

# Scientists decipher source of methane in groundwater near oil and gas operations

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Scientists have invented a new technique to figure out whether methane present in groundwater comes from bacteria or from hydrocarbon reservoirs. Resolving the origin of methane could be helpful for scientists studying the presence of the greenhouse gas in water wells near natural gas drilling sites.

The technique involves using a mass spectrometer designed by scientists at the California Institute of Technology (Caltech), according to the study published yesterday in the journal *Science*.

Homeowners living close to oil and gas extraction have, in recent years, expressed concern that drilling for natural gas, which is primarily composed of methane, could be contaminating their water wells. Methane is a potent greenhouse gas, and scientists have found that it is leaking into the atmosphere and, in very rare cases, into groundwater supplies close to well pads.

In the latter case, the culprit could be faulty drilling processes, such as badly cemented well bores, that release methane directly into aquifers. Or, the methane could migrate through naturally occurring fractures and faults in the ground and reach the aquifers.

Methane can also be present due to bacteria in the aquifer that naturally produce the gas.

## Isotope clumping provides clues

So, given a sample of water and methane, it can be difficult to resolve which of these processes -- natural or man-made -- generated the methane. Some methods are already available to determine the source, but they rely on identifying concentrations of naturally occurring isotopes.

The isotopes are so rare that it makes the process challenging, said John Eilar, professor of geochemistry at Caltech and a co-author of the study.

The new method allows scientists to pinpoint the source of the particular methane more easily.

It is based on the idea that the methane contains within it an imprint of the temperature at which it was formed. Bacteria produce methane at temperatures below 80 degrees Celsius, while methane co-produced with oil forms below 150 C. Methane from kerogen is generated above 150 C.

At low temperatures, rare, heavy isotopes of methane tend to stick together to form a clumped molecule. At higher temperatures, the methane isotopes have enough energy to overcome their inertia and break away from the clump. Overall, the extent to which isotopes clump together reveals the temperature at which the gas formed.

## \$2 million price tag

A specially designed mass spectrometer was able to image these clumps and get an idea of the temperature when the gas first formed. Scientists could match these results with samples collected from various sources to reveal the origin of the methane.

"This is a really interesting application of isotope chemistry. If the result holds broadly, it should help us

identify the source of methane in many instances," said Rob Jackson, professor of earth sciences at Stanford University, who was unaffiliated with the study.

Jackson has been involved in various studies in Pennsylvania's gas-rich Marcellus Shale reservoir where he and his colleagues have tried to resolve methane in shallow drinking water wells within a kilometer of gas drilling sites. To do so, they used older methods, which suggested the methane had originated either in the Marcellus Shale or from the shallower Upper Devonian formation.

The new mass spectrometer could be used in such studies to resolve between the two origins. It could also reveal whether the gas in the Upper Devonian was originally from the Marcellus Shale and had migrated from the depths into the shallower formation over geologic time, said Fred Baldassare, a geoscientist with Echelon Applied Geoscience Consulting. Baldassare is employed by both the Pennsylvania Department of Environmental Protection and by industry for stray gas investigations.

Eilar said the research team has used the spectrometer to resolve gases in the Antrim Shale of Michigan and it has worked accurately.

"There are many cases where it is unclear whether methane in a sample of groundwater is the product of subsurface biological communities or has leaked from petroleum-forming systems," Eilar said in a statement. "Our results from the Antrim Shale indicate that this clumped isotope technique will be useful for distinguishing between these possible sources."

But the instrument will not be very useful for homeowners concerned about the gas in their groundwater given its hefty price tag of \$2 million. It was built specially for Caltech by Thermo Fisher Scientific.