

Chemical tracers untangle natural from agricultural methane emissions

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COCCON (Collaborative Carbon Column Observing Network) network of column sensors to measure excess columns of methane (CH₄) during tests atop the NCAR Foothills Laboratory. Credit: Mahesh Kumar Sha/KIT/BIRA-IASB

With natural gas booming across the Front Range, drilling rigs may operate within feet from cattle farms. That shared land use can confound attempts to understand trends in methane, a greenhouse gas and air pollutant—the gases emitted from these different sources blend together.

To untangle them, a CIRES-led team has innovated a new, cost-effective technique to efficiently measure [methane](#) and a cocktail of associated chemicals in the atmosphere, and to create a kind of chemical identification tag for methane sources.

"Methane is an important [greenhouse gas](#). But it has a high global concentration so it can be challenging to see its specific sources," said Natalie Kille, CIRES Ph.D. student and lead author on the study published today in the AGU journal *Geophysical Research Letters*. "This technique allows us to remove the background methane concentrations in our analysis to clearly see unique chemical tracers."

"Tracers" are chemicals unique to a single source: ethane is a great tracer for oil and gas operations,

for example; and ammonia is a tracer for cattle farms, responsible for that unmistakable cow smell. Measuring levels of those two tracers helped the team disentangle sources of methane produced locally by both agriculture and oil and gas operations.

Using instruments that sit on the ground and measure the air above, they can instantly capture a snapshot of chemical concentrations for methane and its tracers in the column of air reaching from the surface all the way up to the top of the atmosphere. The team then uses this information to remove the methane background—a concept known as "excess column"—so that the tracers can take center stage.

"This was the first study to measure excess columns of all these molecules simultaneously," said Rainer Volkamer, CIRES Fellow, CU associate professor of chemistry, and corresponding author on the study. "This gives us a better handle to separate and quantify methane sources on a regional scale."

The team set up a network of these small instruments across Colorado's Front Range. Frank Hase and Thomas Blumenstock with the German Karlsruhe Institute of Technology developed a novel, portable spectrometer capable of highly precise methane measurements. And CIRES/CU Boulder provided Volkamer's University of Colorado "CU mobile Solar Occultation Flux" instrument that measured the chemical tracers ethane and ammonia. Both devices harness sunlight to identify each molecule by its light absorption fingerprint.



In Colorado, oil and gas operations sit within feet from cattle farms. Credit: Frank Flocke/NCAR

"These two instruments were set up side-by-side in Eaton, Colorado, within what we call the 'methane dome' of the Denver-Julesburg Basin," said Volkamer. "In the areas where [natural gas](#) and cattle farming sites are present, methane is emitted, and mixes together from both sources, forming a bubble inside the atmospheric boundary layer that expands and contracts as if its breathing."

To measure the background concentrations of methane, the team set up two additional KIT instruments (one operated by the National Center for Atmospheric Research) outside the methane dome, in Boulder and Westminster, each about 60 miles away from Eaton. These data helped Kille' calculate—and then remove—the background concentration of methane to isolate locally produced methane and those two key chemical tracers.

In previous work to untangle sources of methane, scientists have often collected flask samples of air, either from the ground or by aircraft, for detailed

analysis back in a laboratory. But some chemicals, including ammonia, can stick to the insides of some canisters, creating challenges.

In this work, the small and portable instruments could be deployed almost anywhere for real-time measurements of the open atmosphere. In Eaton, the team set up in the parking lot behind a bed and breakfast.

Based on data from five days' worth of measurements in 2015, the team found oil and natural gas operations were responsible for most of the methane produced in the Denver-Julesburg Basin, with agricultural sources providing an important but minor source.

The study also uncovered some baffling observations that will require further exploration: for example, when methane concentrations are very low, the agricultural sources are relatively more significant.

These results could help natural gas operators, cattle farmers, and their regulators make more informed decisions about methane mitigation.

In the future, the researchers hope to generate a long-term time series over multiple seasons to see how methane sources in the region change over time—a feat that becomes possible with low-cost, autonomous sensor networks like this. Scientists could also work towards comparing these data with those gathered from satellites, to develop best practices to inform satellite observations, said Volkamer.

More information: Natalie Kille et al. Separation of methane emissions from agricultural and natural gas sources in the Colorado Front Range, *Geophysical Research Letters* (2019). [DOI: 10.1029/2019GL082132](https://doi.org/10.1029/2019GL082132)

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