NG emissions on ozone production in the NCFR is exacerbated by the dominant summertime air circulation patterns that tend to transport pollution-enriched air from the DJB towards the foothills. Continuing ozone production in these accumulated air masses causes peak ozone values along the westerly parts of the plains stretching from Highlands, along Golden, Boulder, Longmont to Fort Collins and westwards a few miles into the mountain slopes. Boulder County is particularly vulnerable, being the closest and most directly downwind located area of the DJB. This conclusion was stated in the NCAR FRAPPE summary report: "On average, oil and gas emissions show a stronger influence in the northern part of the NFRMA and the northern foothills, while mobile emissions dominate farther south and in the southern foothills. Both sectors contribute, on average, 30–40% each to total NFRMA ozone production on high ozone days."

Peer-reviewed literature is consistent in emphasizing that NCFR ozone exceedances are caused by the locally produced ozone that is added to the ozone background that is transported into the State. For Denver, this background is up to 14 ppb higher in comparison to other U.S. cities [*EPA*, 2008], which lowers the amount of ozone that can be added locally to reach exceedance of the standard. This margin is smaller than for other U.S. NAA, making meeting the standard more challenging. However, the local ozone production is mostly within the control of the State. Meeting the standard is calling for a concerted and aggressive effort in curbing regional ozone precursor emissions.

Recommendations

O&NG emissions are impacting air quality in the NCFR in multiple ways and at several scales. Exposures in close proximity arise from primary emissions. Current assessments indicate that the most concerning health impacts are from aromatic VOCs (BTEX), and for citizens living within a 1000 feet radius of wells and O&NG operations. On the order of 3.5 million Colorado residents live in the NCFR ozone NAA. Despite efforts to reduce ozone precursor emissions, and gains made in certain important emission sectors, including transportation and electrical power generation, the region is still subjected to an abundance of elevated ozone occurrences and exceedances of the NAAQS every year. This calls for concerted efforts for better characterizing emissions and air quality impacts of O&NG emissions and for emissions regulation. Specific recommendations are:

- The lack of long-term NO_x monitoring within the DJB hampers the assessment of the contribution of O&NG emissions to regional NO_x. NO_x monitoring should be implemented at key locations upwind, within, and downwind of the DJB. More research is needed to better define NO_x point emissions from O&NG facilities. Remote sensing tools and data should be included in the evaluation of O&NG NO_x sources and emission trends.
- Very little research has been done on evaluating and quantifying the contribution of O&NG emissions to atmospheric particulates. The prospect of 25–49 premature annual human deaths in Colorado from exposure to particles caused by O&NG emissions under current industry growth scenarios by 2025 [*Fann et al.* 2018] should motivate a concerted effort to investigate and better define particulates pollution, and to regulate particulates and secondary aerosol precursor emissions from the industry.
- VOC data, mostly from occasional and campaign-type observations, as well as the CDPHE monitoring at Platteville, clearly show a strong contribution from O&NG operations on total VOCs and the ozone-producing VOC reactivity in the region. VOC monitoring is crucial for assessing O&NG air quality impacts. The current distribution of monitoring sites has a number of shortcomings for evaluating and monitoring changes of O&NG emissions. VOC monitoring is needed near operations to assess facility emissions and exposure risks of nearby residencies. This monitoring needs to be expanded to activities such as flowback, liquid unloading, and wastewater separation, which appear to be associated with high emissions and which have been mostly neglected or been underrepresented in previous assessments. In order to capture the high variability of these emission, this monitoring should be at high time resolution, ideally in real time. VOC monitoring needs to be tailored for characterizing emission trends, representative for a wide regional footprint. This can, for instance, be achieved by sampling at elevated sites or/and from inlets high above the surface, and best during mid-day to afternoon hours, when chances to sample mixed boundary layer air are highest. This monitoring would be most promising if it is conducted continuously, and at highest possible accuracy. Continuous, concurrent, and coordinated monitoring at strategically selected sites upwind and downwind of the DJB would allow assessing changes in basin-wide emissions.
- VOCs emitted from O&NG sources constitute the majority of the OH reactivity in the DJB north of the DMA. These emissions contribute to a temporal and locally variable ozone production. Summertime elevated ozone occurrences show a high correlation to transport from O&NG extraction regions and atmospheric O&NG influences. Due to the ozone production dynamics and air circulation patterns, the daytime peak maximum ozone values are often observed along the NCFR foothills, tens of kilometers downwind of the

O&NG emissions source regions, and thereby impacting communities outside of the production regions. These downwind air quality impacts from O&NG industries should be a strong consideration in the design of monitoring networks and decision-making on regulating existing and new O&NG development in the region.

– Several independent measurements near O&NG operations have shown spikes with highly elevated concentrations of BTEX compounds that exceed health risks thresholds for nearby residents. Highest concentrations have been reported downwind of disposal facilities, rather than from well pads. Available data are mostly from short episodic measurements. This clearly demonstrates that characterization of BTEX emissions warrants more attention. This needs to include continuous monitoring and consideration of the diverse types of O&NG facilities. Thus far, health assessments have predominantly focused on well pads. Further research is needed on incorporating these other emissions sources given the growing body of literature showing their significant emissions and resulting elevated downwind concentrations.
– Bottom-up inventories have large uncertainties, neglect temporal variation, and consistently appear to be lower than top-down emissions determinations. The increase in well sites, the size and number of wells per pad, changes in operational practices, and new regulations make bottom-up emission inventories an ever changing challenge. Inconsistencies between national and state inventories persist. There appears to have been little progress in improving agreement between bottom-up inventory estimates and top-down estimates during the past decade. Experimental tools for aircraft basin-wide top-down emissions determination have improved remarkably during the past five years. A concerted effort building on these capabilities by regularly (e.g. monthly) light aircraft profiling, could, within a short time frame, yield significant improvements of the basin-wide total emissions characterization.
– Assessments of ozone contribution from O&NG emissions will have high uncertainty, and will under-predict the true ozone production as long as they rely on underestimated O&NG inventory emissions. Ozone impact studies need to be revisited with consideration of the most realistic NO_x and VOC emissions from O&NG industry sources.
– Ozone pollution in the NCFR is well within the range where ecosystem impacts and production yield losses in agriculture are predicted. Given the size of the agricultural industry, and from available literature on ozone effects on crops, it is expected that the economic loss to the State's farming industry from the O&NG-contributed ozone may be quite significant. A quantification of the actual revenue loss is needed for evaluating these adverse economic impacts of O&NG industry emissions.
– There has been a remarkable growth in the number of peer-review studies on air quality impacts from O&NG emissions. Consideration of the findings from these resources, and closer communication and collaboration between state regulators and academic and federal researchers will likely be beneficial for directing Colorado's O&NG policy development, guiding policy implementation, and for monitoring and assessing policy effectiveness.

Supplemental file

The supplemental file for this article can be found as follows:

- **Text S1.** CDPHE Comment Letter to EPA. Determination of Colorado Summer Background Ozone. DOI: https://doi.org/10.1525/elementa.398.s1

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Author contributions

DH directed the study, reviewed the literature, and prepared the manuscript.

References

Abdi-Oskouei, M, Pfister, G, Flocke, F, Sobhani, N, Saide, P, Fried, A, Richter, D, Weibring, P, Walega, J and **Carmichael, G.** 2018. Impacts of physical parameterization on prediction of ethane concentrations for oil and gas emissions in WRF-Chem. *Atmospheric Chemistry and Physics* **18**: 16863–16883. DOI: https://doi.org/10.5194/acp-18-16863-2018

Abeleira, A, Pollack, IB, Sive, B, Zhou, Y, Fischer, EV and **Farmer, DK.** 2017. Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015. *Journal of Geophysical Research* **122**: 3595–3613. DOI: https://doi.org/10.1002/2016JD026227

Abeleira, AJ and **Farmer, DK.** 2017. Summer ozone in the northern Front Range metropolitan area: weekend-weekday effects, temperature dependences, and the impact of drought. *Atmospheric Chemistry and Physics* **17**: 6517–6529. DOI: https://doi.org/10.5194/acp-17-6517-2017

Adgate, JL, Goldstein, BD and **McKenzie, LM.** 2014. Potential public health hazards, exposures and health effects from unconventional natural gas development. *Environmental Science & Technology* **48**: 8307–8320. DOI: https://doi.org/10.1021/es404621d

Archibald, AT, Ordonez, C, Brent, E and **Williams, ML.** 2018. Potential impacts of emissions associated with unconventional hydrocarbon extraction on UK air quality and human health. *Air Quality Atmosphere and Health* **11**: 627–637. DOI: https://doi.org/10.1007/s11869-018-0570-8

Avnery, S, Mauzerall, DL, Liu, JF and **Horowitz, LW.** 2011. Global crop yield reductions due to surface ozone exposure: 1. Year 2000 crop production losses and economic damage. *Atmospheric Environment* **45**: 2284–2296. DOI: https://doi.org/10.1016/j.atmosenv.2010.11.045

Bahreini, R, Ahmadov, R, McKeen, SA, Vu, KT, Dingle, JH, Apel, EC, Blake, DR, Blake, N, Campos, TL, Cantrell, C, Flocke, F, Fried, A, Gilman, JB, Hills, AJ, Hornbrook, RS, Huey, G, Kaser, L, Lerner, BM, Mauldin, RL, Meinardi, S, Montzka, DD, Richter, D, Schroeder, JR, Stell, M, Tanner, D, Walega, J, Weibring, P and **Weinheimer, A.** 2018. Sources and characteristics of summertime organic aerosol in the Colorado Front Range: perspective from measurements and WRF-Chem modeling. *Atmospheric Chemistry and Physics* **18**: 8293–8312. DOI: https://doi.org/10.5194/acp-18-8293-2018

Baier, BC, Brune, WH, Miller, DO, Blake, D, Long, R, Wisthaler, A, Cantrell, C, Fried, A, Heikes, B, Brown, S, McDuffie, E, Flocke, F, Apel, E, Kaser, L and **Weinheimer, A.** 2017. Higher measured than modeled ozone production at increased NO_x levels in the Colorado Front Range. *Atmospheric Chemistry and Physics* **17**: 11273–11292. DOI: https://doi.org/10.5194/acp-17-11273-2017

Bar-Ilan, A, Grant, J, Friesen, R, Pollack, AK, Henderer, D, Pring, D and **Sgamma, K.** 2008. Development of baseline 2006 emissions from oil and gas activity in the Denver-Julesburg Basin. *Environ Technical Report.* https://www.wrapair.org/forums/ogwg/documents/2008-04_'06_Baseline_Emissions_DJ_Basin_Technical_Memo_(04-30).pdf. 34 pp.

Barkley, ZR, Lauvaux, T, Davis, KJ, Deng, A, Fried, A, Weibring, P, Richter, D, Walega, JG, DiGangi, J, Ehrman, SH, Ren, X and **Dickerson, RR.** 2019. Estimating methane emissions from underground coal and natural gas production in Southwestern Pennsylvania. *Geophysical Research Letters* **46**: 4531–4540. DOI: https://doi.org/10.1029/2019GL082131

Bell, ML, Dominici, F and **Samet, JM.** 2005. Meta-analysis of ozone and mortality. *Epidemiology* **16**: S35–S35. DOI: https://doi.org/10.1097/00001648-200509000-00075

Benedict, KB, Prenni, AJ, Sullivan, AP, Evanoski-Cole, AR, Fischer, EV, Callahan, S, Sive, BC, Zhou, Y, Schichtel, BA and **Collett, JL, Jr.** 2018. Impact of Front Range sources on reactive nitrogen concentrations and deposition in Rocky Mountain National Park. *PeerJ* **6**: e4759. DOI: https://doi.org/10.7717/peerj.4759

Benedict, KB, Zhou, Y, Sive, BC, Prenni, AJ, Gebhart, KA, Fischer, EV, Evanoski-Cole, A, Sullivan, AP, Callahan, S, Schichtel, BA, Mao, HT, Zhou, Y and **Collett, JL.** 2019. Volatile organic compounds and ozone in Rocky Mountain National Park during FRAPPE. *Atmospheric Chemistry and Physics* **19**: 499–521. DOI: https://doi.org/10.5194/acp-19-499-2019

Bien, T and **Helmig, D.** 2018. Changes in summertime ozone in Colorado during 2000–2015. *Elementa-Science of the Anthropocene* **6**: 1–25. DOI: https://doi.org/10.1525/elementa.300

Bishop, G and **Stedman, DH.** 2008. A decade of on-road emissions measurements. *Environ. Sci. Technol.* **45**: 1651–1656. DOI: https://doi.org/10.1021/es702413b

Bogacki, M and **Macuda, J.** 2014. The influence of shale rock fracturing equipment operation on atmospheric air quality. *Archives of Mining Sciences* **59**: 897–912. DOI: https://doi.org/10.2478/amsc-2014-0062

Brimmer, A. 2019. Overview of 2011/2017 NO_x and VOC Emissions Inventory. *Regional Air Quality Council, Mobile Sources and Fuels Commitee Meeting Presentation*, February 27.

Brodin, M, Helmig, D and **Oltmans, S.** 2010. Seasonal ozone behavior along an elevation gradient in the Colorado Front Range Mountains. *Atmospheric Environment* **44**: 5305–5315. DOI: https://doi.org/10.1016/j.atmosenv.2010.06.033

Brown, SS, Thornton, JA, Keene, WC, Pszenny, AAP, Sive, BC, Dube, WP, Wagner, NL, Young, CJ, Riedel, TP, Roberts, JM, VandenBoer, TC, Bahreini, R, Ozturk, F, Middlebrook, AM, Kim, S, Hubler, G and **Wolfe, DE.** 2013. Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT): Overview of a wintertime air chemistry field study in the front range urban corridor of Colorado. *Journal of Geophysical Research-Atmospheres* **118**: 8067–8085. DOI: https://doi.org/10.1002/jgrd.50537

CDPHE. 2008. Denver Metropolitan Area and North Front Range 8-Hour Ozone State Implementation Plan, http://www.colorado.gov/airquality/documents/deno308/woe_DraftFinal_w%20preface.pdf, Draft Final, October 29, 2008, 1–85.

CDPHE. 2019a. History of Ozone in Colorado, https://www.colorado.gov/pacific/cdphe/

ozone-planning-chronology, Accessed September 2019.

CDPHE. 2019b. North Front Range Ozone Precursor Monitoring, https://www.colorado.gov/airquality/tech_doc_repository.aspx#ozone_precursor_data, Accessed Februrary 3, 2019.

CDPHE. 2019c. Oil and Gas Compliance and Recordkeeping, https://www.colorado.gov/pacific/cdphe/air/oil-and-gas-compliance, Accessed February 3, 2019.

Chang, KL, Petropavlovskikh, I, Cooper, OR, Schultz, MG and **Wang, T.** 2017. Regional trend analysis of surface ozone observations from monitoring networks in eastern North America, Europe and East Asia. *Elementa-Science of the Anthropocene* **5**. DOI: https://doi.org/10.1525/elementa.243

Cheadle, LC, Oltmans, SJ, Pétron, G, Schnell, RC, Mattson, EJ, Herndon, SCC, Thompson, AM, Blake, DR and **McClure-Begley, A.** 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*, 1–23. DOI: https://doi.org/10.1525/elementa.254

Colborn, T, Schultz, K, Herrick, L and **Kwiatkowski, C.** 2014. An exploratory study of air quality near natural gas operations. *Human and Ecological Risk Assessment: An International Journal* **20**: 86–105. DOI: https://doi.org/10.1080/10807039.2012.749447

Cooper, OR, Gao, R-S, Tarasick, D, Leblanc, T and **Sweeney, C.** 2012. Long-term ozone trends at rural ozone monitoring sites across the United States, 1990–2010. *Journal of Geophysical Research: Atmospheres* **117**: n/a–n/a. DOI: https://doi.org/10.1029/2012JD018261

Cooper, OR, Langford, AO, Parrish, DD and **Fahey, DW.** 2015. Challenges of a lowered US ozone standard. *Science* **348**: 1096–1097. DOI: https://doi.org/10.1126/science.aaa5748

Dingle, JH, Vu, K, Bahreini, R, Apel, EC, Campos, TL, Flocke, F, Fried, A, Herndon, S, Hills, AJ, Hornbrook, RS, Huey, G, Kaser, L, Montzka, DD, Nowak, JB, Reeves, M, Richter, D, Roscioli, JR, Shertz, S, Stell, M, Tanner, D, Tyndall, G, Walega, J, Weibring, P and **Weinheimer, A.** 2016. Aerosol optical extinction during the Front Range Air Pollution and Photochemistry Experiment (FRAPPE) 2014 summertime field campaign, Colorado, USA. *Atmospheric Chemistry and Physics* **16**: 11. DOI: https://doi.org/10.5194/acp-16-11207-2016

DISCOVER-AQ. 2013. Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality https://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html, Accessed January 11, 2019.

Drilling-Edge. 2019. Oil & Gas Production in Weld County, CO, http://www.drillingedge.com/colorado/weld-county, Accessed January 31, 2019.

Edie, R, Robertson, AM, Murphy, S, Petron, G, Madronich, M and **Vaughn, B.** 2019. Could O&G wastewater be a significant source of air toxics in the Northern Colorado Front Range? *NOAA Earth Systems Research Laboratory Global Monitoring Division Annual Conference*, May 21–22. Boulder, CO. Abstract Page 48.

EIA. 2009. Household Energy Use in Colorado, https://www.eia.gov/consumption/residential/reports/2009/state_briefs/pdf/CO.pdf.

EPA. 2008. Policy Assessment for the Review of the Ozone National Ambient Air Quality Standards, http://www.epa.gov/ttn/naaqs/standards/ozone/s_o3_2008_pa.html, Accessed October 2019.

EPA. 2019. News Releases from Region 08. EPA reclassifies Denver area to "Serious" non-attainment for ozone, https://www.epa.gov/newsreleases/epa-reclassifies-denver-area-serious-nonattainment-ozone, Accessed December 16, 2019.

Evans, JM and **Helmig, D.** 2017. Investigation of the influence of transport from oil and natural gas regions on elevated ozone levels in the northern Colorado front range. *Journal of the Air & Waste Management Association* **67**: 196–211. DOI: https://doi.org/10.1080/10962247.2016.1226989

Fann, N, Baker, KR, Chan, EAW, Eyth, A, Macpherson, A, Miller, E and **Snyder, J.** 2018. Assessing human health PM2.5 and ozone impacts from US oil and natural gas sector emissions in 2025. *Environmental Science & Technology* **52**: 8095–8103. DOI: https://doi.org/10.1021/acs.est.8b02050

Ferman, MA, Wolff, GT and **Kelly, NA.** 1981. An assessment of the gaseous-pollutants and meteorological conditions associated with Denver Brown Cloud. *Journal of Environmental Science and Health Part A-Environmental Science and Engineering & Toxic and Hazardous Substance Control* **16**: 315–339. DOI: https://doi.org/10.1080/10934528109374984

Field, RA, Soltis, J and **Murphy, S.** 2014. Air quality concerns of unconventional oil and natural gas production. *Environmental Science-Processes & Impacts* **16**: 954–969. DOI: https://doi.org/10.1039/C4EM00081A

Fleming, ZL, Doherty, RM, von Schneidemesser, E, Malley, CS, Cooper, OR, Pinto, JP, Colette, A, Xu, XB, Simpson, D, Schultz, MG, Lefohn, AS, Hamad, S, Moolla, R, Solberg, S and **Feng, ZZ.** 2018. Tropospheric Ozone Assessment Report: Present-day ozone distribution and trends relevant to human health. *Elementa-Science of the Anthropocene* **6**. DOI: https://doi.org/10.1525/elementa.273

Franco, B, Mahieu, E, Emmons, LK, Tzompa-Sosa, ZA, Fischer, EV, Sudo, K, Bovy, B, Conway, S, Griffin, D, Hannigan, J, Strong, K and **Walker, KA.** 2016. Evaluating ethane and methane emissions associated with the development of oil and natural gas extraction in North America. *Environmental Research Letters* **11**: 1–11. DOI: https://doi.org/10.1088/1748-9326/11/4/044010

Frankenberg, C, Thorpe, AK, Thompson, DR, Hulley, G, Kort, EA, Vance, N, Borchardt, J, Krings, T, Gerilowski, K, Sweeney, C, Conley, S, Bue, BD, Aubrey, AD, Hook, S and **Green, RO.** 2016. Airborne methane remote measurements reveal heavy-tail flux distribution in Four Corners region. *Proceedings of the National Academy of Sciences* **113**: 9734–9739. DOI: https://doi.org/10.1073/pnas.1605617113

FRAPPE. 2013. FRAPPÉ – Front Range Air Pollution and Photochemistry Experiment, https://www2.acom.ucar.edu/frappe, Accessed January 11, 2019.

Gilman, JB, Lerner, BM, Kuster, WC and **de Gouw, JA.** 2013. Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado. *Environmental Science & Technology* **47**: 1297–1305. DOI: https://doi.org/10.1021/es304119a

Groblicki, PJ, Wolff, GT and **Countess, RJ.** 1981. Visibility-reducing species in the Denver Brown Cloud. 1. Relationships between extinction and chemical composition. *Atmospheric Environment* **15**: 2473–2484. DOI: https://doi.org/10.1016/0004-6981(81)90063-9

Gryparis, A, Forsberg, B, Katsouyanni, K, Analitis, A, Touloumi, G, Schwartz, J, Samoli, E, Medina, S, Anderson, HR, Niciu, EM, Wichmann, HE, Kriz, B, Kosnik, M, Skorkovsky, J, Vonk, JM and **Dortbudak, Z.** 2004. Acute effects of ozone on mortality from the "Air pollution and health: A European approach" project. *American Journal of Respiratory and Critical Care Medicine* **170**: 1080–1087. DOI: https://doi.org/10.1164/rccm.200403-333OC

Halliday, HS, Thompson, AM, Wisthaler, A, Blake, DR, Hornbrook, RS, Mikoviny, T, Muller, M, Eichler, P, Apel, EC and **Hills, AJ.** 2016. Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014. *Journal of Geophysical Research-Atmospheres* **121**: 11055–11074. DOI: https://doi.org/10.1002/2016JD025327

Heck, WW, Taylor, OC, Adams, R, Bingham, G, Miller, J, Preston, E and **Weinstein, L.** 1982. Assesment of crop loss from ozone. *Journal of the Air Pollution Control Association* **32**: 353–361. DOI: https://doi.org/10.1080/00022470.1982.10465408

HEI. 2019. Potential Human Health Effects Associated with Unconventional Oil and Gas Development: A Systematic Review of the Epidemiology Literature (FINAL REPORT), https://hei-energy.org/publication/potential-human-health-effects-associated-unconventional-oil-and-gas-development, Accessed October 25, 2019.

Helmig, D, Blanchard, B and **Hueber, A.** 2018. Contrasting behavior of slow and fast photoreactive gases during the August 21, 2017, solar eclipse. *Elementa-Science of the Anthropocene* **6**. DOI: https://doi.org/10.1525/elementa.322

Helmig, D, Hannigan, M, Milford, J and **Gordon, J.** 2015. Air Quality Monitoring to Assess Exposure to Volatile Organic Compounds and Develop Cost-Efficient Monitoring Techniques. *Final Report to Boulder County*, 1–50.

Helmig, D, Hueber, J, Blanchard, B, Chopra, JX and **Angot, H.** 2020. Volatile organic compounds and their relation to oil and natural gas sources at the Boulder Reservoir, Colorado. Manuscript in preparation.

Helmig, D, Rossabi, S, Hueber, J, Tans, P, Montzka, S, Masarie, K, Thoning, K, Plass-Duelmer, C, Claude, A, Carpenter, L, Lewis, AC, Punjabi, S, Reimann, S, Vollmer, M, Steinbrecher, R, Hannigan, J, Emmons, L, Mahieu, E, Franco, B, Smale, D and **Pozzer, A.** 2016. Reversal of global atmospheric ethane and propane trends largely due to US Oil and natural gas production. *Nature Geoscience* **9**: 490–495. DOI: https://doi.org/10.1038/ngeo2721

Holder, C, Hader, J, Avanasi, R, Hong, T, Carr, E, Mendez, B, Wignall, J, Glen, G, Guelden, B and **Wei, Y.** 2019. Evaluating potential human health risks from modeled inhalation exposures to volatile organic compounds emitted from oil and gas operations. *Journal of the Air & Waste Management Association*. DOI: https://doi.org/10.1080/10962247.2019.1680459

Hood, G. 2019. Colorado talks a mean game on methane. Bad data, no best practices say otherwise. *Colorado Public Radio News*. https://www.cpr.org/2019/12/05/colorado-talks-a-mean-game-on-methane-bad-data-no-best-practices-say-otherwise/, Accessed December 5, 2019.

Jaffe, DA, Cooper, OR, Fiore, AM, Henderson, BH, Tonnesen, GS, Russell, AG, Henze, DK, Langford, AO, Lin, MY and **Moore, T.** 2018. Scientific assessment of background ozone over the US: Implications for air quality management. *Elementa-Science of the Anthropocene* **6**: 1–30. DOI: https://doi.org/10.1525/elementa.309

Jaffe, DA, Wigder, N, Downey, N, Pfister, G, Boynard, A and **Reid, SB.** 2013. Impact of wildfires on ozone exceptional events in the Western US. *Environmental Science & Technology* **47**: 11065–11072. DOI: https://doi.org/10.1021/es402164f

Jaffe, DA and **Wigder, NL.** 2012. Ozone production from wildfires: A critical review. *Atmospheric Environment* **51**: 1–10. DOI: https://doi.org/10.1016/j.atmosenv.2011.11.063

Johnson, R and **Toth, JJ.** 1982. A climatology of the July 1981 surface flow over northeast Colorado. *Department of Atmospheric Science, Colorado State University*, Paper No. 342.

Karion, A, Sweeney, C, Kort, EA, Shepson, PB, Brewer, A, Cambaliza, M, Conley, SA, Davis, K, Deng, A, Hardesty, M, Herndon, SC, Lauvaux, T, Lavoie, T, Lyon, D, Newberger, T, Petron, G, Rella, C, Smith, M, Wolter, S, Yacovitch, TI and **Tans, P.** 2015. Aircraft-based estimate of total methane emissions from the Barnett Shale region. *Environmental Science & Technology* **49**: 8124–8131. DOI: https://doi.org/10.1021/acs.est.5b00217

Karion, A, Sweeney, C, Petron, G, Frost, G, Hardesty, M, Kofler, J, Miller, BR, Newberger, T, Wolter, S, Banta, R, Brewer, A, Dlugkencky, EJ, Lang, P, Montzka, SA, Schnell, RC, Tans, P, Trainer, M, Zomora, R and **Conley, S.** 2013. Methane emissions estimate from airborne measurements over a western United States natural gas field. *Geophysical Research Letters* **40**: 1–5. DOI: https://doi.org/10.1002/grl.50811

Kaser, L, Patton, EG, Pfister, GG, Weinheimer, AJ, Montzka, DD, Flocke, F, Thompson, AM, Stauffer, RM and **Halliday, HS.** 2017. The effect of entrainment through atmospheric boundary layer growth on observed and modeled surface ozone in the Colorado Front Range. *Journal of Geophysical Research: Atmospheres* **122**: 6075–6093. DOI: https://doi.org/10.1002/2016JD026245

Kille, N, Chiu, R, Frey, M, Hase, F, She, MK, Blumenstock, T, Hannigan, JW, Orphal, J, Bon, D and **Volkamer, R.** 2019. Separation of methane emissions from agricultural and natural gas sources in the Colorado Front Range. *Geophysical Research Letters* **46**: 3990–3998. DOI: https://doi.org/10.1029/2019GL082132

Kirschke, S, Bousquet, P, Ciais, P, Saunois, M, Canadell, JG, Dlugokencky, EJ, Bergamaschi, P, Bergmann, D, Blake, DR, Bruhwiler, L, Cameron-Smith, P, Castaldi, S, Chevallier, F, Feng, L, Fraser, A, Heimann, M, Hodson, EL, Houweling, S, Josse, B, Fraser, PJ, Krummel, PB, Lamarque, J-F, Langenfelds, RL, Le Quere, C, Naik, V, O'Doherty, S, Palmer, PI, Pison, I, Plummer, D, Poulter, B, Prinn, RG, Rigby, M, Ringeval, B, Santini, M, Schmidt, M, Shindell, DT, Simpson, IJ, Spahni, R, Steele, LP, Strode, SA, Sudo, K, Szopa, S, van der Werf, GR, Voulgarakis, A, van Weele, M, Weiss, RF, Williams, JE and **Zeng, G.** 2013. Three decades of global methane sources and sinks. *Nature Geoscience* **6**: 813–823. DOI: https://doi.org/10.1038/ngeo1955

Kort, EA, Frankenberg, C, Costigan, KR, Lindenmaier, R, Dubey, MK and **Wunch, D.** 2014. Four corners: The largest US methane anomaly viewed from space. *Geophysical Research Letters* **41**: 6898–6903. DOI: https://doi.org/10.1002/2014GL061503

Koss, A, Yuan, B, Warneke, C, Gilman, JB, Lerner, BM, Veres, PR, Peischl, J, Eilerman, S, Wild, R, Brown, SS, Thompson, CR, Ryerson, T, Hanisco, T, Wolfe, GM, St Clair, JM, Thayer, M, Keutsch, FN, Murphy, S and **de Gouw, J.** 2017. Observations of VOC emissions and photochemical products over US oil- and gas-producing regions using high-resolution H_3O^+ CIMS (PTR-ToF-MS). *Atmospheric Measurement Techniques* **10**: 2941–2968. DOI: https://doi.org/10.5194/amt-10-2941-2017

Kostinek, J, Roiger, A, Davis, KJ, Sweeney, C, DiGangi, JP, Choi, Y, Baier, B, Hase, F, Gross, J, Eckl, M, Klausner, T and **Butz, A.** 2019. Adaptation and performance assessment of a quantum and interband cascade laser spectrometer for simultaneous airborne in situ observation of CH_4, C_2H_6, CO_2, CO and N_2O. *Atmospheric Measurement Techniques* **12**: 1767–1783. DOI: https://doi.org/10.5194/amt-12-1767-2019

LaFranchi, BW, Pétron, G, Miller, JB, Lehman, SJ, Andrews, AE, Dlugokencky, EJ, Hall, B, Miller, BR, Montzka, SA, Neff, W, Novelli, PC, Sweeney, C, Turnbull, JC, Wolfe, DE, Tans, PP, Gurney, KR and **Guilderson, TP.** 2013. Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}CO_2$. *Atmos. Chem. Phys.* **13**: 11101–11120. DOI: https://doi.org/10.5194/acp-13-11101-2013

Lamsal, LN, Duncan, BN, Yoshida, Y, Krotkov, NA, Pickering, KE, Streets, DG and **Lu, Z.** 2015. US. NO_2 trends (2005–2013): EPA Air Quality System (AQS) data versus improved observations from the Ozone Monitoring Instrument (OMI). *Atmospheric Environment* **110**: 130–143. DOI: https://doi.org/10.1016/j.atmosenv.2015.03.055

Langford, AO, Aikin, KC, Eubank, CS and **Williams, EJ.** 2009. Stratospheric contribution to high surface ozone in Colorado during springtime. *Geophysical Research Letters* **36**. DOI: https://doi.org/10.1029/2009GL038367

Lapina, K, Henze, DK, Milford, JB and **Travis, K.** 2016. Impacts of foreign, domestic, and state-level emissions on ozone-induced vegetation loss in the United States. *Environmental Science & Technology* **50**: 806–813. DOI: https://doi.org/10.1021/acs.est.5b04887

Lefohn, AS, Malley, CS, Smith, L, Wells, B, Hazucha, M, Simon, H, Naik, V, Mills, G, Schultz, MG, Paoletti, E, De Marco, A, Xu, XB, Zhang, L, Wang, T, Neufeld, HS, Musselman, RC, Tarasick, D, Brauer, M, Feng, ZZ, Tang, HY, Kobayashi, K, Sicard, P, Solberg, S and **Gerosa, G.** 2018. Tropospheric ozone assessment report: Global ozone metrics for climate change, human health, and crop/ecosystem research. *Elementa-Science of the Anthropocene* **6**. DOI: https://doi.org/10.1525/elementa.279

Levi, MA. 2012. Comment on "Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study" by Gabrielle Pétron et al. *Journal of Geophysical Research: Atmospheres* **117**. DOI: https://doi.org/10.1029/2012JD017686

Lin, M, Horowitz, LW, Payton, R, Fiore, AM and **Tonnesen, G.** 2017. US surface ozone trends and extremes from 1980 to 2014: quantifying the roles of rising Asian emissions, domestic controls, wildfires, and climate. *Atmospheric Chemistry and Physics* **17**: 2943–2970. DOI: https://doi.org/10.5194/acp-17-2943-2017

Lin, MY, Fiore, AM, Horowitz, LW, Langford, AO, Oltmans, SJ, Tarasick, D and **Rieder, HE.** 2015. Climate variability modulates western US ozone air quality in spring via deep stratospheric intrusions. *Nature Communications* **6**. DOI: https://doi.org/10.1038/ncomms8105

Lindaas, J, Farmer, DK, Pollack, IB, Abeleira, A, Flocke, F and **Fischer, EV.** 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*. DOI: https://doi.org/10.1029/2018JD028825

Lu, X, Zhang, L, Yue, X, Zhang, JC, Jaffe, DA, Stohl, A, Zhao, YH and **Shao, JY.** 2016. Wildfire influences on the variability and trend of summer surface ozone in the mountainous western United States. *Atmospheric Chemistry and Physics* **16**: 14687–14702. DOI: https://doi.org/10.5194/acp-16-14687-2016

Macey, GP, Breech, R, Chernaik, M, Cox, C, Larson, D, Thomas, D and **Carpenter, DO.** 2014. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. *Environ. Health* **13**. DOI: https://doi.org/10.1186/1476-069X-13-82

Madronich, M, Crotwell, A, Dlugokencky, E, Giniewek, A, Hall, BD, Handley, P, Kofler, J, Kahn, B, Mielke-Maday, I, Miller, BR, Mund, J, Petron, G and **Thoning, K.** 2019. Measuring BTEX with a commercial GC-PID system in an oil and gas field. *NOAA Earth Systems Research Laboratory Global Monitoring Division Annual Conference*, May 21–22, Abstract P-14.

Majid, A, Martin, MV, Lamsal, LN and **Duncan, BN.** 2017. A decade of changes in nitrogen oxides over regions of oil and natural gas activity in the United States. *Elementa-Science of the Anthropocene* **5**. DOI: https://doi.org/10.1525/elementa.259

McDuffie, EE, Edwards, PM, Gilman, JB, Lerner, BM, Dube, WP, Trainer, M, Wolfe, DE, Angevine, WM, deGouw, J, Williams, EJ, Tevlin, AG, Murphy, JG, Fischer, EV, McKeen, S, Ryerson, TB, Peischl, J, Holloway, JS, Aikin, K, Langford, AO, Senff, CJ, Alvarez, RJ, II, Hall, SR, Ullmann, K, Lantz, KO and **Brown, SS.** 2016. Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range. *Journal of Geophysical Research-Atmospheres* **121**: 8712–8729. DOI: https://doi.org/10.1002/2016JD025265

McKenzie, LM, Allshouse, WB, Burke, T, Blair, BD and **Adgate, JL.** 2016. Population size, growth, and environmental justice near oil and gas wells in Colorado. *Environmental Science & Technology* **50**: 11471–11480. DOI: https://doi.org/10.1021/acs.est.6b04391

McKenzie, LM, Allshouse, WB, Byers, TE, Bedrick, EJ, Serdar, B and **Adgate, JL.** 2017. Childhood hematologic cancer and residential proximity to oil and gas development. *Plos One* **12**. DOI: https://doi.org/10.1371/journal.pone.0170423

McKenzie, LM, Blair, B, Hughes, J, Allshouse, WB, Blake, NJ, Helmig, D, Milmoe, P, Halliday, H, Blake, DR and **Adgate, JL.** 2018. Ambient nonmethane hydrocarbon levels along Colorado's Northern Front Range: Acute and chronic health risks. *Environmental Science & Technology* **52**: 4514–4525. DOI: https://doi.org/10.1021/acs.est.7b05983

McKenzie, LM, Crooks, J, Peel, JL, Biafr, BD, Brindley, S, Allshouse, WB, Malin, S and **Adgate, JL.** 2019. Relationships between indicators of cardiovascular disease and intensity of oil and natural gas activity in Northeastern Colorado. *Environmental Research* **170**: 56–64. DOI: https://doi.org/10.1016/j.envres.2018.12.004

McKenzie, LM, Guo, R, Witter, RZ, Savitz, DA, Newman, LS and **Adgate, JL.** 2014. Birth outcomes and maternal residential proximity to natural gas development in rural Colorado. *Environmental Health Perspectives* **122**: A232–A233. DOI: https://doi.org/10.1289/ehp.1408647R

McKenzie, LM, Witter, RZ, Newman, LS and **Adgate, JL.** 2012. Human health risk assessment of air emissions from development of unconventional natural gas resources. *Science of the Total Environment* **424**: 79–87. DOI: https://doi.org/10.1016/j.scitotenv.2012.02.018

McMullin, TS, Bamber, AM, Bon, D, Vigil, DI and **Van Dyke, M.** 2018. Exposures and health risks from volatile organic compounds in communities located near oil and gas exploration and production activities in Colorado (USA). *International journal of environmental research and public health* **15**. DOI: https://doi.org/10.3390/ijerph15071500

Mielke-Maday, I, Madronich, M, Handley, M, Kofler, J, Hall, BD, Miller, BR, Mund, J, Kitzis, D, Lang, P, Crotwell, A, Crotwell, MJ, Moglia, E, Mefford, TK, Vaughn, B, Schnell, RC and **Petron, G.** 2019. Characterization and quantification of benzene emissions from a new multiwell pad in a Colorado Front Range residential community. *NOAA Earth Systems Research Laboratory Global Monitoring Division Annual Conference*, May 21–22, Abstract P-13.

Mills, G, Pleijel, H, Malley, CS, Sinha, B, Cooper, OR, Schultz, MG, Neufeld, HS, Simpson, D, Sharps, K, Feng, ZZ, Gerosa, G, Harmens, H, Kobayashi, K, Saxena, P, Paoletti, E, Sinha, V and **Xu, XB.** 2018. Tropospheric Ozone Assessment Report: Present-day tropospheric ozone distribution and trends relevant to vegetation. *Elementa-Science of the Anthropocene* **6**. DOI: https://doi.org/10.1525/elementa.302

Morgan, PB, Ainsworth, EA and **Long, SP.** 2003. How does elevated ozone impact soybean? A meta-analysis of photosynthesis, growth and yield. *Plant Cell and Environment* **26**: 1317–1328. DOI: https://doi.org/10.1046/j.0016-8025.2003.01056.x

Neff, WD. 1997. The Denver Brown Cloud studies from the perspective of model assessment needs and the role of meteorology. *Journal of the Air & Waste Management Association* **47**: 269–285. DOI: https://doi.org/10.1080/10473289.1997.10464447

Nicholson, D. 2019. Polis withdraws request to EPA for more time to bring Colorado into compliance with federal air-quality standards. *The Denver Post*, March 7.

Ogburn, SP. 2014. Colorado first state to limit methane pollution from oil and gas wells. *Scientific American*,

https://www.scientificamerican.com/article/colorado-first-state-to-limit-methane-pollution-from-oil-and-gas-wells/, Accessed December 6, 2019.

Oltmans, SJ, Cheadle, LC, Helmig, D, Dlugokencky, E, Petron, G, Montzka, SA, Agnot, H, Andrews, A and **Schnell, RC.** 2020. Oil and natural gas hydrocarbons measured at a tall tower in SW Weld County, CO during 2007–2016 Show little change despite stricter industry emissions regulations. Manuscript in preparation.

Oltmans, SJ, Cheadle, LC, Johnson, BJ, Schnell, RC, Helmig, D, Thompson, AM, Cullis, P, Hall, E, Jordan, A, Sterling, C, McClure-Begley, A, Sullivan, JT, McGee, TJ and **Wolfe, D.** 2019. Boundary layer ozone in the Northern Colorado Front Range in July–August 2014 during FRAPPE and DISCOVER-AQ from vertical profile measurements. *Elememta Science of the Anthropocene* **7**: 1–14. DOI: https://doi.org/10.1525/elementa.345

Peischl, J, Eilerman, SJ, Neuman, JA, Aikin, KC, de Gouw, J, Gilman, JB, Herndon, SC, Nadkarni, R, Trainer, M, Warneke, C and **Ryerson, TB.** 2018. Quantifying methane and ethane emissions to the atmosphere from Central and Western U.S. oil and natural gas production regions. *Journal of Geophysical Research-Atmospheres* **123**: 7725–7740. DOI: https://doi.org/10.1029/2018JD028622

Peischl, J, Ryerson, TB, Aikin, KC, de Gouw, JA, Gilman, JB, Holloway, JS, Lerner, BM, Nadkarni, R, Neuman, JA, Nowak, JB, Trainer, M, Warneke, C and **Parrish, DD.** 2015. Quantifying atmospheric methane emissions from the Haynesville, Fayetteville, and northeastern Marcellus shale gas production regions. *Journal of Geophysical Research-Atmospheres* **120**: 2119–2139. DOI: https://doi.org/10.1002/2014JD022697

Pétron, G, Frost, G, Miller, BR, Hirsch, AI, Montzka, SA, Karion, A, Trainer, M, Sweeney, C, Andrews, AE, Miller, L, Kofler, J, Bar-Ilan, A, Dlugokencky, EJ, Patrick, L, Moore, CT, Ryerson, TB, Siso, C, Kolodzey, W, Lang, PM, Conway, T, Novelli, P, Masarie, K, Hall, B, Guenther, D, Kitzis, D, Miller, J, Welsh, D, Wolfe, D, Neff, W and **Tans, P.** 2012. Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study. *Journal of Geophysical Research-Atmospheres* **117**: 1–19. DOI: https://doi.org/10.1029/2011JD016360

Pétron, G, Frost, GJ, Trainer, MK, Miller, BR, Dlugokencky, EJ and **Tans, P.** 2013. Reply to comment on "Hydrocarbon emissions characterization in the Colorado Front Range-A pilot study" by Michael A. Levi. *Journal of Geophysical Research-Atmospheres* **118**: 236–242. DOI: https://doi.org/10.1029/2012JD018487

Petron, G, Karion, A, Sweeney, C, Miller, BR, Montzka, SA, Frost, GJ, Trainer, M, Tans, P, Andrews, A, Kofler, J, Helmig, D, Guenther, D, Dlugokencky, E, Lang, P, Newberger, T, Wolter, S, Hall, B, Novelli, P, Brewer, A, Conley, S, Hardesty, M, Banta, R, White, A, Noone, D, Wolfe, D and **Schnell, R.** 2014. A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin. *Journal of Geophysical Research-Atmospheres* **119**: 6836–6852. DOI: https://doi.org/10.1002/2013JD021272

Pfister, G, Flocke, F, Hornbrook, RS, Orlando, J and **Lee, S.** 2017a. Process-Based and Regional Source Impact Analysis for FRAPPE and DISCOVER-AQ 2014. *Final Report to the Colorado Department of Public Health and Environment*, 31 July, 2017.

Pfister, GG, Reddy, PJ, Barth, MC, Flocke, FF, Fried, A, Herndon, SC, Sive, BC, Sullivan, JT, Thompson, AM, Yacovitch, TI, Weinheimer, AJ and **Wisthaler, A.** 2017b. Using observations and source-specific model tracers to characterize pollutant transport during FRAPPÉ and DISCOVER-AQ. *Journal of Geophysical Research: Atmospheres* **122**: 10,510–510,538. DOI: https://doi.org/10.1002/2017JD027257

Rasmussen, DJ, Fiore, AM, Naik, V, Horowitz, LW, McGinnis, SJ and **Schultz, MG.** 2012. Surface ozone-temperature relationships in the eastern US: A monthly climatology for evaluating chemistry-climate models. *Atmospheric Environment* **47**: 142–153. DOI: https://doi.org/10.1016/j.atmosenv.2011.11.021

Reddy, PJ and **Pfister, GG.** 2016. Meteorological factors contributing to the interannual variability of midsummer surface ozone in Colorado, Utah, and other western US states. *Journal of Geophysical Research-Atmospheres* **121**: 2434–2456. DOI: https://doi.org/10.1002/2015JD023840

Richter, D, Weibring, P, Walega, JG, Fried, A, Spuler, SM and **Taubman, MS.** 2015. Compact highly sensitive multi-species airborne mid-IR spectrometer. *Applied Physics B* **119**: 119–131. DOI: https://doi.org/10.1007/s00340-015-6038-8

Robertson, AM, Edie, R, Snare, D, Soltis, J, Field, RA, Burkhart, MD, Bell, CS, Zimmerle, D and **Murphy, SM.** 2017. Variation in methane emission rates from well pads in four oil and gas basins with contrasting production volumes and compositions. *Environmental Science & Technology* **51**: 8832–8840. DOI: https://doi.org/10.1021/acs.est.7b00571

Rodriguez, MA, Barna, MG and **Moore, T.** 2009. Regional impacts of oil and gas development on ozone formation in the Western United States. *Journal of the Air & Waste Management Association* **59**: 1111–1118. DOI: https://doi.org/10.3155/1047-3289.59.9.1111

Rossabi, S, Evans, J, Thompson, C, Hueber, J, Smith, K, Reed, T, Wang, W and **Pfister, G.** 2017. Surface observations of volatile organic compounds along an elevation gradient in the Northern Colorado Front Range during FRAPPE. *Presented at FRAPPE Science Team Meeting*, Boulder, CO, May 2–3.

Rossabi, S, Hueber, J, Terrell, R, Smith, K, Wang, W, Millmoe, P and **Helmig, D.** 2020. Atmospheric distribution of volatile organic oil and natural gas compounds in the Northern Colorado Front Range

during FRAPPE and DISCOVERY-AQ. Submitted for publication.

Sloane, CS, Watson, J, Chow, J, Pritchett, L and **Richards, LW.** 1991. Size-segregated fine particle measurements by chemical-species and their impact on visibility impairment in Denver. *Atmospheric Environment* **25**: 1013–1024. DOI: https://doi.org/10.1016/0960-1686(91)90143-U

Smith, ML, Gvakharia, A, Kort, EA, Sweeney, C, Conley, SA, Faloona, IC, Newberger, T, Schnell, R, Schwietzke, S and **Wolter, S.** 2017. Airborne quantification of methane emissions over the Four Corners region. *Environ. Sci. Technol.* DOI: https://doi.org/10.1021/acs.est.6b06107

Sovacool, BK. 2014. Cornucopia or curse? Reviewing the costs and benefits of shale gas hydraulic fracturing (fracking). *Renewable & Sustainable Energy Reviews* **37**: 249–264. DOI: https://doi.org/10.1016/j.rser.2014.04.068

Sullivan, JT, McGee, TJ, Langford, AO, Alvarez, RJ, II, Senff, CJ, Reddy, PJ, Thompson, AM, Twigg, LW, Sumnicht, GK, Lee, P, Weinheimer, A, Knote, C, Long, RW and **Hoff, RM.** 2016. Quantifying the contribution of thermally driven recirculation to a high-ozone event along the Colorado Front Range using lidar. *Journal of Geophysical Research: Atmospheres* **121**: 10,377–310,390. DOI: https://doi.org/10.1002/2016JD025229

Swain, TE. 2018. Weld County Oil & Gas Update February 2018, https://www.weldgov.com/UserFiles/Servers/Server_6/File/Departments/Planning%20&%20Zoning/Oil%20and%20Gas/Updates/Oil%20%20Gas%20Update%20FEB%202018.pdf.

Swarthout, RF, Russo, RS, Zhou, Y, Hart, AH and **Sive, BC.** 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**: 10614–10637. DOI: https://doi.org/10.1002/jgrd.50722

Szoke, EJ. 1991. Eye of the Denver Cyclone. *Monthly Weather Review* **119**: 1283–1292. DOI: https://doi.org/10.1175/1520-0493(1991)119<1283:EOTDC>2.0.CO;2

Thompson, CR, Hueber, J and **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* **3**: 1–17. DOI: https://doi.org/10.12952/journal.elementa.000035

Thompson, TM, Rodriguez, MA, Barna, MG, Gebhart, KA, Hand, JL, Day, DE, Malm, WC, Benedict, KB, Collett, JL and **Schichtel, BA.** 2015. Rocky Mountain National Park reduced nitrogen source apportionment. *Journal of Geophysical Research-Atmospheres* **120**: 4370–4384. DOI: https://doi.org/10.1002/2014JD022675

Townsend-Small, A, Botner, EC, Jimenez, KL, Schroeder, JR, Blake, NJ, Meinardi, S, Blake, DR, Sive, BC, Bon, D, Crawford, JH, Pfister, G and **Flocke, FM.** 2016. Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range. *Geophysical Research Letters* **43**: 11,462–411,471. DOI: https://doi.org/10.1002/2016GL071438

Tzompa-Sosa, ZA, Henderson, BH, Keller, CA, Travis, K, Mahieu, E, Franco, B, Estes, M, Helmig, D, Fried, A, Richter, D, Weibring, P, Walega, J, Blake, DR, Hannigan, JW, Ortega, I, Conway, S, Strong, K and **Fischer, EV.** 2019. Atmospheric implications of large C_2-C_5 alkane emissions from the U.S. oil and gas Industry. *Journal of Geophysical Research* **124**: 1148–1169. DOI: https://doi.org/10.1029/2018JD028955

Tzompa-Sosa, ZA, Mahieu, E, Franco, B, Keller, CA, Turner, AJ, Helmig, D, Fried, A, Richter, D, Weibring, P, Walega, J, Yacovitch, TI, Herndon, SC, Blake, DR, Hase, F, Hannigan, JW, Conway, S, Strong, K, Schneider, M and **Fischer, EV.** 2017. Revisiting global fossil fuel and biofuel emissions of ethane. *Journal of Geophysical Research-Atmospheres* **122**: 2493–2512. DOI: https://doi.org/10.1002/2016JD025767

USDA. 2018. Colorado Agriculturual Statistics 2018, https://www.nass.usda.gov/Statistics_by_State/Colorado/Publications/Annual_Statistical_Bulletin/Bulletin2018.pdf, Accessed October 27, 2019.

Van Dingenen, R, Dentener, FJ, Raes, F, Krol, MC, Emberson, L and **Cofala, J.** 2009. The global impact of ozone on agricultural crop yields under current and future air quality legislation. *Atmospheric Environment* **43**: 604–618. DOI: https://doi.org/10.1016/j.atmosenv.2008.10.033

Vaughn, TL, Bell, CS, Pickering, CK, Schwietzke, S, Heath, GA, Petron, G, Zimmerle, DJ, Schnell, RC and **Nummedal, D.** 2018. Temporal variability largely explains top-down/bottom-up difference in methane emission estimates from a natural gas production region. *Proceedings of the National Academy of Sciences of the United States of America* **115**: 11712–11717. DOI: https://doi.org/10.1073/pnas.1805687115

Verma, DK, Johnson, DM and **McLean, JD.** 2000. Benzene and total hydrocarbon exposures in the upstream petroleum oil and gas industry. *American Industrial Hygiene Association Journal* **61**: 255–263. DOI: https://doi.org/10.1080/15298660008984534

Vu, KT, Dingle, JH, Bahreini, R, Reddy, PJ, Apel, EC, Campos, TL, DiGangi, JP, Diskin, GS, Fried, A, Herndon, SC, Hills, AJ, Hornbrook, RS, Huey, G, Kaser, L, Montzka, DD, Nowak, JB, Pusede, SE, Richter, D, Roscioli, JR, Sachse, GW, Shertz, S, Stell, M, Tanner, D, Tyndall, GS, Walega, J, Weibring, P, Weinheimer, AJ, Pfister, G and **Flocke, F.** 2016. Impacts of the Denver Cyclone on regional air quality and aerosol formation in the Colorado Front Range during FRAPPÉ 2014. *Atmospheric Chemistry and Physics*

16: 12039–12058. DOI: https://doi.org/10.5194/acp-16-12039-2016

Waggoner, AP, Weiss, RE and **Ahlquist, NC.** 1983. The color of Denver haze. *Atmospheric Environment* **17**: 2081–2086. DOI: https://doi.org/10.1016/0004-6981(83)90366-9

West, JJ and **Fiore, AM.** 2005. Management of tropospheric ozone by reducing methane emissions. *Environmental Science & Technology* **39**: 4685–4691. DOI: https://doi.org/10.1021/es048629f

West, JJ, Fiore, AM, Horowitz, LW and **Mauzerall, DL.** 2006. Global health benefits of mitigating ozone pollution with methane emission controls. *Proceedings of the National Academy of Sciences of the United States of America* **103**: 3988–3993. DOI: https://doi.org/10.1073/pnas.0600201103

WHO. 2019a. Air pollution, https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health, Accessed October 30, 2019.

WHO. 2019b. Exposure to Benzene: A major Health Concern, https://www.who.int/ipcs/features/benzene.pdf.

Wilczak, JM and **Christian, TW.** 1990. Case study of an orographically induced mesoscale vortex (Denver Cyclone). *Monthly Weather Review* **118**: 1082–1102. DOI: https://doi.org/10.1175/1520-0493(1990)118<1082:CSOAOI>2.0.CO;2

Wilczak, JM and **Glendening, JW.** 1988. Observations and and mixed-layer modeling of a terrain-induced mesoscale gyre – the Denver Cyclone. *Monthly Weather Review* **116**: 2688–2711. DOI: https://doi.org/10.1175/1520-0493(1988)116<2688:OAMLMO>2.0.CO;2

Witman, S, Holloway, T and **Reddy, P.** 2014. Integrating satellite data into air quality management. *Environmental Manager*, 34–38.

Wolff, GT, Countess, RJ, Groblicki, PJ, Ferman, MA, Cadle, SH and **Muhlbaier, JL.** 1981. Visibility-reducing species in the Denver Brown Cloud. 2. Sources and temporal patterns. *Atmospheric Environment* **15**: 2485–2502. DOI: https://doi.org/10.1016/0004-6981(81)90064-0

WRAP. 2009. Western Regional Air Partnership – Oil & Gas Emissions Workgroup, http://www.wrapair.org/forums/ogwg/index.html, Accessed October 27, 2019.

Yacovitch, TI, Daube, C, Vaughn, TL, Bell, CS, Roscioli, JR, Knighton, WB, Nelson, DD, Zimmerle, D, Pétron, G and **Herndon, SC.** 2017. Natural gas facility methane emissions: measurements by tracer flux ratio in two US natural gas producing basins. *Elementa Science of the Anthropocene*, 1–12. DOI: https://doi.org/10.1525/elementa.251

Yacovitch, TI, Herndon, SC, Petron, G, Kofler, J, Lyon, D, Zahniser, MS and **Kolb, CE.** 2015. Mobile laboratory observations of methane emissions in the Barnett Shale Region. *Environmental Science & Technology* **49**: 7889–7895. DOI: https://doi.org/10.1021/es506352j

Yacovitch, TI, Neininger, B, Herndon, SC, van der Gon, HD, Jonkers, S, Hulskotte, J, Roscioli, JR and **Zavala-Araiza, D.** 2018. Methane emissions in the Netherlands: The Groningen field. *Elementa-Science of the Anthropocene* **6**. DOI: https://doi.org/10.1525/elementa.308

Zaragoza, J, Callahan, S, McDuffie, EE, Kirkland, J, Brophy, P, Durrett, L, Farmer, DK, Zhou, Y, Sive, B, Flocke, F, Pfister, G, Knote, C, Tevlin, A, Murphy, J and **Fischer, EV.** 2017. Observations of acyl peroxy nitrates during the Front Range Air Pollution and Photochemistry Experiment (FRAPPE). *Journal of Geophysical Research-Atmospheres* **122**: 12416–12432. DOI: https://doi.org/10.1002/2017JD027337

Zhang, L, Jacob, DJ, Downey, NV, Wood, DA, Blewitt, D, Carouge, CC, van Donkelaar, A, Jones, DBA, Murray, LT and **Wang, Y.** 2011. Improved estimate of the policy-relevant background ozone in the United States using the GEOS-Chem global model with 1/2 degrees × 2/3 degrees horizontal resolution over North America. *Atmospheric Environment* **45**: 6769–6776. DOI: https://doi.org/10.1016/j.atmosenv.2011.07.054

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APPLIED ECOLOGY

Agriculture is a major source of NO_x pollution in California

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Nitrogen oxides (NO_x = NO + NO_2) are a primary component of air pollution—a leading cause of premature death in humans and biodiversity declines worldwide. Although regulatory policies in California have successfully limited transportation sources of NO_x pollution, several of the United States' worst–air quality districts remain in rural regions of the state. Site-based findings suggest that NO_x emissions from California's agricultural soils could contribute to air quality issues; however, a statewide estimate is hitherto lacking. We show that agricultural soils are a dominant source of NO_x pollution in California, with especially high soil NO_x emissions from the state's Central Valley region. We base our conclusion on two independent approaches: (i) a bottom-up spatial model of soil NO_x emissions and (ii) top-down airborne observations of atmospheric NO_x concentrations over the San Joaquin Valley. These approaches point to a large, overlooked NO_x source from cropland soil, which is estimated to increase the NO_x budget by 20 to 51%. These estimates are consistent with previous studies of point-scale measurements of NO_x emissions from the soil. Our results highlight opportunities to limit NO_x emissions from agriculture by investing in management practices that will bring co-benefits to the economy, ecosystems, and human health in rural areas of California.

INTRODUCTION

Nitrogen oxide (NO_x = NO + NO_2) gases are among the most important components of air pollution, which, according to the World Health Organization, is responsible for one in eight premature deaths worldwide (*1*). These nitrogen (N) gases have been linked to upper respiratory disease, asthma, cancer, birth defects, cardiovascular disease, and sudden infant death syndrome (*2*, *3*). Global studies have pointed to similarities in the magnitude of NO_x emissions from fossil fuel combustion and soil, with the largest soil emissions from regions with heavy N fertilizer applications (*4*–*7*). Despite the significance of soil microbial NO_x emissions at the global scale, policies have focused largely on limiting NO_x from mobile and stationary fossil fuel sources (*8*, *9*). Where agriculture is an important source of NO_x, strategies to reduce nonpoint emissions will need to incorporate soil management approaches and policies that are fundamentally different from fossil fuel sources.

California is considered the world's sixth largest economy in terms of gross national product and supports 12.2% of the U.S. food economy (*10*). The state has instituted policies to reduce NO_x pollution from fossil fuel sources, resulting in NO_x declining by 9% per year in Los Angeles, San Francisco, and Sacramento over the period of 2005 to 2008 (*11*). Recent findings have suggested that agriculture is one of the dominant sources of NO_x in the United States, particularly in the midwest region, where fertilizer inputs are substantial (*6*, *12*). In California, local field measurements have similarly ascribed high NO_x emissions to agricultural soil (*13*). Matson *et al.* (*14*) provided some of the first evidence of substantial NO_x production from agricultural soils in California's Central Valley; however, a statewide assessment, which is needed to drive new policies for NO_x pollution, is hitherto lacking. The California Air Resources Board (CARB) estimates that ~3.8% of the state's NO_x budget can be attributed to cropland soils, but these estimates are based on data limited to farms located within 200 km of Sacramento and miss many of the most heavily fertilized areas in the state (*15*). Moreover, CARB does not include these estimated emissions in their official statewide database for air quality modeling (*16*).

Here, we provide the first large-scale quantification of soil NO_x emissions for California through two different approaches: integrative "bottom-up" spatial modeling and "top-down" airborne NO_x measurements. This two-pronged approach allows us to independently examine the contribution of biogenic NO_x emissions in California while comparing these estimates to local empirical data. Our overarching hypothesis is that biogenic emissions of NO_x from agricultural areas are much higher than we used to believe and could be a major source of atmospheric NO_x statewide. Alternatively, if agricultural sources are of minor significance, then we would expect to find uniformly low emissions throughout natural and agricultural ecosystems.

RESULTS AND DISCUSSION

Our combined bottom-up and top-down estimates uniformly point to high NO_x emissions from California's agricultural soil, revealing a significant unrecognized source of N pollution statewide. Our bottom-up model reveals that 161,100 metric tons of NO_x-N $year^{-1}$ is emitted from California soil with croplands accounting for 79% of total emissions. When combined with data on existing mobile and stationary fossil fuel sources (*16*), our results indicate that fertilized croplands account for 20 to 32% of total NO_x-N emissions from all sectors of the state, whereas natural soils account for 5 to 9% (Fig. 1). A meta-analysis of soil NO_x emissions from the existing literature demonstrates quantitative coherence between our model-based estimates and empirical measurements from different areas of the state (Table 1). Mean NO_x emissions from California cropland soils were 19.8 (±27.3 SD) kg of N ha^{-1} $year^{-1}$ and ranged from 0 to 276 kg of N ha^{-1} $year^{-1}$ (Fig. 2), with $^1/_4$ quartile and $^3/_4$ quartile values of 4.3 and 24.9 kg of N ha^{-1} $year^{-1}$, respectively. NO_x emissions were largest from agricultural soils where N fertilizer applications can reach >600 kg of N ha^{-1} $year^{-1}$ (average N fertilizer

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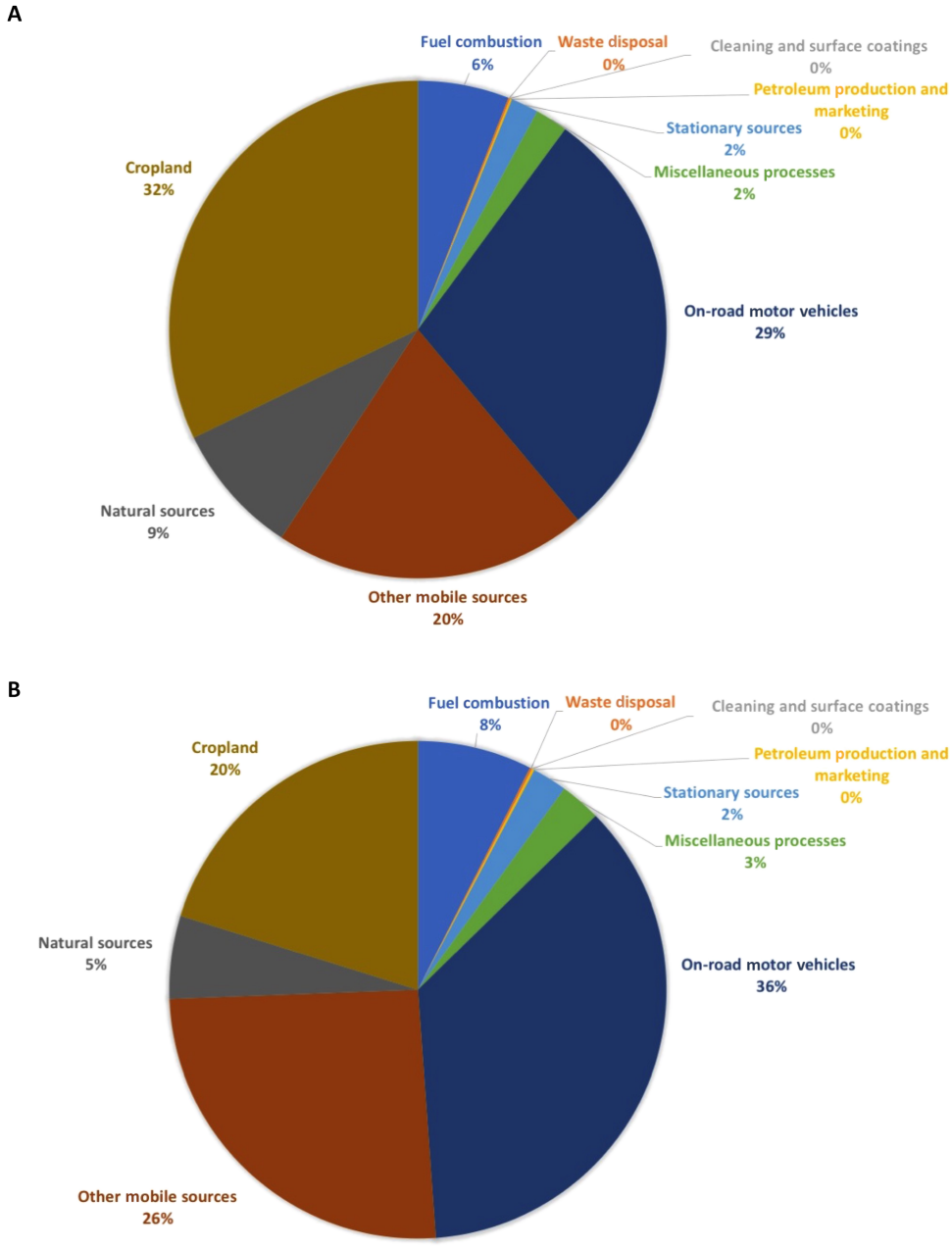

Fig. 1. Contribution of soils to statewide NO_x emissions. Based on CARB emission estimates and IMAGE-modeled emission estimates for cropland and natural ecosystems (**A**) without vegetation scavenging (gross rates) and (**B**) with 50% of NO_x emissions scavenged by vegetation (net rates).

rates for fertilized soils, 131.8 kg of N ha^{-1} $year^{-1}$; Fig. 3). A spatial maximum hot spot of soil NO_x emissions is identified for southern reaches of the state, where climate is relatively hot and arid (*17*). The model also predicts local maxima in the Sacramento Delta region, the Salinas Valley, and the San Joaquin Valley, with the latter being confirmed by aircraft measurements (see below).

Modeled NO_x emissions track N fertilizer applications

Our findings support the hypothesis that biogenic sources represent a significant fraction of NO_x emissions in California, particularly in areas with high N fertilizer applications. Although we report gross soil emission estimates, NO_x uptake by vegetation can cut atmospheric NO_x emissions in half (*4*, *18*). We thereby provide a more conservative estimate that attributes 25% of statewide NO_x to the soil (Fig. 1B), which assumes that half of the soil NO_x is lost to dry deposition within nearby vegetation canopies. Reducing uncertainty regarding the soil contribution of NO_x to the statewide budget will require spatial and temporal assessments that can distinguish between sources.

Our findings for California are consistent with previous global-scale estimates given the tremendous agricultural productivity of the state: Yienger and Levy (*4*) used a model to demonstrate that soils account for 50% of the total NO_x budget in remote agricultural regions of the Northern Hemisphere, Jaeglé *et al.* (*6*) found that soils were

Table 1. Modeled values and observed values collected from the literature of NO emissions in California. LAT, latitude; LONG, longitude; SFREC, Sierra Foothill Research and Extension Center.

Site	LAT	LONG	Modeled NO (kg of N ha^{-1} $year^{-1}$)	Observed NO (kg of N ha^{-1} $year^{-1}$)	Observed NO range (kg of N ha^{-1} $year^{-1}$)	Reference
Imperial Valley	32.8476	−115.5694	20.6	21.0	0–280	(*13*)
SFREC	39.2513	−121.3137	2.5	3.5	4–31	(*27*)
Barton Flats	34.2439	−116.9114	1.1	1.0	0–2	(*28*)
Camp Paivika	34.2429	−117.2683	3.7	5.0	3–7	(*28*)
Stanford	37.4241	−122.1661	1.9	3.5	0–7	(*29*)
San Dimas	34.1797	−117.7681	0.0	3.0	0–19	(*30*)
Bonadelle Ranchos	36.9693	−119.8873	4.5	7.1	4–12	(*14*)
Clovis	36.8252	−119.7029	1.6	0.9	0–3	(*14*)
Corcoran	36.098	−119.5604	0.2	0.1	—	(*14*)
Firebaugh	36.8588	−120.456	27.7	6.7	1–18	(*14*)
Kearny	36.6008	−119.5109	17.3	2.8	0–21	(*14*)
Lindcove	36.3578	−119.0636	19.6	1.3	1–2	(*14*)
Mendota	36.7536	−120.3816	23.9	0.7	0–1	(*14*)
Parlier	36.6116	−119.5271	2.9	5.6	0–22	(*14*)
Plainview	36.144	−119.1326	38.1	13.7	0–46	(*14*)
Riverdale	36.4311	−119.8596	28.3	0.1	0–1	(*14*)
San Joaquin	36.6066	−120.189	5.5	7.2	1–57	(*14*)
Sanger	36.708	−119.556	9.1	9.6	—	(*14*)
Tranquility	36.6488	−120.2527	52.9	2.1	2–3	(*14*)
Tulare	36.2077	−119.3473	20.6	0.1	0–1	(*14*)
Waukena	36.1382	−119.5099	10.4	0.4	0–1	(*14*)

responsible for 22% of worldwide NO_x emissions, Wang *et al.* (*7*) estimated that agricultural soils were responsible for 20 to 30% of global NO_x sources, and Davidson *et al.* (*5*) estimated that soils were responsible for 10% of emissions in the Southeastern United States, with agriculture contributing to 75% of total soil NO_x emissions. Furthermore, our soil NO_x emission estimates are on par with those from agrarian areas in Europe (24 to 62%) (*19*) and during the crop-growing season in the midwestern United States (15 to 40% in June and July) (*12*).

In contrast to high mean efflux from agricultural soils (average, 19.8 kg of N ha^{-1} $year^{-1}$), NO_x emissions from natural ecosystems were much lower (average, 1.0 kg of N ha^{-1} $year^{-1}$). This points to the importance of N inputs (in fertilizer) in accelerating NO_x emissions from soil microbial communities (*20*). Our model-based estimates compared favorably with published literature values for California and beyond, which range from 0 to 25 kg of N ha^{-1} $year^{-1}$ (Table 1). Likewise, in the southern and midwestern regions of the United States, empirically measured NO_x emissions from cultivated soils are on the order of 3 to 14 kg of N ha^{-1} $year^{-1}$ versus 0.1 to 3 kg of N ha^{-1} $year^{-1}$ from nearby unfertilized grasslands (*21*–*25*). Other studies have also demonstrated that cultivated land produces NO_x emissions an order of magnitude larger than forest soils in the same biome (*26*).

Emission estimate variability

Modeled soil NO_x emissions produced ranges that were similar to those reported in the literature (Table 1). Both modeled and observed (in situ chamber measurements) emissions were typically less than 5 kg of N ha^{-1} $year^{-1}$, with larger values in the Imperial Valley (located in Southern California between the Salton Sea and Mexico; Fig. 2). Whereas most observed values were similar to those of the model, NO_x emissions showed marked variability, consistent with spatial heterogeneities of soil microbial processes. Biogenic NO_x emissions can also vary temporally, with the largest emissions spiking when fertilizers are applied (*12*). The timing of fertilization in California varies regionally, considering the variety of crop species grown and the different management practices used. Our model validation was restricted to a handful of empirical studies (*13*, *14*, *27*–*30*), which demonstrate the need for more ground measurements throughout California to better assess the local impact and spatial distribution of soil NO_x emissions.

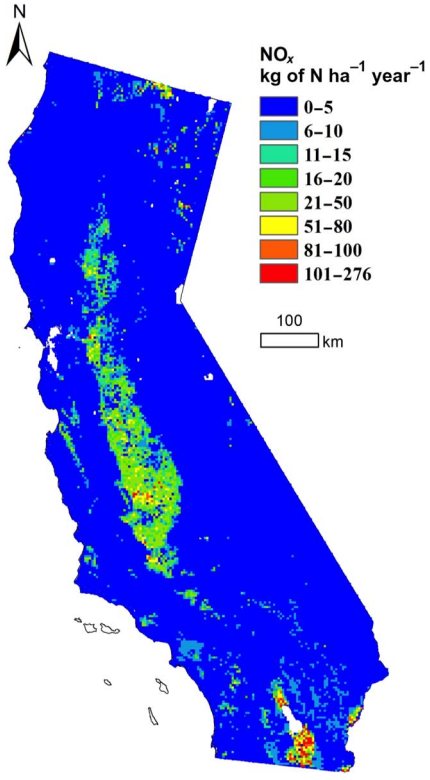

Fig. 2. Estimates of NO_x emissions from California soils (natural and cropland) generated by using stable isotopic modeling and IMAGE model.

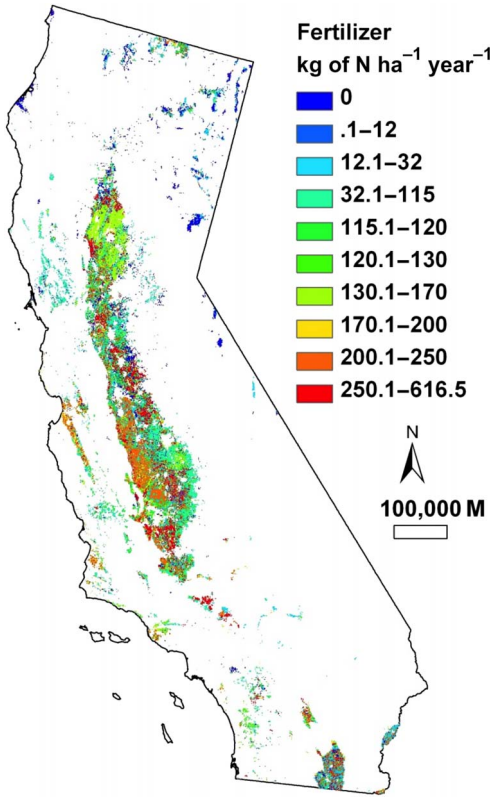

Fig. 3. Nitrogen fertilizer inputs to California soils. Fertilizer application rates are generated based on crop type, using crop-specific data provided by the DWR of California and USDA fertilizer consumption database for 1964 to 2006.

Surface emissions estimates from airborne NO_x observations

We used airborne measurements of NO_x concentrations to estimate regional emissions in the San Joaquin Valley. This allows us to further verify our model and determine how NO_x emissions from the soil might affect regional compliance with ambient air quality standards, which are based on 1-hour and annual average concentration thresholds (*31*). Our top-down approach involved repeated airborne measurements of NO_x made between Fresno and Visalia during the summer of 2016 (fig. S3) in conjunction with the California Baseline Ozone Transport Study (CABOTS) coordinated by CARB. Careful accounting of the height of the atmospheric boundary, coupled with direct measurements and some judicious estimates of all the terms in the NO_x concentration budget equation, allowed us to estimate surface emissions (*32*) of NO_x in the region of the flight experiment (see the Supplementary Materials). The average of six flight days (three at the end of July and three at the beginning of August) over a region of ~720,000 ha yielded a NO_x emission estimate of 190 ± 130 metric tons day^{-1}. According to the CARB California Emissions Projection Analysis Model (CEPAM) (*33*), which includes fossil fuel but not natural sources, the sum of average summertime NO_x emissions over all three counties in the surrounding area (Fresno, Tulare, and Kings covering over 3.1 million ha) amounts to 100 metric tons day^{-1}. Although the exact area and diurnal timing of the emissions from the CEPAM inventory cannot be precisely compared to the spatial and temporal footprint of our airborne sampling, the comparison between the CEPAM inventory and airborne sampling shows that soil emissions are likely a very important source of atmospheric NO_x, especially in the agriculturally intensive San Joaquin Valley. In this case, the agricultural soil source would need to account for at least 47% of the total NO_x emissions or a regional flux of 12.4 kg of N ha^{-1} $year^{-1}$ (table S4). We consider this to be a conservative estimate because the county inventories make up a much larger area than the flight domain. Furthermore, the flights did not span either commuter rush hour, when NO_x emissions are at their daily peak. We conclude that soils most likely contribute a majority of all NO_x emissions to the atmosphere in the agriculturally intensive central San Joaquin Valley.

Comparing emissions estimates between methods

We compared surface emissions estimates for the San Joaquin Valley with soil model estimates for the same region (fig. S3 and table S4). Using year-round mean emissions for both natural and cropland soils, our model generated an annual flux of 24 kg of N ha^{-1} $year^{-1}$ for the central San Joaquin Valley, between Fresno and Visalia, and as high as 36 kg of N ha^{-1} $year^{-1}$ during the season of the airborne measurements (July to August), which yielded fluxes ranging from 14 to 39 kg of N ha^{-1} $year^{-1}$. The correspondence between the bottom-up and top-down estimates builds robustness into our estimates for statewide NO_x emissions and confirms our working conclusion for substantial NO_x emissions from fertilized croplands in the Central Valley.

Our soil model estimates are slightly higher than, although comparable with, the few number of empirical measurements of NO_x emissions from the San Joaquin Valley's cropland soils (made between July and September of 1995) (*14*), which ranged from 0.1 to 14 kg of N ha^{-1} $year^{-1}$ (Table 1). That we estimate higher soil NO_x fluxes via the top-down and bottom-up approaches is consistent with more recent empirical measurements (*13*), suggesting that increases in N fertilizer

use and population growth have likely accelerated soil NO_x emissions since the last time empirical measurements were reported for the region, some 20 years ago (*14*).

Controls on soil NO_x emissions

Previous studies have demonstrated that NO_x emissions are controlled by water-filled pore space (influenced by precipitation, irrigation, and soil texture) (*34*), N availability (*20*), and temperature (*13*), all of which were fundamental parameters in our model-based estimate of soil NO_x emissions in California (that is, the model relies on functions related to soil organic carbon, soil texture, drainage, temperature, and precipitation). We performed a model sensitivity analysis by evaluating the response of cropland denitrification rates to model input parameters at the ±10% level and examined the effect size of this parameter variation on NO_x emissions. We found that soil NO_x emissions were least sensitive to changes in soil carbon and were much more responsive to changes in soil texture, soil drainage, and climate (fig. S2).

Nitrogen input rates and climate were primary determinants of soil NO_x emissions in our model. The largest chamber-based measurements of soil NO_x emissions come from the Imperial Valley in Southern California (Table 1) (*12*), which was accurately predicted by our model, implying that our model is capable of detecting hot spot emissions. High emissions in the Imperial Valley are likely explained by three factors. First, a biogenic source in these soils suggests a kinetic response to high temperatures that occur in this region. Second, arid soils not only produce more NO_x relative to N_2O and N_2 but also allow for the build-up of inorganic N via nitrification; N that will then be released in large quantities when soils are irrigated and microbial denitrification is triggered. Third, high fertilizer inputs that increase N availability in the soil may help soils to develop a healthy community of nitrifying bacteria, providing a positive feedback to N availability and subsequent loss.

Implications for California

The CARB emission inventory provides an assessment of air pollution magnitudes and sources in California. Sources are inventoried based on four main categories: mobile, stationary, area-wide, and natural. In the current CARB NO_x inventory, mobile emissions are thought to predominate (83%), whereas soil emissions are currently considered negligible (*16*). Here, we show that agricultural soils contribute a substantial amount of NO_x to the atmosphere. We can expect to see the significance of biogenic NO_x emissions increase as N fertilizer inputs increase to keep pace with food demands (*35*) and automotive NO_x controls continue to attenuate mobile fossil fuel sources. Our findings suggest the need to reconsider the role of soil NO_x sources and provide a pathway to constrain these diffuse pathways into CARB inventory analyses. Recent climate changes in California have caused pronounced heat waves and drought, factors which could exacerbate biogenic NO_x emissions, leading to increased air pollution and N deposition rates in natural ecosystems (*8*). Considering the limited number of field-based NO_x measurements and the difficulty involved with partitioning soil versus fossil fuel sources through satellite imagery, a more robust field sampling strategy of soil NO_x emissions throughout the state could aid in efforts to understand agricultural impacts on air pollution in the Central Valley.

Several existing approaches could be used to reduce soil NO_x emissions from fertilized croplands. There are many strategies to improve fertilizer efficiencies, which would minimize the unwanted risks of N fertilizer spillovers into the environment and benefit farmers by reducing fertilizer costs. Where mineral fertilizers are used exclusively, for example, applying different forms of fertilizer (for example, slow-release fertilizers) (*36*) or lowering N applications and using precision agriculture to target developmental stages (*37*), have been shown to cut N fertilizer losses from cropland soil. Where organic amendments are applied, separating the application timing of mineral N and organic fertilizer has been shown to reduce N emissions (*38*). Precision fertilization, as opposed to broadcasting, can also increase N uptake and minimize losses (*39*). Cover crops that consume residual N, which can subsequently be incorporated into the soil, are another option for reducing N fertilizer application rates (*40*). A complementary institutional strategy would be to incentivize plant production for human versus livestock consumption because livestock manure and the N used to grow livestock feed are major sources of N pollution in the air and water (*3*). Another strategy would be to promote the reduction of NO_x to an environmentally benign gas such as dinitrogen (N_2), which can be achieved by installing riparian zones to collect fertilizer runoff or introducing nitrification inhibitors to stem denitrification rates (*3*, *41*). The ratio in which harmful (NO_x and N_2O) and inert (N_2) gases are emitted from soils depends heavily on N availability, soil moisture, and temperature; thus, irrigation strategies are another important step to reduce N losses from agriculture.

These and many other strategies can help to reduce potentially harmful N losses from agriculture (*3*, *42*, *43*). Losses of N fertilizer are not only costly to farmers but can also create economic costs to the greater United States on the order of $210 billion dollars per year in health and environmental damages (*43*, *44*). Reducing NO_x emissions therefore offers a win-win situation for farmers, environmental health, and the economy.

CONCLUSIONS

This study builds on local point-scale measurements (*14*) to provide the first spatially explicit evidence of substantial NO_x emissions from agricultural soils in California, a previously unrecognized source that is estimated to contribute 20 to 51% of the state's total NO_x budget. These soil NO_x emissions are sourced to N fertilizer applications in Central Valley croplands. The effect of large soil NO_x emissions on air quality and human health remain unclear, but the magnitude of the flux alone raises concern about its potential impact, particularly in rural California. Where biogenic sources affect air quality and health, the implementation of strategies to reduce these emissions will be imperative. A better understanding of the sources, distribution, and impact of biogenically produced NO_x will improve our ability to mitigate emissions in the future.

MATERIALS AND METHODS

To model the spatial distribution of soil NO_x emissions, we used an N isotope model (*17*, *45*) in natural areas and an Integrated Model for the Assessment of the Global Environment (IMAGE) (*46*) in cropland areas to estimate total N losses from soils based on the surplus of N in the environment [see the study of Wang *et al.* (*7*) for model details]. The N surplus was a function of N inputs (deposition, fixation, fertilizer, and irrigation) minus N outputs besides denitrification and leaching (crop harvest and ammonia volatilization). Manure and grazing were not included as inputs/outputs; instead, we considered them as recycling functions of internal N cycling. Surplus N was then partitioned between leaching and gaseous losses based on temperature, precipitation

(irrigation), evapotranspiration, soil texture, soil drainage, soil organic carbon content, soil total available water content, and land cover (see the Supplementary Materials). Gaseous losses were partitioned between NO, N_2O, and N_2 based on water-filled pore space (fig. S1). The resulting NO flux in California was between 0 and 276 kg of N ha^{-1} $year^{-1}$ with one outlier (525.7 kg of N ha^{-1} $year^{-1}$) being removed.

All data sets were transformed to 4000-m × 4000-m spatial grids before model runs. We used the California Augmented Multisource Land Cover Map published by the Information Center for the Environment, University of California, Davis (UC Davis). Temperature and precipitation data (mean from 1971 to 2000) were from the PRISM (Parameter-elevation Regressions on Independent Slopes Model) Climate Group, Oregon State University, created on 4 June 2010 (*47*). Nitrogen deposition data were based on the Community Multiscale Air Quality model by Tonnesen *et al.* (*48*). Nitrogen fertilizer application rates were from the Department of Water Resources (DWR) of California and U.S. Department of Agriculture (USDA) fertilizer consumption database for 1964 to 2006. Nitrogen harvest was calculated by multiplying crop production by percent dry matter by percent N for each crop type at each year. We then used the mean value for each crop type from 1980 to 2007. The data were from the USDA National Agricultural Statistics Service (2012) and the UC Davis Agricultural and Resource Economics. Nitrogen irrigation data were from the DWR irrigation database for 2001, assuming that N content in irrigation water was 1 mg of N $liter^{-1}$ water. We used a fixed N fixation rate for different crops: rice, 2.5 kg of N ha^{-1} $year^{-1}$; beans, 40 kg of N ha^{-1} $year^{-1}$; alfalfa, 400 kg of N ha^{-1} $year^{-1}$; clover, 15 kg of N ha^{-1} $year^{-1}$; and natural vegetation, 5 kg of N ha^{-1} $year^{-1}$ (*10*). The ammonia volatilization rate was estimated to be 3.6% of N fertilizer, as reported in the California Department of Food and Agriculture Fertilizer Research and Education Program, and to be 15 kg of N ha^{-1} $year^{-1}$ in manure applied areas and 1.6 kg of N ha^{-1} $year^{-1}$ in urban areas (*49*). Soil properties data, including soil texture, soil drainage, SOC (soil organic carbon) content, and total available water content, were from the USDA Soil Survey. We collected data from the literature, which we then compared to our model generated fluxes. Data were collected using Google Scholar and some combination of the following search terms: "NO_x," "nitrogen oxides," "nitric oxide," "emissions," "trace gas," "California," and "site name." References were then followed from papers that were found to be useful.

The airborne NO measurements were made with an Eco Physics (model CLD 88) chemiluminescence instrument with a stabilized photomultiplier tube and reaction chamber temperatures and other operating parameters to ensure a steady calibration point and high reproducibility. A blue-light light-emitting diode photolytic converter (Model 42i BLC2-395 manufactured by Air Quality Design Inc.) was used to selectively convert NO_2 to NO for alternating measurements of NO_x (= NO + NO_2). Further, a Teflon prereaction chamber was installed to run the chemiluminescence reaction to completion before the detection cell to keep track of any interferences or changes in the background signal, thereby increasing the confidence in the measurements and lowering the detection limit generally to less than 0.05 parts per billion by volume. The instrument was cycled through the three states of NO and NO_x, and background measurements were done every 20 s. Calibrations were performed by O_3 titration with a National Institute of Standards and Technology traceable NO standard (Scott-Marrin Inc.) certified to within 5%. Full calibrations were performed before and after the entire flight series, with zero and span checks run routinely before and after each flight. The aircraft used to conduct the experiment is operated by Scientific Aviation Inc. (http://scientificaviation.com/overview/).

Emission estimates were made using a simple boundary layer budget equation for NO_x (see the Supplementary Materials). This technique was outlined in the study of Lenschow *et al.* (*50*), can be generalized to any scalar (*51*–*54*), and was recently used to estimate regional methane emissions in the San Joaquin Valley (*32*). The technique involves thoroughly probing the atmospheric boundary layer (ABL) over a particular region via aircraft, horizontally and vertically, to determine the time rate of change, horizontal advection, and vertical mixing for various scalars, as well as the boundary layer height and its growth. This technique permits the calculation of residual terms within the scalar budgets for the region of interest (*32*). See the Supplementary Materials and Trousdell *et al.* (*32*) for greater details of the budget method, error estimates, and the other aircraft measurements.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/1/eaao3477/DC1

Supplementary Methods

table S1. Crop classification and fertilizer rate data (mean for 1964 to 2006) collected from the DWR of California and USDA fertilizer consumption database.

table S2. ABL heights, z_i, and budget terms for the six flights.

table S3. NO_x budget table and the consequent total regional emissions for each flight.

table S4. Flight estimates of total NO_x and soil NO_x and model estimates of soil NO_x for the flight area in fig. S3 [Coordinates box: (36°51′52.09″N, 120°43′19.65″W), (37°0′6.85″ N, 119°50′53.87″W), (35°57′49.03″N, 120°1′37.93″W), and (36°5′27.03″N, 118°58′2.91″W) compared with CARB inventory of total NO_x].

fig. S1. Model of how nitrogen oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2) partitioning varies with water-filled pore space.

fig. S2. Sensitivity of NO emission from croplands to different input parameters: soil organic carbon (fsoc), soil texture (ftxt), soil drainage (fdrain), and climate (fclim).

fig. S3. Airborne NO_x observation sampling area.

References (*55*–*58*)

REFERENCES AND NOTES

1. World Health Organization (2014); www.who.int/mediacentre/news/releases/2014/air-pollution/en/.
2. A. R. Townsend, R. W. Howarth, F. A. Bazzaz, M. S. Booth, C. C. Cleveland, S. K. Collinge, A. P. Dobson, P. R. Epstein, E. A. Holland, D. R. Keeney, M. A. Mallin, C. A. Rogers, P. Wayne, A. H. Wolfe, Human health effects of a changing global nitrogen cycle. *Front. Ecol. Environ.* **1**, 240–246 (2003).
3. E. A. Davidson, M. B. David, J. N. Galloway, C. L. Goodale, R. Haeuber, J. A. Harrison, R. W. Howarth, D. B. Jaynes, R. R. Lowrance, N. B. Thomas, J. L. Peel, R. W. Pinder, E. Porter, C. S. Snyder, A. R. Townsend, M. H. Ward, Excess nitrogen in the US environment: Trends, risks, and solutions. *Issues Ecol.* **15**, 1–16 (2011).
4. J. J. Yienger, H. Levy II, Empirical model of global soil-biogenic NO_x emissions. *J. Geophys. Res.* **100**, 11447–11464 (1995).
5. E. A. Davidson, C. S. Potter, P. Schlesinger, S. A. Klooster, Model estimates of regional nitric oxide emissions from soils of the southeastern United States. *Ecol. Appl.* **8**, 748–759 (1998).
6. L. Jaeglé, L. Steinberger, R. V. Martin, K. Chance, Global partitioning of NO_x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions. *Faraday Discuss.* **130**, 407–423 (2005).
7. C. Wang, B. Z. Houlton, W. W. Dai, E. Bai, Growth in the global N_2 sink attributed to N fertilizer inputs over 1860 to 2000. *Sci. Total Environ.* **574**, 1044–1053 (2017).
8. Y. Li, B. A. Schichtel, J. T. Walker, D. B. Schwede, X. Chen, C. M. B. Lehmann, M. A. Puchalski, D. A. Gay, J. L. Collett Jr., Increasing importance of deposition of reduced nitrogen in the United States. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 5874–5879 (2016).
9. Environmental Protection Agency, "Nitrogen Oxide Trends"; www.epa.gov/air-trends/nitrogen-dioxide-trends.
10. T. P. Tomich, K. M. Scow, *The California Nitrogen Assessment: Challenges and Solutions for People, Agriculture, and the Environment* (University of California Press, 2016).
11. A. R. Russell, L. C. Valin, E. J. Bucsela, M. O. Wenig, R. C. Cohen, Space-based constraints on spatial and temporal patterns of NO_x emissions in California, 2005–2008. *Environ. Sci. Technol.* **44**, 3608–3615 (2010).

12. R. C. Hudman, N. E. Moore, A. K. Mebust, R. V. Martin, A. R. Russell, L. C. Valin, R. C. Cohen, Steps towards a mechanistic model of global soil nitric oxide emissions: Implementation and space based-constraints. *Atmos. Chem. Phys.* **12**, 7779–7795 (2012).
13. P. Y. Oikawa, C. Ge, J. Wang, J. R. Eberwein, L. L. Liang, L. A. Allsman, D. A. Grantz, G. D. Jenerette, Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region. *Nat. Commun.* **6**, 8753 (2015).
14. P. A. Matson, M. Firestone, D. Herman, T. Billow, N. Kiang, T. Benning, J. Burns, "Agricultural systems in the San Joaquin Valley: Development of emissions estimates for nitrogen oxides" (Technical Report Contract No. 94–732, California Environmental Protection Agency, Air Resources Board, Technical Support Division, 1997).
15. M. Burger, W. R. Horwath, "Assessment of NO_x Emissions from Soil in California Cropping Systems" (Contract No. 09-329, 2013).
16. California Environmental Protection Agency - Air Resources Board, *The California Almanac of Emissions and Air Quality* (Sacramento, California, 2013); www.arb.ca.gov/aqd/almanac/almanac13/almanac13.htm.
17. E. Bai, B. Z. Houlton, Y. P. Wang, Isotopic identification of nitrogen hotspots across natural terrestrial ecosystems. *Biogeosciences* **9**, 3287–3304 (2012).
18. L. N. Ganzeveld, J. Lelieveld, F. J. Dentener, M. C. Krol, A. J. Bouwman, G.-J. Roelofs, Global soil-biogenic NO_x emissions and the role of canopy processes. *J. Geophys. Res. Atmos.* **107**, ACH 9-1–ACH 9-17 (2002).
19. D. Simpson, Biogenic VOC emissions in Europe: Modeling the implications for ozone control strategies, paper presented at the AWMA Conference, San Diego, CA, 8 to 14 November 1993.
20. M. K. Firestone, E. A. Davidson, Microbiological basis of NO and N_2O production and consumption in soil, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, M. O. Andreae, David Steven Schimel, Eds. (Wiley, 1989), vol. 47, pp. 7–21.
21. I. C. Anderson, J. S. Levine, Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide. *J. Geophys. Res. Atmos.* **92**, 965–976 (1987).
22. E. J. Williams, G. L. Hutchinson, F. C. Fehsenfeld, NO_x and N_2O emissions from soil. *Global Biogeochem. Cycles* **6**, 351–388 (1992).
23. D. D. Parrish, E. J. Williams, D. W. Fahey, S. C. Liu, F. C. Fehsenfeld, Measurement of nitrogen oxide fluxes from soils: Intercomparison of enclosure and gradient measurement techniques. *J. Geophys. Res. Atmos.* **92**, 2165–2171 (1987).
24. E. J. Williams, D. D. Parrish, F. C. Fehsenfeld, Determination of nitrogen oxide emissions from soils: Results from a grassland site in Colorado, United States. *J. Geophys. Res. Atmos.* **92**, 2173–2179 (1987).
25. P. M. Homyak, J. C. Blankinship, K. Marchus, D. M. Lucero, J. O. Sickman, J. P. Schimel, Aridity and plant uptake interact to make dryland soils hotspots for nitric oxide (NO) emissions. *Proc. Natl. Acad. Sci. U.S.A.* **113**, E2608–E2616 (2016).
26. E. A. Davidson, W. Kingerlee, A global inventory of nitric oxide emissions from soils. *Nutr. Cycling Agroecosyst.* **48**, 37–50 (1997).
27. E. A. Davidson, Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Sci. Soc. Am. J.* **56**, 95–102 (1992).
28. M. E. Fenn, M. A. Poth, D. W. Johnson, Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. *For. Ecol. Manage.* **82**, 211–230 (1996).
29. B. A. Hungate, C. P. Lund, H. L. Pearson, F. S. Chapin III, Elevated CO_2 and nutrient addition after soil N cycling and N trace gas fluxes with early season wet-up in a California annual grassland. *Biogeochemistry* **37**, 89–109 (1997).
30. I. C. Anderson, M. A. Poth, Semiannual losses of nitrogen as NO and N_2O from unburned and burned chaparral. *Global Biogeochem. Cycles* **3**, 121–135 (1989).
31. Environmental Protection Agency, "NAAQS Table"; www.epa.gov/criteria-air-pollutants/naaqs-table.
32. J. F. Trousdell, S. A. Conley, A. Post, I. C. Faloona, Observing entrainment mixing, photochemical ozone production, and regional methane emissions by aircraft using a simple mixed-layer framework. *Atmos. Chem. Phys.* **16**, 15433–15450 (2016).
33. California Environmental Protection Agency - Air Resources Board, "The California Emissions Projection Analysis Model", (Sacramento, California, 2013); www.arb.ca.gov/app/emsinv/fcemssumcat/fcemssumcat2016.php.
34. E. A. Davidson, M. Keller, H. E. Erickson, L. V. Verchot, E. Veldkamp, Testing a conceptual model of soil emissions of nitrous and nitric oxides: Using two functions based on soil nitrogen availability and soil water content, the hole-in-the-pipe model characterizes a large fraction of the observed variation of nitric oxide and nitrous oxide emissions from soils. *Bioscience* **50**, 667–680 (2000).
35. D. Tilman, J. Fargione, B. Wolff, C. D'Antonio, A. Dobson, R. Howarth, D. Schindler, W. H. Schlesinger, D. Simberloff, D. Swackhamer, Forecasting agriculturally driven global environmental change. *Science* **292**, 281–284 (2001).
36. R. Harrison, J. Webb, A review of the effect of N fertilizer type on gaseous emissions. *Adv. Agron.* **73**, 65–108 (2001).
37. P. A. Matson, R. Naylor, I. Ortiz-Monasterio, Integration of environmental, agronomic, and economic aspects of fertilizer management. *Science* **280**, 112–115 (1998).
38. K. L. McGeough, R. J. Laughlin, C. J. Watson, C. Müller, M. Ernfors, E. Cahalan, K. G. Richards, The effect of cattle slurry in combination with nitrate and the nitrification inhibitor dicyandiamide on in situ nitrous oxide and dinitrogen emissions. *Biogeosciences* **9**, 4909–4919 (2012).
39. K. A. Smith, D. R. Jackson, T. H. Misselbrook, B. F. Pain, R. A. Johnson, PA—Precision agriculture: Reduction of ammonia emission by slurry application techniques. *J. Agric. Eng. Res.* **77**, 277–287 (2000).
40. M. J. Helmers, J. L. Baker, Strategies for nitrate reduction: The Cedar River case study, paper presented at the Integrated Crop Management Conference, Iowa State University, Ames, Iowa, 1 to 2 December 2010.
41. H. J. Di, K. C. Cameron, R. R. Sherlock, Comparison of the effectiveness of a nitrification inhibitor, dicyandiamide, in reducing nitrous oxide emissions in four different soils under different climatic and management conditions. *Soil Use Manage.* **23**, 1–9 (2007).
42. M. A. Sutton, C. M. Howard, J. W. Erisman, G. Billen, A. Bleeker, P. Grennfelt, H. Van Grinsven, B. Grizzetti, *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives* (Cambridge Univ. Press, 2011).
43. B. Z. Houlton. E. Boyer, A. Finzi, J. Galloway, A. Leach, D. Liptzin, J. Melillo, T. S. Rosenstock, D. Sobota, A. R. Townsend, Intentional versus unintentional nitrogen use in the United States: Trends, efficiency and implications. *Biogeochemistry* **114**, 11–23 (2013).
44. D. J. Sobota, J. E. Compton, M. L. McCrackin, S. Singh, Cost of reactive nitrogen release from human activities to the environment in the United States. *Environ. Res. Lett.* **10**, 025006 (2015).
45. B. Z. Houlton, E. Bai, Imprint of denitrifying bacteria on the global terrestrial biosphere. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 21713–21716 (2009).
46. G. Van Drecht, A. F. Bouwman, J. M. Knoop, A. H. W. Beusen, C. R. Meinardi, Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. *Global Biogeochem. Cycles* **17**, 1115 (2003).
47. PRISM Climate Group, Oregon State University, http://prism.oregonstate.edu, created 4 February 2004.
48. G. Tonnesen, Z. Wang, M. Omary, C. J. Chien, "Assessment of Nitrogen Deposition: Modeling and Habitat Assessment," (CEC-500-2006-032, California Energy Commission, PIER Energy-Related Environmental Research, 2007).
49. G. R. Cass, S. Gharib, M. Peterson, J. W. Tilden, "The origin of ammonia emissions to the atmosphere in an urban area," (Open file report 82–6, Environmental Quality Laboratory, California, Institute of Technology, 1982).
50. D. H. Lenschow, P. B. Krummel, S. T. Siems, Measuring entrainment, divergence, and vorticity on the mesoscale from aircraft. *J. Atmos. Oceanic Tech.* **16**, 1384–1400 (1999).
51. S. R. Kawa, R. Pearson Jr., Ozone budgets from the dynamics and chemistry of marine stratocumulus experiment. *J. Geophys. Res.* **94**, 9809–9817 (1989).
52. A. Bandy, I. C. Faloona, B. W. Blomquist, B. J. Huebert, A. D. Clarke, S. G. Howell, R. L. Mauldin, C. A. Cantrell, J. G. Hudson, B. G. Heikes, J. T. Merrill, Y. Wang, D. W. O'Sullivan, W. Nadler, D. D. Davis, Pacific atmospheric sulfur experiment (PASE): Dynamics and chemistry of the south pacific tropical trade wind regime. *J. Atmos. Chem.* **68**, 5–25 (2011).
53. S. A. Conley, I. Faloona, G. H. Miller, D. H. Lenschow, B. Blomquist, A. Bandy, Closing the dimethyl sulfide budget in the tropical marine boundary layer during the pacific atmospheric sulfur experiment. *Atmos. Chem. Phys.* **9**, 8745–8756 (2009).
54. I. Faloona, S. A. Conley, B. Blomquist, A. D. Clarke, V. Kapustin, S. Howell, D. H. Lenschow, A. R. Bandy, Sulfur dioxide in the tropical marine boundary layer: Dry deposition and heterogeneous oxidation observed during the pacific atmospheric sulfur experiment. *J. Atmos. Chem.* **63**, 13–32 (2009).
55. J. B. Burkholder, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation No. 18, JPL Publication 15–10* (Jet Propulsion Laboratory, 2009); http://jpldataeval.jpl.nasa.gov.
56. W. H. Brune, B. C. Baier, J. Thomas, X. Ren, R. C. Cohen, S. E. Pusede, E. C. Browne, A. H. Goldstein, D. R. Gentner, F. N. Keutsch, J. A. Thornton, Ozone production chemistry in the presence of urban plumes. *Faraday Discuss.* **189**, 169–189 (2016).
57. T. Karl, P. K. Misztal, H. H. Jonsson, S. Shertz, A. H. Goldstein, A. B. Guenther, Airborne flux measurements of BVOCs above Californian oak forests: Experimental investigation of surface and entrainment fluxes, OH densities, and Damköhler numbers. *J. Atmos. Sci.* **70**, 3277–3287 (2013).
58. Soberanes Fires; http://cdfdata.fire.ca.gov/incidents/incidents_details_info?incident_id=1348.

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Agriculture is a major source of NO_x pollution in California

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Colorado Field Production of Crude Oil
https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=MCRFPCO1&f=M
15:06:43 GMT-0600 (Mountain Daylight Time)
Source: U.S. Energy Information Administration

Month	Colorado Field Production of Crude Oil Thousand Barrels
Mar-20	15224
Feb-20	14611
Jan-20	16117
Dec-19	16692
Nov-19	16904
Oct-19	17234
Sep-19	15494
Aug-19	16190
Jul-19	15791
Jun-19	15562
May-19	15432
Apr-19	14568
Mar-19	14556
Feb-19	13624
Jan-19	15516
Dec-18	16775
Nov-18	16487
Oct-18	16890
Sep-18	15951
Aug-18	16075
Jul-18	13986
Jun-18	13119
May-18	14215
Apr-18	13924
Mar-18	13966
Feb-18	12467
Jan-18	13962
Dec-17	13918
Nov-17	13095
Oct-17	12951
Sep-17	12187
Aug-17	12039
Jul-17	10980
Jun-17	10147
May-17	10487
Apr-17	9841
Mar-17	9568
Feb-17	8386
Jan-17	9297
Dec-16	9417
Nov-16	9595
Oct-16	11183

Sep-16	9742
Aug-16	10042
Jul-16	9965
Jun-16	9285
May-16	9667
Apr-16	9505
Mar-16	9906
Feb-16	9484
Jan-16	10326
Dec-15	10320
Nov-15	10271
Oct-15	10735
Sep-15	10252
Aug-15	10866
Jul-15	10676
Jun-15	10156
May-15	10572
Apr-15	10164
Mar-15	10335
Feb-15	9163
Jan-15	9865
Dec-14	9629
Nov-14	8853
Oct-14	9025
Sep-14	8335
Aug-14	8709
Jul-14	8394
Jun-14	7895
May-14	7833
Apr-14	7123
Mar-14	7192
Feb-14	6017
Jan-14	6554
Dec-13	6492
Nov-13	6448
Oct-13	6478
Sep-13	5682
Aug-13	5842
Jul-13	5554
Jun-13	5080
May-13	5156
Apr-13	5053
Mar-13	5074
Feb-13	4526
Jan-13	4839
Dec-12	5000
Nov-12	4791

Oct-12	4775
Sep-12	4177
Aug-12	4107
Jul-12	4034
Jun-12	3794
May-12	4089
Apr-12	3683
Mar-12	3927
Feb-12	3551
Jan-12	3717
Dec-11	3639
Nov-11	3551
Oct-11	3558
Sep-11	3406
Aug-11	3440
Jul-11	3296
Jun-11	3226
May-11	3286
Apr-11	3208
Mar-11	3234
Feb-11	2748
Jan-11	2898
Dec-10	3020
Nov-10	2897
Oct-10	2950
Sep-10	2870
Aug-10	2876
Jul-10	2564
Jun-10	2574
May-10	2773
Apr-10	2650
Mar-10	2725
Feb-10	2473
Jan-10	2681
Dec-09	2531
Nov-09	2552
Oct-09	2515
Sep-09	2488
Aug-09	2555
Jul-09	2519
Jun-09	2503
May-09	2552
Apr-09	2445
Mar-09	2662
Feb-09	2448
Jan-09	2625
Dec-08	2588

Nov-08	2619
Oct-08	2662
Sep-08	2648
Aug-08	2540
Jul-08	2518
Jun-08	2471
May-08	2521
Apr-08	2434
Mar-08	2472
Feb-08	2224
Jan-08	2250
Dec-07	2235
Nov-07	2295
Oct-07	2361
Sep-07	2157
Aug-07	2303
Jul-07	2231
Jun-07	2187
May-07	2308
Apr-07	2225
Mar-07	2191
Feb-07	1802
Jan-07	1890
Dec-06	1969
Nov-06	2073
Oct-06	2171
Sep-06	2026
Aug-06	2096
Jul-06	2097
Jun-06	2015
May-06	2136
Apr-06	2022
Mar-06	2098
Feb-06	1830
Jan-06	1968
Dec-05	1931
Nov-05	1967
Oct-05	2016
Sep-05	1930
Aug-05	2016
Jul-05	1933
Jun-05	1912
May-05	2035
Apr-05	1873
Mar-05	1962
Feb-05	1760
Jan-05	1893

Dec-04	1894
Nov-04	1831
Oct-04	1879
Sep-04	1839
Aug-04	1919
Jul-04	1885
Jun-04	1899
May-04	1943
Apr-04	1901
Mar-04	1939
Feb-04	1773
Jan-04	1832
Dec-03	1892
Nov-03	1778
Oct-03	1850
Sep-03	1830
Aug-03	1801
Jul-03	1788
Jun-03	1779
May-03	1813
Apr-03	1766
Mar-03	1780
Feb-03	1633
Jan-03	1800
Dec-02	1815
Nov-02	1701
Oct-02	1770
Sep-02	1716
Aug-02	1715
Jul-02	1668
Jun-02	1643
May-02	1730
Apr-02	1709
Mar-02	1740
Feb-02	1581
Jan-02	1733
Dec-01	1349
Nov-01	1314
Oct-01	1367
Sep-01	1333
Aug-01	1387
Jul-01	1397
Jun-01	1362
May-01	1418
Apr-01	1383
Mar-01	1440
Feb-01	1291

Jan-01	1479
Dec-00	1523
Nov-00	1480
Oct-00	1536
Sep-00	1495
Aug-00	1553
Jul-00	1555
Jun-00	1510
May-00	1568
Apr-00	1521
Mar-00	1615
Feb-00	1494
Jan-00	1631
Dec-99	1538
Nov-99	1484
Oct-99	1561
Sep-99	1483
Aug-99	1540
Jul-99	1532
Jun-99	1539
May-99	1513
Apr-99	1484
Mar-99	1659
Feb-99	1464
Jan-99	1672
Dec-98	1852
Nov-98	1700
Oct-98	1670
Sep-98	1785
Aug-98	1849
Jul-98	1838
Jun-98	1836
May-98	1949
Apr-98	1930
Mar-98	2044
Feb-98	1873
Jan-98	2038
Dec-97	2293
Nov-97	2069
Oct-97	2055
Sep-97	2062
Aug-97	2096
Jul-97	2113
Jun-97	2138
May-97	2135
Apr-97	2189
Mar-97	2275

Feb-97	2023
Jan-97	2169
Dec-96	2023
Nov-96	1945
Oct-96	2107
Sep-96	2039
Aug-96	2029
Jul-96	2152
Jun-96	2063
May-96	2085
Apr-96	2135
Mar-96	2138
Feb-96	2054
Jan-96	2183
Dec-95	2339
Nov-95	2269
Oct-95	2207
Sep-95	2179
Aug-95	2256
Jul-95	2273
Jun-95	2162
May-95	2421
Apr-95	2421
Mar-95	2573
Feb-95	2311
Jan-95	2566
Dec-94	2407
Nov-94	2255
Oct-94	2326
Sep-94	2315
Aug-94	2379
Jul-94	2396
Jun-94	2381
May-94	2562
Apr-94	2381
Mar-94	2533
Feb-94	2283
Jan-94	2395
Dec-93	2526
Nov-93	2452
Oct-93	2433
Sep-93	2347
Aug-93	2426
Jul-93	2429
Jun-93	2369
May-93	2870
Apr-93	2239

Mar-93	2573
Feb-93	2280
Jan-93	2454
Dec-92	2418
Nov-92	2335
Oct-92	2557
Sep-92	2468
Aug-92	2434
Jul-92	2477
Jun-92	2458
May-92	2561
Apr-92	2546
Mar-92	2532
Feb-92	2435
Jan-92	2566
Dec-91	2716
Nov-91	2557
Oct-91	2623
Sep-91	2551
Aug-91	2643
Jul-91	2646
Jun-91	2634
May-91	2720
Apr-91	2608
Mar-91	2664
Feb-91	2418
Jan-91	2602
Dec-90	2417
Nov-90	2505
Oct-90	2598
Sep-90	2528
Aug-90	2552
Jul-90	2561
Jun-90	2514
May-90	2659
Apr-90	2557
Mar-90	2646
Feb-90	2349
Jan-90	2567
Dec-89	2451
Nov-89	2478
Oct-89	2580
Sep-89	2424
Aug-89	2557
Jul-89	2546
Jun-89	2553
May-89	2666

Apr-89	2622
Mar-89	2680
Feb-89	2368
Jan-89	2730
Dec-88	2675
Nov-88	2649
Oct-88	2758
Sep-88	2671
Aug-88	2789
Jul-88	2796
Jun-88	2760
May-88	2753
Apr-88	2719
Mar-88	2743
Feb-88	2510
Jan-88	2528
Dec-87	2520
Nov-87	2307
Oct-87	2492
Sep-87	2423
Aug-87	2465
Jul-87	2468
Jun-87	2396
May-87	2409
Apr-87	2349
Mar-87	2422
Feb-87	2169
Jan-87	2382
Dec-86	2391
Nov-86	2322
Oct-86	2431
Sep-86	2316
Aug-86	2410
Jul-86	2406
Jun-86	2393
May-86	2529
Apr-86	2473
Mar-86	2640
Feb-86	2358
Jan-86	2640
Dec-85	2527
Nov-85	2457
Oct-85	2552
Sep-85	2455
Aug-85	2539
Jul-85	2486
Jun-85	2462

May-85	2608
Apr-85	2569
Mar-85	2626
Feb-85	2301
Jan-85	2664
Dec-84	2424
Nov-84	2343
Oct-84	2424
Sep-84	2346
Aug-84	2368
Jul-84	2395
Jun-84	2433
May-84	2500
Apr-84	2435
Mar-84	2522
Feb-84	2288
Jan-84	2367
Dec-83	2343
Nov-83	2459
Oct-83	2557
Sep-83	2473
Aug-83	2447
Jul-83	2634
Jun-83	2321
May-83	2400
Apr-83	2313
Mar-83	2384
Feb-83	2218
Jan-83	2501
Dec-82	2387
Nov-82	2401
Oct-82	2534
Sep-82	2469
Aug-82	2554
Jul-82	2600
Jun-82	2621
May-82	2654
Apr-82	2639
Mar-82	2725
Feb-82	2352
Jan-82	2609
Dec-81	2708
Nov-81	2630
Oct-81	2774
Sep-81	2464
Aug-81	2495
Jul-81	2523

Jun-81	2445
May-81	2498
Apr-81	2478
Mar-81	2527
Feb-81	2255
Jan-81	2506