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Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range

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Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range

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Abstract Global atmospheric concentrations of methane (CH4), a powerful greenhouse gas, are increasing, but because there are many natural and anthropogenic sources of CH4, it is difficult to assess which sources may be increasing in magnitude. Here we present a data set of δ2H-CH4 measurements of individual sources and air in the Colorado Front Range, USA. We show that δ2H-CH4 but not δ13C signatures are consistent in air sampled downwind of landfills, cattle feedlots, and oil and gas wells in the region. Applying these signatures to air in ground and aircraft samples indicates that at least 50% of CH4 emitted in the region is biogenic, perhaps because regulatory restrictions on leaking oil and natural gas wells are helping to reduce this source of CH4. Source apportionment tracers such as δ2H may help close the gap between CH4 observations and inventories, which may underestimate biogenic as well as thermogenic sources.

1. Introduction

Methane (CH4) is a potent greenhouse gas with multiple natural and anthropogenic sources. Human activities have increased atmospheric CH4 concentrations directly through biogenic processes such as cultivation of ruminant cattle, rice agriculture, and landfills; thermogenic CH4 is released as a consequence of the extraction of fossil fuels [Kirschke et al., 2013]. Human activities may also indirectly increase biogenic CH4 emissions through climate warming and changing precipitation, which may increase CH4 emissions from permafrost [Schuur et al., 2015] and hypoxic lakes and reservoirs [Beaulieu et al., 2014; Saunois et al., 2016; Townsend-Small et al., 2016a]. Global CH4 concentrations are rising despite a hiatus in concentration growth rate in the beginning of this century: some recent analyses have concluded that emissions from oil and gas operations are underestimated [Miller et al., 2013; Brandt et al., 2014; Rice et al., 2016], but other studies have pointed to increased agricultural intensification or enhanced natural biogenic sources [Nisbet et al., 2016; Schaefer et al., 2016].

Methane emissions are estimated in two ways. “Bottom-up” techniques measure CH4 emission rate from individual sources and then multiply the average emission by the number of sources [e.g., Lamb et al., 2015; Marchese et al., 2015; United States Environmental Protection Agency, 2016]. Bottom-up measurements can provide accurate data for individual sources but may miss the largest emitters [Zavala-Araiza et al., 2015] and also do not address natural sources, including those that may be enhanced by human activities. “Top-down” techniques involve the measurement of total regional emissions from a tower or aircraft [Kovacs et al., 2013, 2015; Peischl et al., 2013, 2015]. This technique integrates multiple emissions sources, but it is difficult to distinguish different CH4 sources.

Reconciliation of bottom-up and top-down estimates generally either involves the use of emission inventories to calculate the percentage of CH4 emissions from each sector [Petron et al., 2014; Lyon et al., 2015; Saunois et al., 2016] or the use of source apportionment tracers such as alkane ratios (generally ethane [C2H6]/CH4) [Peischl et al., 2013; Smith et al., 2015] or stable isotope ratios (δ13C and δ2H) [Townsend-Small et al., 2012, 2015]. Ethane/methane and carbon-13 ratios have also been applied to global CH4 budgets [Aydin et al., 2011; Kai et al., 2011; Simpson et al., 2012; Schwietzke et al., 2014; Nisbet et al., 2016; Rice et al., 2016; Schaefer et al., 2016]. In general, biogenic and thermogenic processes impart distinctive 13C and 2H signatures to emitted CH4 [Whiticar, 1999; Townsend-Small et al., 2012, 2015], and only thermogenic, not...
biogenic, CH₄ sources are also sources of heavier alkanes such as C₂H₆ [Simpson et al., 2012; Townsend-Small et al., 2015]. However, the isotopic and alkane composition of CH₄ can vary based on thermal maturity and whether it has been subject to oxidation [Whiticar, 1999; Osborn and McIntosh, 2010; Zumbege et al., 2012]. Previous work has indicated that δ²H is a more consistent tracer of atmospheric fossil fuel CH₄ sources than δ¹³C [Townsend-Small et al., 2012], and that C₂H₆/CH₄ in natural gas sources can be highly variable in a single region, complicating the use of alkane ratios for CH₄ source apportionment [Townsend-Small et al., 2015; Lamb et al., 2016].

Here we present a data set of stable isotopic composition of CH₄ sources in the Colorado Front Range and use δ²H source signatures to constrain the proportion of biogenic and thermogenic CH₄ to total emissions in the region using samples taken both on the ground and via aircraft.

2. Methods

2.1. Study Area

The study area includes the city of Denver and smaller cities of Boulder, Fort Collins, Longmont, and Greeley, with a combined population of over 2,000,000 people (Figure 1). These urban areas have landfills, natural gas distribution systems, and sewage/wastewater treatment plants that are sources of atmospheric CH₄ [Townsend-Small et al., 2012]. Some landfills in Colorado have controls on odor, smoke, and non-CH₄ organic carbon emissions, which may also reduce emissions of CH₄, but older landfills may not have emissions controls (Figure 1). Wastewater treatment can be a significant source of CH₄ in urban areas, particularly if the treatment process includes anoxic processes such as sludge digestion or denitrification [Schneider et al., 2015]. The adjacent Denver-Julesburg Basin has ~ 100,000 oil and natural gas wells including conventional, abandoned, and unconventional hydraulic fracturing wells [Colorado Oil and Gas Conservation Commission, 2016]. Finally, there are large dairy and beef feedlots in the northeastern part of the Denver area. Cattle and dairy are the two largest agricultural commodities in Colorado, and the top five counties in terms of agricultural sales (Weld, Yuma, Morgan, Logan, and Kit Carson) are all located in our study area [United States Department of Agriculture, USDA, 2016]. The most recent USDA Census of Agriculture [2012] indicates there are more than 1.3 million cattle and calves in these five counties [United States Department of Agriculture, USDA, 2012]. There are presumably few natural CH₄ sources, as the region is semiarid with no flooded soils or wetlands, although there are reservoirs, which may emit biogenic CH₄ [Beaulieu et al., 2014].

Oil and gas well locations are taken from the Colorado Oil and Gas Conservation Commission (http://cogcc.state.co.us) as of May 2016. Producing wells are shown in red points in Figure 1; other categories of oil and gas wells are in blue. Other categories include abandoned, active, closed, dry, drilling, injecting, plugged and abandoned, shut in, and temporarily abandoned, as well as wells in the active drilling phase and waiting for well completions. Data for locations and permitted sizes (where available) of cattle feedlots, landfills, and wastewater treatment plants are from the Colorado Department of Public Health and Environment (Figure 1).

2.2. Sample Collection

Sampling occurred in July and August 2014 as part of the National Center for Atmospheric Research (NCAR) Front Range Air Pollution and Photochemistry Experiment (FRAPPE) campaign in conjunction with the NASA DISCOVER-AQ campaign. Three different types of whole air samples were collected: (1) samples upwind and downwind of known CH₄ sources (Figure S1 in the supporting information), (2) samples at fixed ground locations (Golden, Platteville, Chatfield, and Rocky Mountain National Park; Figure 1), and (3) aircraft samples taken aboard the NCAR C-130. Ground samples were collected using an oil-free bellows pump in 2 L stainless steel canisters that were preevacuated to 10⁻² Torr, with sampling times of about ~1 min. Aircraft samples were taken in stainless steel preevacuated canisters using the Advanced Whole Air Sampler (https://www.eol.ucar.edu/instruments/advanced-whole-air-sampler). Aircraft canister filling times were from 5 to 15 s and therefore represent an average of air composition over the distance that the aircraft covered while the canister was open. Aircraft samples for isotopic analysis were chosen to represent samples from upwind and downwind of the region along a range of CH₄ concentrations.

Samples were taken on the ground from three types of CH₄ sources: oil and gas sources (n = 32), landfills (n = 18), and cattle (n = 14) (Figure S1). Oil and gas samples were taken throughout the high-density extraction area in Weld County. These samples include canisters filled downwind of production, gathering, processing, and
pipeline sites, as well as several samples downwind of processing and produced water disposal sites. Landfill samples were taken in Weld and Larimer counties. Cattle samples were taken near several large feedlots in Morgan and Weld counties and represent CH$_4$ emitted directly from cattle as well as that produced in manure disposal pits. In all three cases, samples were taken both upwind and downwind of the sources for better attribution of source signatures. We also took triplicate samples of at least one sample from each source category; our isotopic measurements were within the instrument reproducibility for each set of triplicate samples.

We also took samples throughout the campaign at three fixed ground sites and throughout Rocky Mountain National Park. Sites at Golden, Platteville, and Chatfield corresponded with aircraft sampling spirals in the DISCOVER-AQ campaign. The Platteville site ($n = 35$) is surrounded by both oil and gas activity and cattle feedlots (Figure 1). Golden ($n = 73$) is located in the foothills of the Front Range directly to the west of Denver, with very little oil and gas activity or cattle present (Figure 1). Samples at these two sites were taken during NASA flight spirals throughout July and August of 2014. The ground site at Chatfield Reservoir is an air quality monitoring station operated by the Colorado Department of Public Health and Environment (http://www.colorado.gov/airquality/report.aspx), and we report data from six samples taken at this site on 26 to 27 July 2014. The Golden and Chatfield sites are located near landfills and wastewater treatment plants (Figure 1). Samples were taken throughout Rocky Mountain National Park ($n = 30$) at a variety of altitudes and locations throughout the campaign.

Figure 1. Map of the study area with oil and gas wells, landfills, wastewater treatment plants, and cattle feedlots. Inset map shows the location in northeastern Colorado. Also shown are ground sampling sites (black stars) at Platteville, Rocky Mountain National Park, Chatfield, and Golden. Dairy and beef feedlots are depicted with the maximum permitted head. Wastewater treatment plants are shown in sizes relative to the volume of waste treated (millions of gallons per day). Landfills are categorized according to whether CH$_4$ emissions are controlled. Producing oil and gas wells are shown in red, all other wells (inactive, abandoned, drilling, and permitted) are shown in blue.
2.3. Sample Analysis

Methane concentrations were measured via gas chromatography (GC) flame ionization detection at the University of California, Irvine, with a precision of 0.1% and an accuracy of 0.1% and with calibration standards linked to National Institute of Standards and Technology and subject to frequent intercalibration [Townsend-Small et al., 2015]. Methane concentrations in flight canisters were not measured via GC; these values were calculated using continuous CH4 measurements made during flights via cavity ring down spectroscopy (CRDS) using a Picarro G1301-f, which has a precision of < 1 ppb for CH4. The 1 s data from the CRDS instrument were averaged over the time period that canisters were open for sampling. Subsamples of each canister were transferred via vacuum line for aircraft samples or, for pressurized samples, manually via syringe to preevacuated 12 mL glass vials for stable isotopic analysis of CH4 via isotope ratio mass spectrometry (IRMS) at the University of Cincinnati [Yarnes, 2013]. Isotope ratios are expressed in delta notation with respect to Vienna Peedee belemnite (for $^{13}$C) and Vienna SMOW (for $^2$H) standards. The IRMS instrument is calibrated several times daily with standards bracketing the isotopic composition of samples and with standards matched to the concentration of samples to avoid linearity issues. The reproducibility of $\delta^{13}$C and $\delta^2$H is 0.2‰ and 4‰, respectively.

2.4. Data Analysis and Statistics

We determined isotopic composition of three categories of CH4 sources (oil and gas, landfills, and cattle) using the “Keeling plot” technique, where $\delta^{13}$C or $\delta^2$H composition of CH4 from individual source samples is plotted against the reciprocal of the CH4 concentration in each sample, and where the y axis intercept of a significant regression line indicates the isotopic composition of the CH4 source [Keeling, 1958, 1961; Pataki et al., 2003]. We used the Model II standard major axis regression technique to estimate the intercept values for each source and then used the 95% confidence interval estimate of the intercept from the Model I regression (also known as the ordinary least squares regression) for uncertainty analysis [Pataki et al., 2003]. The same techniques were used for source apportionment for samples from fixed ground and aircraft sites. Because intercept confidence intervals were larger for flights and fixed ground sites than for CH4 sources, standard errors for each flight and fixed ground site were used for calculating ranges of possible source contributions. Statistical analyses were done in R using the lmodel2 package [Legendre, 2013]. Previous studies have also applied other statistical tools to combat heteroscedasticity, or the change in relative error of isotopic measurements with changing CH4 concentration [Zazzeri et al., 2015], but, as described above, our method includes calibration steps that eliminate these correlated errors.

3. Results and Discussion

3.1. Source Signatures

Isotopic composition of the three main CH4 sources is shown in Figure 2. There was a significant relationship ($p < 0.05$) between isotopic composition and $1/[CH_4]$ for all sources and isotopes, except for $\delta^{13}$C-CH4 of oil and gas sources (Figure 2). We have previously observed this pattern of $\delta^{13}$C-CH4 from natural gas mixed with air [Townsend-Small et al., 2015], likely due to the similarity of natural gas $\delta^{13}$C signatures to background atmospheric CH4 ($\sim -47$‰), so that small changes in boundary layer height and background concentrations diminish the ability to consistently distinguish source signatures from background air. Natural gas produced in the region has $\delta^{13}$C values ranging from $-40$‰ to $-50$‰ [Sherwood et al., 2016], consistent with our results (Figure 2b).

Methane from oil and gas sources had a $\delta^2$H of $-209\pm 9$‰ (Figure 2a), generally consistent with previous studies of thermogenic CH4 [Whiticar, 1999]. Our finding of a narrowly defined end-member ($-218$ to $-200$‰) is somewhat surprising, although we found a similar pattern in the Barnett Shale [Townsend-Small et al., 2015]. The stable isotopic composition of natural gas can vary based on thermal maturity and reservoir depth and age, even within a single geographic region [Osborn and McIntosh, 2010]. However, we attribute our consistent $\delta^2$H-CH4 results to the predominance of a single formation, the Niobrara Shale, in current natural gas production in the Front Range [Pétron et al., 2014]. More work is needed to confirm whether $\delta^2$H-CH4 is consistent in natural gas in the region, including direct measurements and sampling from production sites in the Niobrara Shale and other formations in the Denver Basin.

Biogenic CH4 emitted from landfills ($\delta^2$H = $-290\pm 4$‰, Figure 2c) and cattle feedlots ($\delta^2$H = $-302\pm 16$‰, Figure 2e) was depleted in $^2$H relative to natural gas CH4. The $\delta^2$H signatures for the two biogenic sources are
close to within 4‰, the reproducibility of our measurement method, of each other; therefore, biogenic sources are lumped together with a δ²H of $-296%_{\text{o}} \pm 16%_{\text{o}}$ for regional source apportionment. Regressions on Keeling plots for δ¹³C of CH₄ from landfills and feedlots were also significant, with source signatures of $-58.1%_{\text{o}} \pm 1.4%_{\text{o}}$ and $-56.2%_{\text{o}} \pm 1.2%_{\text{o}}$, respectively (Figures 2d and 2f). δ¹³C and δ²H end-members for biogenic CH₄ in the Front Range are similar to values for these sources in other regions [Cicerone and Oremland, 1988; Whiticar, 1999; Townsend-Small et al., 2012, 2015].

### 3.2. Source Apportionment at Ground Sites

Percent of biogenic (landfill and cattle, average δ²H = $-296%_{\text{o}}$) and thermogenic (oil and gas, δ²H = $-209%_{\text{o}}$) CH₄ sampled at each fixed ground monitoring site was assessed using Keeling plots of δ²H (Figure 3). There
was a significant relationship \((p < 0.05)\) between \(\delta^2\text{H}\) and the inverse of \(\text{CH}_4\) concentration at three sites, with \(\delta^2\text{H}\) end-members of \(-256\% \pm 13\%\), \(-365\% \pm 69\%\), and \(-297\% \pm 74\%\) at Platteville, Golden, and Chatfield, respectively (Figure 3). This corresponds to 54\% of \(\text{CH}_4\) observed in Platteville of biogenic origin, with a range (calculated using 95\% confidence intervals of the intercept) of 39\% to 69\% biogenic \(\text{CH}_4\). For the Golden site, the intercept was lower than the observed signature of biogenic \(\text{CH}_4\), with a range of percent biogenic \(\text{CH}_4\) between 100\% and 259\%, indicating that oxidation of biogenic \(\text{CH}_4\) in the atmosphere contributes to lower isotopic values observed at this site [Townsend-Small et al., 2012]. Similarly, at the Chatfield site, where confidence intervals were also high, we find a range of percent biogenic \(\text{CH}_4\) at this site ranging from 16\% to 186\%, with a mean value of 100\% biogenic \(\text{CH}_4\). There was a significant relationship of \(\delta^{13}\text{C}\) with \(1/\text{CH}_4\) at the Platteville and Chatfield sites (but not in Golden), although with less robust correlation coefficients, but it is difficult to calculate the exact proportion of biogenic and thermogenic sources without a firm end-member for natural gas \(\delta^{13}\text{C}\) in the basin (Figure S2).

Samples taken throughout the campaign in Rocky Mountain National Park had a significant relationship between both isotopes and the inverse of \(\text{CH}_4\) concentration \((p < 0.05)\), and both the \(\delta^2\text{H}\) and \(\delta^{13}\text{C}\) end-members were below the range of measured biogenic \(\text{CH}_4\) (Figure S3).

While the Platteville site is in an area with large numbers of oil and gas wells, there are also several large cattle feedlots in the area (Figure 1). In Golden, farther from oil and gas activity, there are several landfills and a large wastewater treatment plant nearby (Figure 1). Chatfield is located farthest from oil and gas activity and near a drinking water and flood control reservoir, which may be a source of biogenic \(\text{CH}_4\) [Beaulieu et al., 2014; Townsend-Small et al., 2016a], particularly in the summer months when hypoxia is present [Chatfield Watershed Authority, 2016].
3.3. Source Apportionment From Aircraft Flights

There were 10 campaign flights categorized as “emission” flights, where the C-130 flew parallel to the Front Range at various distances east of the continental divide (see supporting information). Of the flights with samples in the Front Range only, four had a significant ($p < 0.5$) relationship of $\delta^2$H versus $1/\text{CH}_4$: RF03, RF05, RF06, and RF14, with $y$ intercepts ($\pm 95\%$ CI) of $-362\%\pm 101\%o$, $-303\%\pm 71\%o$, $-362\%\pm 152\%o$, and $-421\%\pm 152\%o$, respectively (Figure 3d and Table S1). These results indicate that CH$_4$ in the region is between 27% and greater than 100% biogenic CH$_4$. Two other “emission” flights where $\delta^13$C was not measured, RF11 and RF12, have $y$ intercepts corresponding with $\delta^{13}$C values of $-54.0\%\pm 2.3\%$ and $-51.8\%\pm 1.2\%$, respectively (Table S1), close to $\delta^{13}$C values of biogenic CH$_4$. These data indicate that, despite the high number of oil and gas wells in the area, biogenic sources still account for a significant portion of CH$_4$ emissions. The variability in composition between flight days may represent normal daily variations in oil and gas emissions, which, unlike CH$_4$ emissions from cattle and landfills, are generally dominated by a few large, short-term sources [e.g., Lamb et al., 2015; Zavala-Araiza et al., 2015].

Two other flights with samples taken outside of the study area in northeastern Colorado include RF09 and RF10, including portions of western Nebraska and southeastern Colorado. These flights have similar $\delta^2$H end-members to samples taken within the Front Range (Table S1), indicating greater than 100% (range = 7% to 211%) and 61% (range 0% to 153%) biogenic CH$_4$, respectively.

Interestingly, data from two aircraft flights indicated that nearby basins have a larger proportion of thermogenic CH$_4$ than in the Front Range. In flight RF08, which included the Piceance basin of northwestern Colorado and portions of the Uintah Basin in eastern Utah, $\delta^2$H measurements indicated a source signature of $-245\%\pm 102\%o$ (Table S1), indicating a larger portion (59%) of thermogenic CH$_4$ than in aircraft samples taken in the Front Range only (see above). A similar flight path later in the campaign (RF15) showed similar results, with a $y$ intercept of $-269\%\pm 38\%o$ (Table S1). A previous study in the Uintah basin indicated a high leak rate from oil and gas operations and also suggested a higher leak rate in the Piceance basin relative to the Denver-Julesburg basin [Karion et al., 2013]. That study also indicated that the Uintah basin had lower CH$_4$ emissions from cattle than the Denver-Julesburg basin [Karion et al., 2013; Pétron et al., 2014].

Flight RF04 also includes samples from outside the Denver-Julesburg basin, including in the Green River basin of southeastern Wyoming. The $\delta^2$H end-member for samples collected on this flight has a strong biogenic signal ($-465\%\pm 306$, Table S1). This may be indicative of cattle ranching in this area. There are also coalbed CH$_4$ wells and coal mines in this area, which may be a source of biogenic CH$_4$ [Townsend-Small et al., 2016b]. There are few studies of CH$_4$ sources in this area, but the San Juan basin in southwestern Colorado is a large source of biogenic coalbed and natural gas CH$_4$ [Kort et al., 2014; Arata et al., 2016].

3.4. Methane Emissions in the Colorado Front Range

Results from aircraft samples and ground sampling sites in the Front Range are in good agreement, showing that biogenic CH$_4$ comprised about 50% of total CH$_4$ observed in the active oil and gas extraction region, with a larger proportion of biogenic CH$_4$ in regions farther from active drilling regions, including urban and south suburban Denver. These results indicate that thermogenic CH$_4$ emissions may be declining in the Colorado Front Range, as a previous study (using alkane ratios for thermogenic CH$_4$ source apportionment and inventory data for biogenic CH$_4$ sources) estimated that only 27% of CH$_4$ emissions in Weld County (location of our Platteville sampling site) were biogenic [Pétron et al., 2014]. This decline may be due to increased inspection and leak repair at oil and gas production sites or reduced production rates in response to declining oil and natural gas prices.

Other studies in the Front Range have used VOC concentrations to compare urban, agricultural, and oil and gas sources of air pollution. For example, previous studies have used the ratio of i-pentane to n-pentane in air to show that oil and gas infrastructure, not urban vehicular emissions, is the dominant source of these alkanes in the Denver area [Gilman et al., 2013; Swarthout et al., 2013]. Other studies have measured VOCs in the Platteville region and found that oil and gas signatures dominated there [Thompson et al., 2014; Halliday et al., 2016], implying that oil and gas sources may be the dominant source of CH$_4$ as well. These studies are valuable because many VOCs can have direct and indirect implications for human health [Colborn et al., 2014; Marrero et al., 2016]. However, because these methods do not include tracers of biogenic CH$_4$. 
it can be problematic to use hydrocarbon measurements as proxies of CH$_4$ sources. For example, our previous work has shown that the ratio of CH$_4$ to other alkanes can be variable within a single basin, particularly basins that have a combination of wet gas, dry gas, and oil wells [Townsend-Small et al., 2015]. For this reason, the $\delta^{2}H$ composition of CH$_4$ may be a more accurate tracer of CH$_4$ sources.

One caveat to the utility of $\delta^{2}H$ composition of CH$_4$ for source apportionment is that, as mentioned above, oil and gas extraction can be a source of biogenic and thermogenic CH$_4$, and biogenic coalbed CH$_4$ can also escape via natural seepage or during coal mining [Zazzeri et al., 2015]. Biogenic coalbed gas is a source of CH$_4$ in groundwater in oil and gas extraction regions of Colorado [Sherwood et al., 2016], and there is active coalbed CH$_4$ extraction in southwestern Colorado and southern Wyoming [Kort et al., 2014; Arata et al., 2016]. Furthermore, legacy wells in Colorado are a source of both biogenic and thermogenic CH$_4$ [Townsend-Small et al., 2016b], and drilling through subsurface coal formations may release coalbed CH$_4$ [Cañada et al., 2014]. However, in the 33 samples we collected downwind of oil and gas facilities in the Front Range (Figures 2a and 2b), we did not detect a strong biogenic signature. More work is needed on the relative contributions of biogenic and thermogenic CH$_4$ to total CH$_4$ emissions from oil and gas regionally and globally, as emissions of biogenic coalbed CH$_4$ will also decrease the effectiveness of other source apportionment techniques such as C$_2$H$_6$:CH$_4$. Additional sampling of CH$_4$ from natural gas supply chain activity in the Front Range, including direct measurements, could determine if natural gas with a depleted isotopic signature [e.g., Osborn and McIntosh, 2010] is prevalent in the region.

3.5. Implications for Regional and Global CH$_4$ Sources

Our results indicate two possible conclusions. Previous studies of CH$_4$ emissions in the region may have underestimated the contribution of biogenic sources. Alternatively, thermogenic CH$_4$ emissions have decreased in the area either in response to regulatory constraints and more frequent inspection of oil and gas wells with subsequent leak repair or due to lower production rates triggered by falling oil and natural gas prices. If the former case is true, top-down studies in this and other regions may have overestimated the contribution of thermogenic CH$_4$, particularly if those studies have used $\delta^{13}C$ or hydrocarbon ratios to estimate thermogenic contributions. Additional studies utilizing $\delta^{2}H$ to distinguish CH$_4$ sources are needed regionally and globally: if biogenic CH$_4$ emissions are underestimated [e.g., Nisbet et al., 2016; Schaefer et al., 2015], these studies may help to close the gap between bottom-up and top-down studies [e.g., Miller et al., 2013; Brandt et al., 2014]. Because increasing sensitivity of isotope ratio mass spectrometry methods has led to smaller volume requirements for CH$_4$ isotope analysis, we can now analyze many samples in a short period of time, which allows for a new look at CH$_4$ sources as well as changing atmospheric CH$_4$ concentrations.

References


Colorado Oil and Gas Conservation Commission (2016), Production data inquiry. [Available at http://cogcc.state.co.us/data/html/#cogis].


Supplemental Information

Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range

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Figure S1A. Location of samples taken at oil and gas facilities (in black). Legend and scale are as in Figure 1.
Figure S1B. Location of samples taken at landfills (in black). Legend and scale are as in Figure 1.
Figure S1C. Location of samples taken at cattle facilities (in black). Legend and scale are as in Figure 1.
Figure S2 – δ\(^{13}\)C signatures of samples taken at Platteville, Golden, and Chatfield
Figure S3 – δ²H and δ¹³C signatures of samples taken in Rocky Mountain National Park
Table S1. Flights and isotopic endmembers with 95% confidence intervals (for p > 0.05 only). For significant relationships, the number of samples is also shown. All flights are within the Front Range of Northeastern Colorado except where noted. Flight tracks can be viewed in Google Earth using the following link: http://www-air.larc.nasa.gov/missions/discover-aq/kmz/FRAPPE_C130_2014_ALL_July26-August18.kmz

<table>
<thead>
<tr>
<th>Flight</th>
<th>Date</th>
<th>Approximate flight area (km²)</th>
<th>δ¹³C endmember (%)</th>
<th>δ¹⁸H endmember (%) (± SE)</th>
<th>Notes on flight path</th>
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<td>7/26/14</td>
<td>2.1 x 10⁴</td>
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<tr>
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<td>1.6 x 10⁴</td>
<td>Not significant</td>
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<tr>
<td>RF03</td>
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<td>Not significant</td>
<td>-362 ± 101 (n = 24)</td>
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<tr>
<td>RF04</td>
<td>7/29/14</td>
<td>4.0 x 10⁴</td>
<td>Not significant</td>
<td>-465 ± 306 (n = 11)</td>
<td>includes south-central Wyoming</td>
</tr>
<tr>
<td>RF05</td>
<td>7/31/14</td>
<td>2.1 x 10⁴</td>
<td>Not significant</td>
<td>-303 ± 71 (n = 10)</td>
<td></td>
</tr>
<tr>
<td>RF06</td>
<td>8/2/14</td>
<td>2.1 x 10⁴</td>
<td>Not significant</td>
<td>-362 ± 152 (n = 20)</td>
<td></td>
</tr>
<tr>
<td>RF07</td>
<td>8/3/14</td>
<td>2.2 x 10⁴</td>
<td>Not significant</td>
<td>Not significant</td>
<td></td>
</tr>
<tr>
<td>RF08</td>
<td>8/6/14</td>
<td>5.1 x 10⁴</td>
<td>Not measured</td>
<td>-245 ± 102 (n = 14)</td>
<td>includes Piceance basin, northwest Colorado and western Utah</td>
</tr>
<tr>
<td>RF09</td>
<td>8/7/14</td>
<td>1.9 x 10⁴</td>
<td>Not measured</td>
<td>-305 ± 89 (n = 15)</td>
<td>includes western Nebraska</td>
</tr>
<tr>
<td>RF10</td>
<td>8/8/14</td>
<td>3.0 x 10⁴</td>
<td>Not significant</td>
<td>-262 ± 81 (n = 8)</td>
<td>includes western Nebraska, south-central Colorado</td>
</tr>
<tr>
<td>RF11</td>
<td>8/11/14</td>
<td>2.0 x 10⁴</td>
<td>-54.0 ± 2.3 (n = 15)</td>
<td>Not measured</td>
<td></td>
</tr>
<tr>
<td>RF12</td>
<td>8/12/14</td>
<td>2.1 x 10⁴</td>
<td>-51.8 ± 1.2 (n = 19)</td>
<td>Not measured</td>
<td></td>
</tr>
<tr>
<td>RF13</td>
<td>8/15/14</td>
<td>9.4 x 10⁴</td>
<td>Not measured</td>
<td>Not significant</td>
<td>includes northwest Colorado, southern Wyoming, western Kansas, and southwest Nebraska</td>
</tr>
<tr>
<td>RF14</td>
<td>8/16/14</td>
<td>3.3 x 10⁴</td>
<td>Not significant</td>
<td>-421 ± 152 (n = 12)</td>
<td></td>
</tr>
<tr>
<td>RF15</td>
<td>8/18/14</td>
<td>7.7 x 10⁴</td>
<td>Not significant</td>
<td>-269 ± 38 (n = 18)</td>
<td>includes northwest Colorado</td>
</tr>
</tbody>
</table>