

2016

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

Amy Townsend-Small
University of Cincinnati

E. Claire Botner
University of Cincinnati

Kristine L. Jimenez
University of Cincinnati

Jason R. Schroeder
University of California, Irvine

Nicola J. Blake
University of California, Irvine

See next page for additional authors

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Townsend-Small, Amy; Botner, E. Claire; Jimenez, Kristine L.; Schroeder, Jason R.; Blake, Nicola J.; Meinardi, Simone; Blake, Donald R.; Sive, Barkley C.; Bon, Daniel; Crawford, James H.; Pfister, Gabriele; and Flocke, Frank M., "Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range" (2016). *U.S. National Park Service Publications and Papers*. 138.
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Authors

Amy Townsend-Small, E. Claire Botner, Kristine L. Jimenez, Jason R. Schroeder, Nicola J. Blake, Simone Meinardi, Donald R. Blake, Barkley C. Sive, Daniel Bon, James H. Crawford, Gabriele Pfister, and Frank M. Flocke



RESEARCH LETTER

10.1002/2016GL071438

Key Points:

- Biogenic and thermogenic CH₄ have distinct hydrogen isotopic ratios in Colorado
- Hydrogen isotopes indicate that biogenic sources comprise at least 50% of CH₄ in the Front Range
- Potential for resolving differences between methane inventories and observations regionally and globally

Supporting Information:

- Supporting Information S1

Correspondence to:

A. Townsend-Small,
amy.townsend-small@uc.edu

Citation:

Townsend-Small, A., et al. (2016), Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: A case study from the Colorado Front Range, *Geophys. Res. Lett.*, 43, 11,462–11,471, doi:10.1002/2016GL071438.

Received 4 OCT 2016

Accepted 27 OCT 2016

Accepted article online 28 OCT 2016

Published online 15 NOV 2016

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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

Amy Townsend-Small¹, E. Claire Botner¹, Kristine L. Jimenez¹, Jason R. Schroeder^{2,3}, Nicola J. Blake², Simone Meinardi², Donald R. Blake², Barkley C. Sive⁴, Daniel Bon⁵, James H. Crawford³, Gabriele Pfister⁶, and Frank M. Flocke⁶

¹Department of Geology, University of Cincinnati, Cincinnati, Ohio, USA, ²Department of Chemistry, University of California, Irvine, California, USA, ³NASA Langley Research Center, Hampton, Virginia, USA, ⁴United States National Park Service, Denver, Colorado, USA, ⁵Colorado Department of Public Health and Environment, Denver, Colorado, USA, ⁶National Center for Atmospheric Research, Boulder, Colorado, USA

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 source 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; Saunio 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 [Karion 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 [Pétron et al., 2014; Lyon et al., 2015; Saunio 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; Zumberge *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 (FRAPPÉ) 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

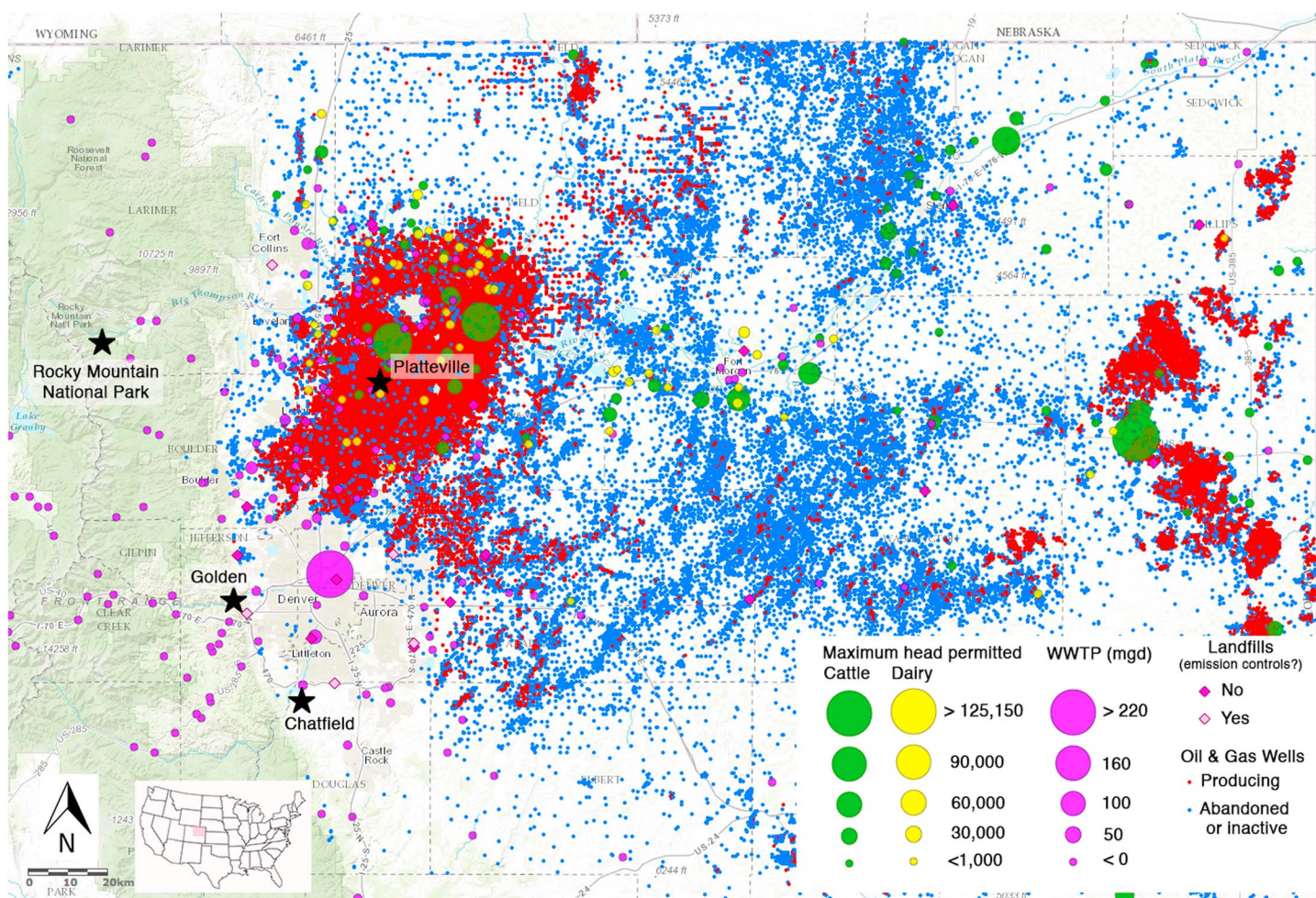


Figure 1. Map of the study area with oil and gas wells, landfills, wastewater treatment plants, and cattle feedlots. Inset map shows the location in northeastern Colorado. Also shown are ground sampling sites (black stars) at Platteville, Rocky Mountain National Park, Chatfield, and Golden. Dairy and 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 CH₄ emissions are controlled. Producing oil and gas wells are shown in red, all other wells (inactive, abandoned, drilling, and permitted) are shown in blue.

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 CH₄ 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.

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 Pee Dee belemnite (for ¹³C) and Vienna SMOW (for ²H) 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 δ¹³C and δ²H 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 δ¹³C or δ²H 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 δ¹³C-CH₄ of oil and gas sources (Figure 2). We have previously observed this pattern of δ¹³C-CH₄ from natural gas mixed with air [Townsend-Small *et al.*, 2015], likely due to the similarity of natural gas δ¹³C signatures to background atmospheric CH₄ (~ -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 δ¹³C values ranging from -40‰ to -50‰ [Sherwood *et al.*, 2016], consistent with our results (Figure 2b).

Methane from oil and gas sources had a δ²H of -209‰ ± 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 δ²H-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 δ²H-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 (δ²H = -290‰ ± 4‰, Figure 2c) and cattle feedlots (δ²H = -302‰ ± 16‰, Figure 2e) was depleted in ²H relative to natural gas CH₄. The δ²H signatures for the two biogenic sources are

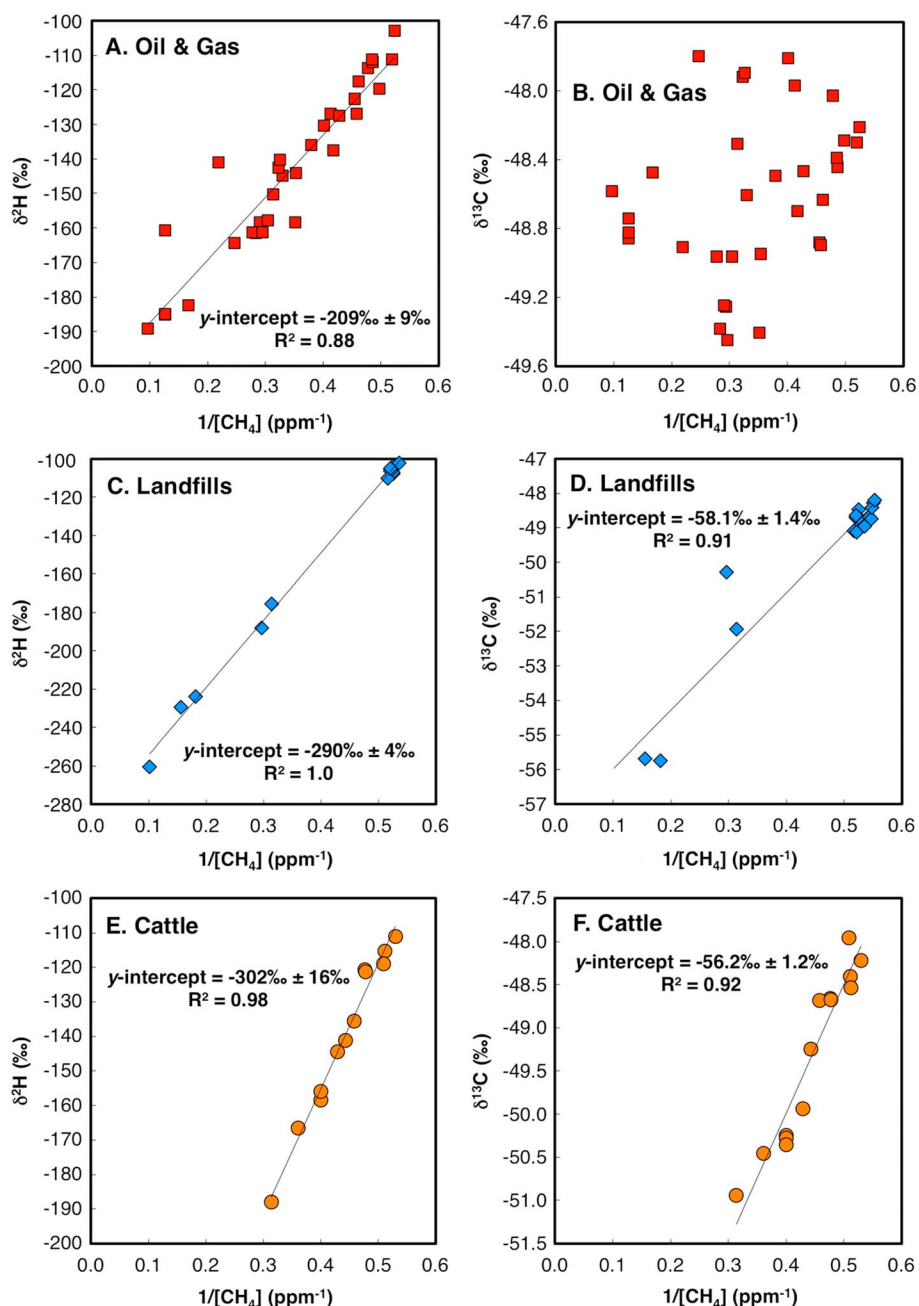


Figure 2. Keeling plots of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ composition of CH_4 versus $1/[\text{CH}_4]$ (ppm⁻¹) collected downwind of (a and b) oil and gas, (c and d) landfill, and (e and f) cattle sources. Each point represents an individual sample.

close to within 4‰, the reproducibility of our measurement method, of each other; therefore, biogenic sources are lumped together with a $\delta^2\text{H}$ of $-296\text{‰} \pm 16\text{‰}$ for regional source apportionment. Regressions on Keeling plots for $\delta^{13}\text{C}$ of CH_4 from landfills and feedlots were also significant, with source signatures of $-58.1\text{‰} \pm 1.4\text{‰}$ and $-56.2\text{‰} \pm 1.2\text{‰}$, respectively (Figures 2d and 2f). $\delta^{13}\text{C}$ and $\delta^2\text{H}$ end-members for biogenic CH_4 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 $\delta^2\text{H} = -296\text{‰}$) and thermogenic (oil and gas, $\delta^2\text{H} = -209\text{‰}$) CH_4 sampled at each fixed ground monitoring site was assessed using Keeling plots of $\delta^2\text{H}$ (Figure 3). There

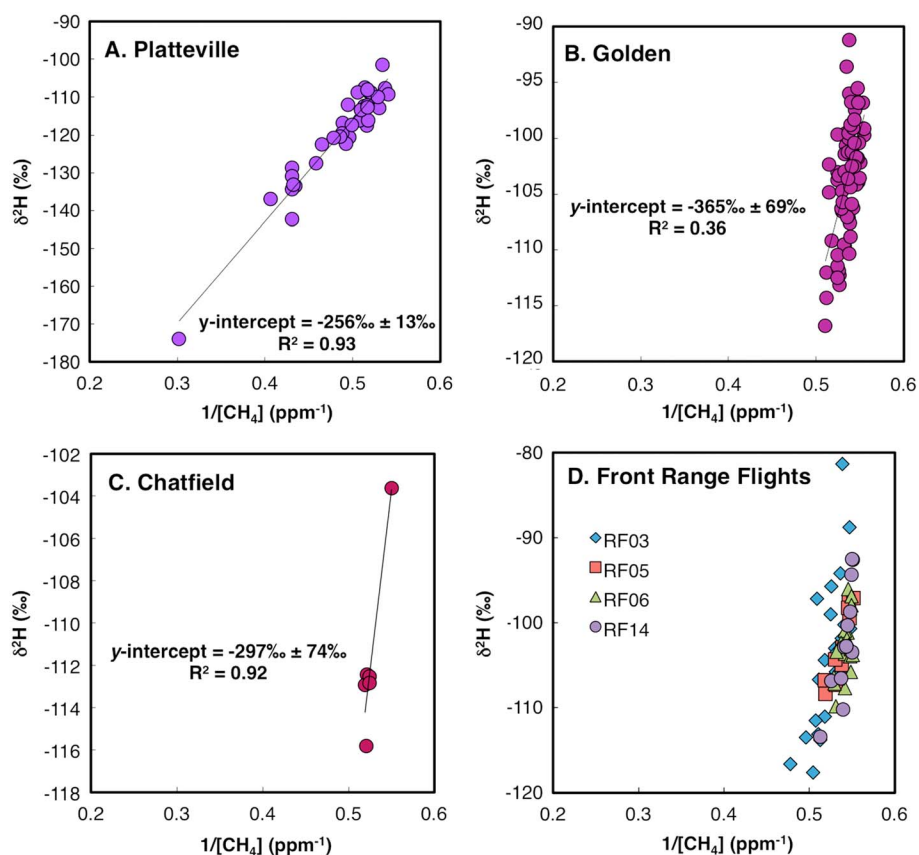


Figure 3. (a–c) Keeling plots of $\delta^2\text{H}$ composition of CH_4 at three ground sites in the Front Range (sampling locations are shown in Figure 1). (d) $\delta^2\text{H}$ - CH_4 for samples taken during aircraft flights within the Front Range. All flights shown are significant at $p < 0.05$. Flight tracks can be viewed using the following link: http://www-air.larc.nasa.gov/missions/discover-aq/kmz/FRAPPE_C130_2014_ALL_July26-August18.kmz. Source CH_4 end-members for flight samples are shown in Table S1.

was a significant relationship ($p < 0.05$) between $\delta^2\text{H}$ and the inverse of CH_4 concentration at three sites, with $\delta^2\text{H}$ end-members of $-256\text{‰} \pm 13\text{‰}$, $-365\text{‰} \pm 69\text{‰}$, and $-297\text{‰} \pm 74\text{‰}$ at Platteville, Golden, and Chatfield, respectively (Figure 3). This corresponds to 54% of CH_4 observed in Platteville of biogenic origin, with a range (calculated using 95% confidence intervals of the intercept) of 39% to 69% biogenic CH_4 . For the Golden site, the intercept was lower than the observed signature of biogenic CH_4 , with a range of percent biogenic CH_4 between 100% and 259%, indicating that oxidation of biogenic 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 CH_4 at this site ranging from 16% to 186%, with a mean value of 100% biogenic 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 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 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 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 $\delta^2\text{H}$ versus $1/[\text{CH}_4]$: RF03, RF05, RF06, and RF14, with y intercepts ($\pm 95\%$ CI) of $-362\text{‰} \pm 101\text{‰}$, $-303\text{‰} \pm 71\text{‰}$, $-362\text{‰} \pm 152\text{‰}$, and $-421\text{‰} \pm 152\text{‰}$, 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 $\delta^2\text{H}$ was not measured, RF11 and RF12, have y intercepts corresponding with $\delta^{13}\text{C}$ values of $-54.0\text{‰} \pm 2.3\text{‰}$ and $-51.8\text{‰} \pm 1.2\text{‰}$, respectively (Table S1), close to $\delta^{13}\text{C}$ 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 $\delta^2\text{H}$ 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, $\delta^2\text{H}$ measurements indicated a source signature of $-245\text{‰} \pm 102\text{‰}$ (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 $-269\text{‰} \pm 38\text{‰}$ (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 $\delta^2\text{H}$ end-member for samples collected on this flight has a strong biogenic signal ($-465\text{‰} \pm 306$, 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 CH₄ sources. For example, our previous work has shown that the ratio of CH₄ 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 δ²H composition of CH₄ may be a more accurate tracer of CH₄ sources.

One caveat to the utility of δ²H composition of CH₄ for source apportionment is that, as mentioned above, oil and gas extraction can be a source of biogenic and thermogenic CH₄, and biogenic coalbed CH₄ can also escape via natural seepage or during coal mining [Zazzeri *et al.*, 2015]. Biogenic coalbed gas is a source of CH₄ in groundwater in oil and gas extraction regions of Colorado [Sherwood *et al.*, 2016], and there is active coalbed CH₄ 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 CH₄ [Townsend-Small *et al.*, 2016b], and drilling through subsurface coal formations may release coalbed CH₄ [Caulton *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 CH₄ to total CH₄ emissions from oil and gas regionally and globally, as emissions of biogenic coalbed CH₄ will also decrease the effectiveness of other source apportionment techniques such as C₂H₆:CH₄. Additional sampling of CH₄ 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 CH₄ Sources

Our results indicate two possible conclusions. Previous studies of CH₄ emissions in the region may have underestimated the contribution of biogenic sources. Alternatively, thermogenic CH₄ 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 CH₄, particularly if those studies have used δ¹³C or hydrocarbon ratios to estimate thermogenic contributions. Additional studies utilizing δ²H to distinguish CH₄ sources are needed regionally and globally: if biogenic CH₄ emissions are underestimated [e.g., Nisbet *et al.*, 2016; Schaefer *et al.*, 2016], 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 CH₄ isotope analysis, we can now analyze many samples in a short period of time, which allows for a new look at δ¹³C and δ²H signatures of CH₄ sources as well as changing atmospheric CH₄ concentrations.

Acknowledgments

Funding for this project was supplied by the Colorado Department of Public Health and Environment, with additional resources from the NASA DISCOVER-AQ project. Isotope instrumentation was funded by the National Science Foundation (award 1229114). We would like to thank Gabrielle Pétron (NOAA) and Anne Thompson, Hannah Halliday, and Bianca Baier (Penn State) for their assistance with ground sampling. The manuscript was also improved thanks to the help of Steve Pelikan (UC) and the comments of two anonymous reviewers. All of the data in this paper are available to the public at <http://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html>. 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. The authors declare no conflict of interest.

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1 **Supplemental Information**

2
3 **Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric**
4 **methane sources: A case study from the Colorado Front Range**

5
6 Amy Townsend-Small^{1*}, E. Claire Botner¹, Kristine L. Jimenez¹, Jason R. Schroeder^{2,5}, Nicola J.
7 Blake², Simone Meinardi², Donald R. Blake², Barkley C. Sive³, Daniel M. Bon⁴, James H.
8 Crawford⁵, Gabriele Pfister⁶, and Frank M. Flocke⁶

9
10 ¹Department of Geology, University of Cincinnati, Cincinnati, Ohio

11 ²Department of Chemistry, University of California, Irvine California

12 ³United States National Park Service, Denver, Colorado

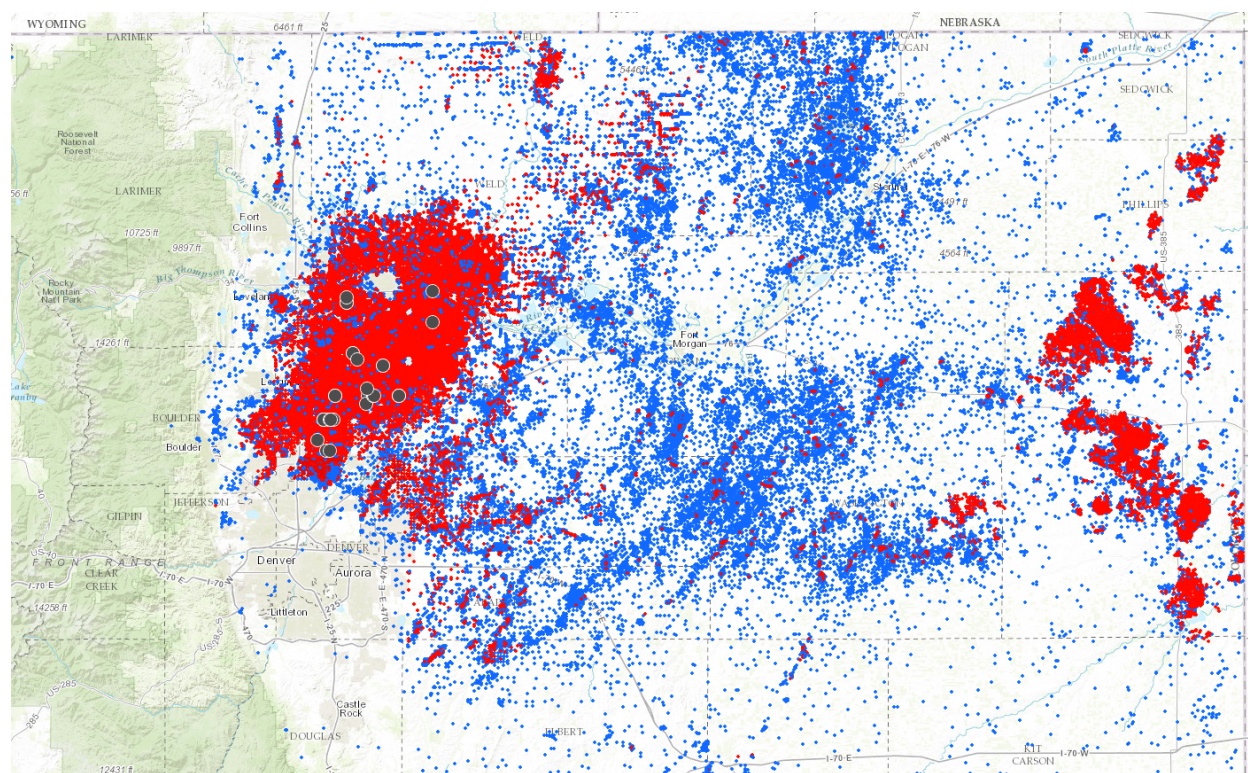
13 ⁴Colorado Department of Public Health and Environment, Denver, Colorado

14 ⁵NASA Langley Research Center, Hampton, Virginia

15 ⁶National Center for Atmospheric Research, Boulder, Colorado

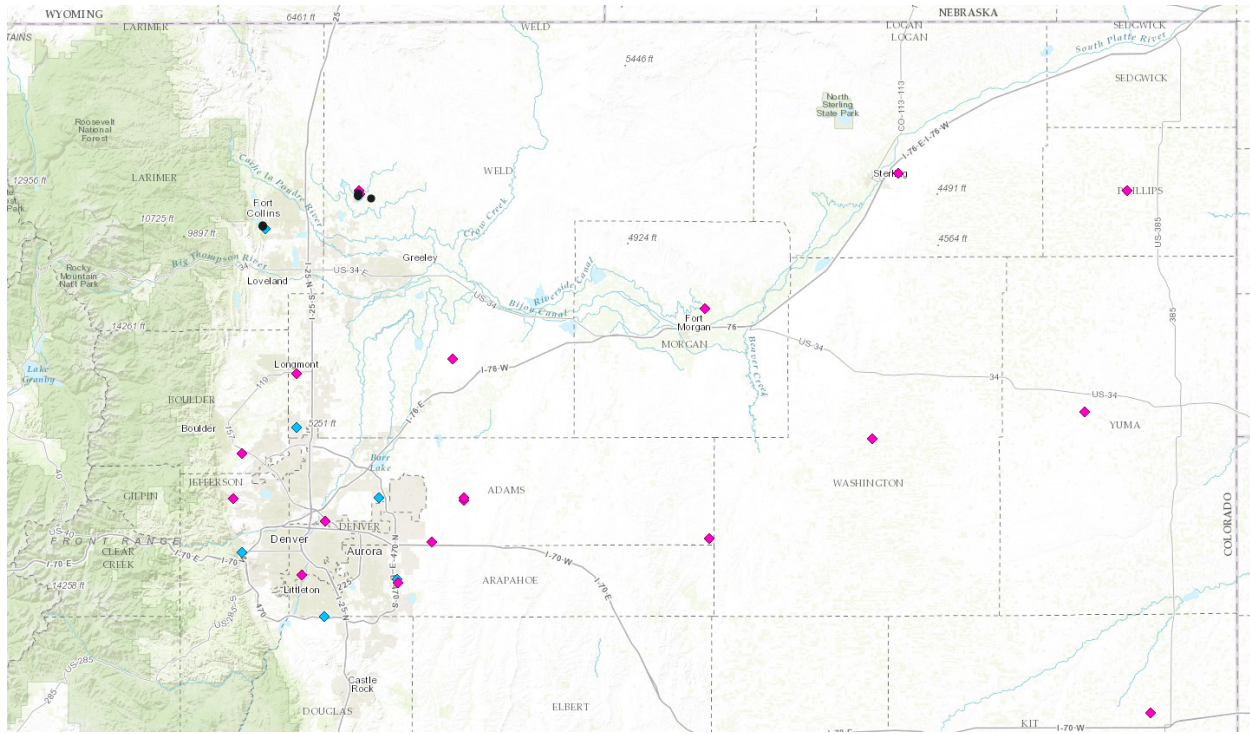
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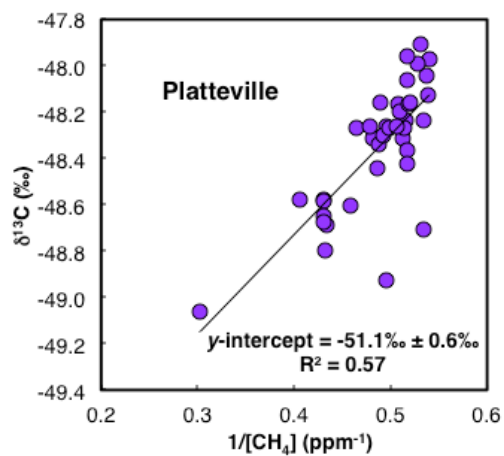
Figure S1A. Location of samples taken at oil and gas facilities (in black). Legend and scale are as in Figure 1.



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Figure S1B. Location of samples taken at landfills (in black). Legend and scale are as in Figure 1.

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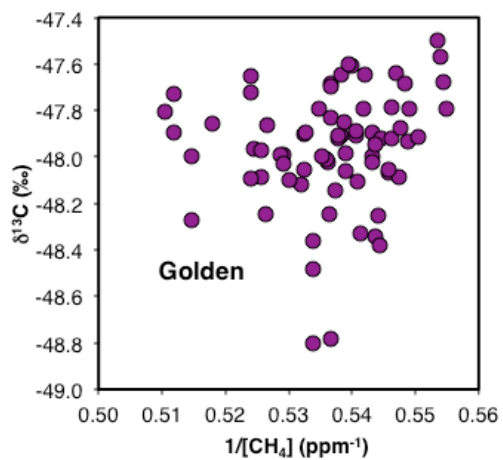
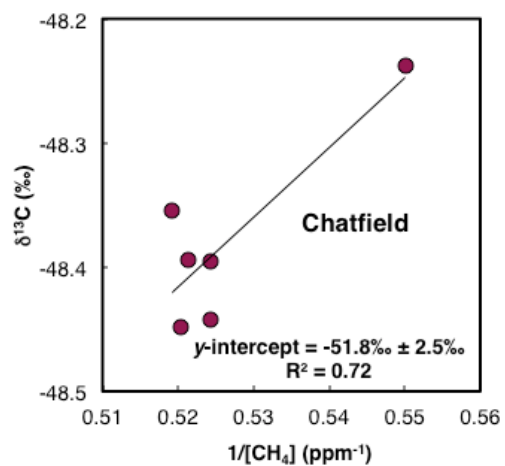
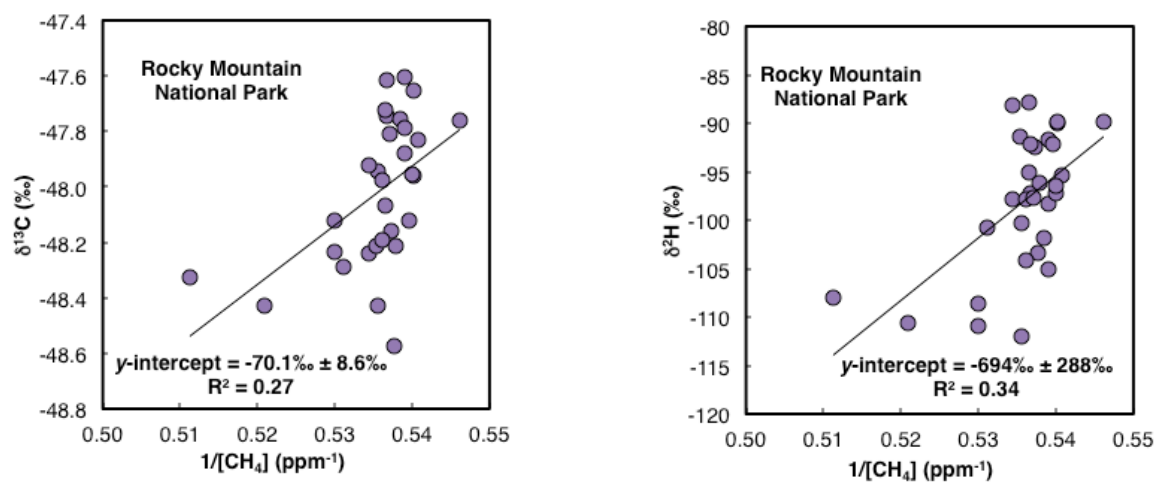


Figure S2 – $\delta^{13}\text{C}$ signatures of samples taken at Platteville, Golden, and Chatfield



44 **Figure S3 – $\delta^2\text{H}$ and $\delta^{13}\text{C}$ signatures of samples taken in Rocky Mountain National Park**

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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

Flight	Date	Approximate flight area (km ²)	$\delta^{13}\text{C}$ end-member (‰)	$\delta^2\text{H}$ endmember (‰) (\pm SE)	Notes on flight path
RF01	7/26/14	2.1×10^4	Not significant	Not significant	
RF02	7/27/14	1.6×10^4	Not significant	Not measured	
RF03	7/28/14	1.8×10^4	Not significant	-362 ± 101 (n = 24)	
RF04	7/29/14	4.0×10^4	Not significant	-465 ± 306 (n = 11)	includes south-central Wyoming
RF05	7/31/14	2.1×10^4	Not significant	-303 ± 71 (n = 10)	
RF06	8/2/14	2.1×10^4	Not significant	-362 ± 152 (n = 20)	
RF07	8/3/14	2.2×10^4	Not significant	Not significant	
RF08	8/6/14	5.1×10^4	Not measured	-245 ± 102 (n = 14)	includes Piceance basin, northwest Colorado and western Utah
RF09	8/7/14	1.9×10^4	Not measured	-305 ± 89 (n = 15)	includes western Nebraska
RF10	8/8/14	3.0×10^4	Not significant	-262 ± 81 (n = 8)	includes western Nebraska, south-central Colorado
RF11	8/11/14	2.0×10^4	-54.0 ± 2.3 (n = 15)	Not measured	
RF12	8/12/14	2.1×10^4	-51.8 ± 1.2 (n = 19)	Not measured	
RF13	8/15/14	9.4×10^4	Not measured	Not significant	includes northwest Colorado, southern Wyoming, western Kansas, and southwest Nebraska
RF14	8/16/14	3.3×10^4	Not significant	-421 ± 152 (n = 12)	
RF15	8/18/14	7.7×10^4	Not significant	-269 ± 38 (n = 18)	includes northwest Colorado

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