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COMMENTARY

Slaying the methane minotaur

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Despite atmospheric methane's significance in driving climate change, the global methane budget is still poorly constrained (1–4). Neither sources nor sinks are accurately quantified, and the rapid year-on-year changes remain poorly understood (5). It is difficult to determine how much methane is from natural microbial sources, how much from human agriculture and waste, and how much from fossil fuel use and natural geological sources. Variations in the ratio of ^{13}C to ^{12}C (expressed as $\delta^{13}C_{CH4}$) and ^{2}H to ^{1}H (δD_{CH4}) in methane provide powerful insights into this problem, but wide uncertainties remain. Now Haghnegahdar et al. (6) demonstrate the potential value of methane's "clumped" isotopologues, such as $^{13}CH_3D$, $^{12}CH_2D_2$, etc. in distinguishing between microbial and fossil fuel sources, thereby placing better constraints on global and regional emissions.

Atmospheric methane is less than 2 parts per million of ambient air. Nearly 99% of that is $^{12}CH_4$. About 1% is $^{13}CH_4$, usually reported in $\delta^{13}C_{CH4}$ terms. A tiny amount contains deuterium, $^{12}CH_3D$, reported as δD_{CH4}. Even rarer in ambient air are the clumped isotopes: minute amounts of doubly substituted $^{13}CH_3D$, $^{12}CH_2D_2$, infinitesimal amounts of triply substituted $^{13}CH_2D_2$ and $^{12}CHD_3$, and "trillionths of millionths" of $^{13}CD_4$ (7, 8). To use clumped isotopes to track the sources and sinks of methane, the analytical demands are extreme. Large samples of ambient air and advanced (i.e., expensive) mass spectrometry facilities are needed. Despite these challenges, Haghnegahdar et al. (6) show clumped isotopologues have a great deal to offer when we try to enter the labyrinth of the methane budget.

Atmospheric Methane is like the ancient minotaur, dominantly human, partly natural, with more than a whiff of cow breath. Anthropogenic sources include gas, oil, and coal industry leaks and vents, landfills, biodigesters, and sewage, as well as a wide range of agricultural sources including the breath of

Table 1. Summary of observational pathways and needs to improve our understanding of the global methane budget, validate emissions inventories, and assess compliance with the Global Methane Pledge

Measurement parameter	Information delivered	Current measurement	Needs	Importance in reduction and mitigation efforts
Mole fraction	Methane burden and Greenhouse impact. Geographic spread of emissions and transport (15).	Global collaborative network of in situ monitoring stations led by NOAA. Few tropical stations.	More tropical stations, with more continuous measurement. Mid-troposphere measurement.	Measurement is essential to verify progress to Global Methane Pledge goals.
$\delta^{13}C_{CH4}$	Helps differentiate between biogenic, fossil fuel, and fire sources. Tests global and regional emission inventories for isotopic balance.	Local mobile measurement and regional sampling. Very thin global network of few stations, led by NOAA.	More mobile measurement to find and quantify local sources. More background sampling and source signatures.	Essential if sources are to be separately quantified.
$\delta^{2}H_{CH4}$	Potentially adds strong constraints to Bayesian inversion studies assessing changing emissions and sinks.	Minimal—few monitoring stations, few source signatures, especially for tropical (C4) wetlands.	More sampling stations, colocated with $\delta^{13}C_{CH4}$ network. Better source signatures.	Powerful and inexpensive way to improve budget studies and inventory verification.
Clumped isotopes	Potentially powerful help discriminating between sources, and improving sink quantification	Few laboratories capable of measuring clumped isotopes. Few source signature studies.	Needs a basic global monitoring network. Needs better knowledge of source signatures and sink impacts.	Potentially very useful for quantifying sources, tracking mitigation efforts, and verifying inventories.
Satellite observation	Observation and rough quantification of fossil fuel and wetland emissions during non-cloudy weather. Important in identifying gas industry and waste emissions (e.g., large landfills).	Increasingly useful in spotting poorly quantified or little-known large sources, especially where local regulatory control may be weak.	Better observation; better quantification. Ground-based Total Carbon Observing Network needs support, to validate satellite retrievals.	Essential, especially to monitor nations that have not joined or are not compliant with the Global Methane Pledge.

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farmed ruminants like cattle, sheep, and goats, animal manures, and in smoke from deliberate burning of crop waste, grassland, and forest. Although these anthropogenic emissions are still imprecisely known, international agreements such as the UN's Framework Convention on Climate Change (UNFCCC), Paris Agreement, and Global Methane Pledge (9) have driven development of detailed national emissions inventories.

"Natural" emissions, difficult to quantify accurately, mainly come from decaying organic matter in wetlands and other anaerobic settings, from natural ruminants, natural (lightning-lit) biomass fires, termites, permafrost, and geological sources. Many natural emissions may show strong feedbacks to climatic forcing (e.g., increases of precipitation and temperature), as well as responding to human interventions such as fertilizer run-off into wetlands (5). Methane's main sink is atmospheric oxidation by hydroxyl [OH], with some removal by atmospheric chlorine and methanotrophic soil bacteria, and loss to the stratosphere (1, 5, 10). Humans can have significant impact on sinks, through factors like air pollution (e.g., by CO or NO_x) that influence the atmosphere's oxidative capacity or land use changes.

> **Haghnegahdar et al. demonstrate the potential value of methane's "clumped" isotopologues, such as $^{13}CH_3D$, $^{12}CH_2D_2$, etc. in distinguishing between microbial and fossil fuel sources, thereby placing better constraints on global and regional emissions.**

"Bottom up" estimates of emissions are based on statistical data such as cattle populations, coal and gas production, and summative estimates from field studies of natural emissions from wetlands or biomass fires (1, 3). In contrast, "Top-down" studies (2–4) use models to estimate emissions at global, regional, and national scales, coupling prior estimates of emissions with geographically spread measurements of methane's mixing ratio and chemical transport models of methane destruction in the air. However, budget inversions remain ill-constrained. Some results are difficult to reconcile with measurements of the actual isotopic compositions and isotopic trends of methane present in air. The problem of solving the methane budget remains open, with very wide uncertainties, both in quantifying sources and in assessing sink impacts. Fresh threads of insight are needed into methane's labyrinth.

Each isotopologue of methane brings a different perspective to the quantification of the methane budget. The $\delta^{13}C_{CH4}$ isotopic constraints are now being used to constrain inversions (2, 11) and to discriminate between biogenic methane (e.g., wetlands, agriculture, and waste), and methane emitted from fossil fuel use and from fires. While δD_{CH4} measurements are more sparse, they also discriminate between sources. Moreover, because δD_{CH4} of biogenic methane depends both on the D/H ratio of rainwater (which varies with latitude) and on whether methanogenesis is hydrogenotrophic or acetoclastic (12–14), δD_{CH4} potentially carries information about latitudes of biogenic sources and about source processes (13, 14).

Table 1 summarises various ways to improve our understanding of global and regional methane budgets. Significant advances are likely in optical measurement of $\delta^{13}C_{CH4}$, helping rapid identification and quantification of local sources. National inventories need to be tested for consistency with the $\delta^{13}C_{CH4}$ of methane actually in the air: Isotopic verification of UNFCCC declarations is now becoming feasible. The use of δD_{CH4} to reduce uncertainties in global budgets is also possible by piggy-backing on existing $\delta^{13}C_{CH4}$ flask sampling from remote in situ sites. However methane budget inversions can only improve if there is better knowledge of source signatures for both $\delta^{13}C_{CH4}$ and δD_{CH4}, especially in the tropics. This will need measurement of methane collected in the free-moving air, not just in closed chambers or waters where active methanotrophy is in progress.

To make methane's clumped isotopes useful, the challenges are enormous: Few groups have budgets large enough to fund equipment nor can many teams routinely support long-term monitoring by collecting large air samples from remote locations. However, as Haghnegahdar et al and colleagues demonstrate (6–8, 12, 16, 17), clumped isotopes offer much promise in reducing uncertainties in budget analyses. Their data and model analyses show (6) that clumped isotopes can indeed successfully distinguish between emission scenarios based on different versions of the EDGAR (Emissions Database for Global Atmospheric Research) database (18), improving our understanding of the relative contributions of fossil fuel and microbial sources of methane.

Better measurement skills and improved regional and global budget determinations offer hope for accurate identification and quantification of anthropogenic methane emissions, essential if they are to be reduced. That is the aim of the Global Methane Pledge, which over 150 nations have signed (9). However, many nations with large emissions have not signed the pledge. Though cattle are central to South Asian and African culture (15), there are many other ways (19) to cut emissions without affecting food supply or economic growth, for example, covering landfills, mitigating manure and sewage emissions, removing methane from coal mine vents, and stopping crop waste burning in Africa and India, a source both of methane and widespread health-damaging pollution. The task is urgent (20).

Today, atmospheric methane is growing extremely rapidly (5, 10), with evidence for strongly increasing emissions from natural feedbacks to climate warming (2–5). Unless effective global action is urgently taken to reduce emissions, including by nations that have not signed the Global Methane Pledge, it is likely the Paris Agreement will fail (19). Fully knowing methane's sources and sinks is the essential proximate requirement if methane is to be controlled. The costs of much better understanding, including clumped isotope analysis, are small compared to the rewards of ameliorating climate change. "Trust, but verify" said Ronald Reagan. The Nuclear Test Ban Treaty and the Montreal Protocol prevailed because signatory nations committed to verification. To succeed, the Global Methane Pledge now needs that same strong national commitment to verification.

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