The Isotopic Fingerprint of Human-Emitted Methane

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Background, Purpose and Hypothesis:

There are two primary types of methane: biogenic and thermogenic. Biogenic methane is created by bacteria in an anaerobic (without oxygen) environment. Bacteria produce methane as a by-product when reducing organic materials. Thermogenic methane is produced by the decay of higher level hydrocarbons in the earth's crust at elevated temperatures.

Humans produce biogenic methane. The methane is produced in the colon when specialized bacteria utilize food residue. Humans produce 0.5-1.5 litres of gas per day! Only a small amount of this gas is actually methane.

The purpose of this project was to answer the question: "Does anybody know of data for ^{13}C compositions of methane from human emissions?" This question was posted on the internet by Dr. Dave Mattey (Geology Department, Royal Holloway College, London, England) who is collecting samples of CO_2 and methane isotopes in cave air. He was looking for explanations for "one or two anomalous data points", perhaps of human origin.

There are two stable carbon isotopes, ^{12}C and ^{13}C. Only one of approximately ninety-nine carbon molecules are ^{13}C molecules. An isotope ratio is the ratio of ^{13}C to ^{12}C compared to an international standard. The more negative the value is, the less ^{13}C it has. The isotope ratio varies depending on the source.

My hypothesis is that human-emitted methane can be distinguished from atmospheric methane because it is produced biogenically. Therefore, the use of isotope ratios will allow the methane to be "fingerprinted".

Variables:

Independent Variable: People to sample / types of samples

Dependent Variable: Isotope ratio

Controlled Variable: Collection method

Procedure:

1. Sample containers (bottles, vials) were labeled and evacuated using a vacuum pump.
2. Methane samples were collected: breath, regurgitated gas (burps) and colonic gas (farts). Breath and burp samples were collected in a syringe. Once collected, the sample was injected into an evacuated container. Colonic methane samples were first collected using an evacuated bottle. A second method involved collecting the methane in a bag and transferring it to an evacuated bottle.
3. Samples were analyzed at the University of Waterloo by gas chromatography and isotope ratio mass spectrometry.
4. Data was analyzed, graphed and prepared for presentation.

Results and Discussion:

In order to measure the isotopes, a 0.5 ml sample with at least 1000 ppm methane was needed. All breath samples were close to atmospheric concentration (Figure 1). These samples could not be measured with the equipment available. Given my results, it is currently impossible to tell the difference between breath samples and the atmosphere so it is very unlikely that Dr. Mattey's samples were contaminated by someone's breath. All regurgitated methane (burp) samples were slightly higher than atmospheric concentration (Figure 2), but the concentrations were still too low to allow measurement of an isotope ratio. So regurgitated methane would also unlikely be a contaminant of Dr. Mattey's samples.

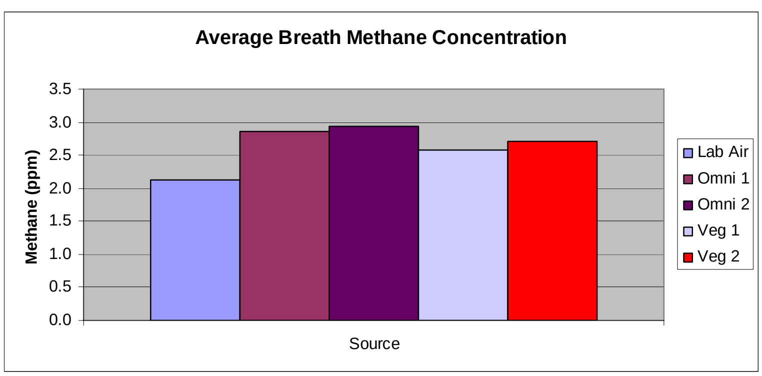

Figure 1: Average Breath Methane Concentration

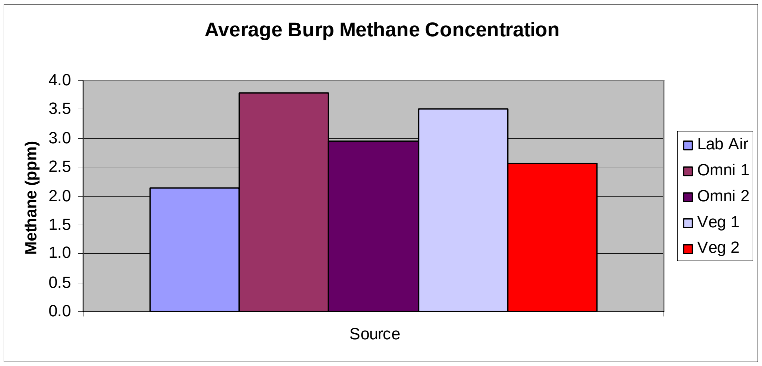

Figure 2: Average Burp Methane Concentration

Almost all colonic methane samples (farts) were below 30ppm (Figure 3 and 4); however, several vegetarian samples had extremely high concentrations (Figure 4).

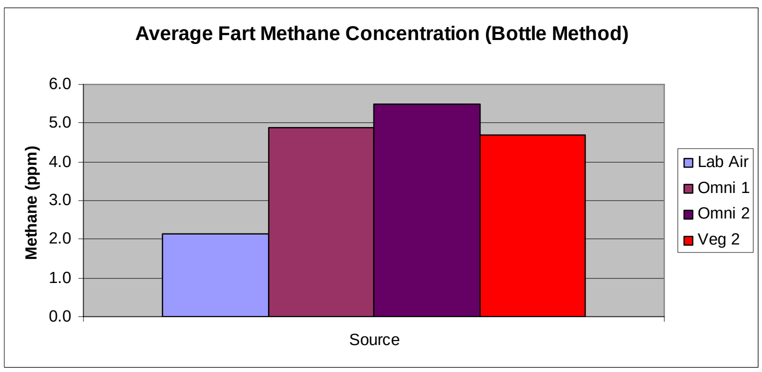

Figure 3: Average Fart Methane Concentration (Bottle Method)

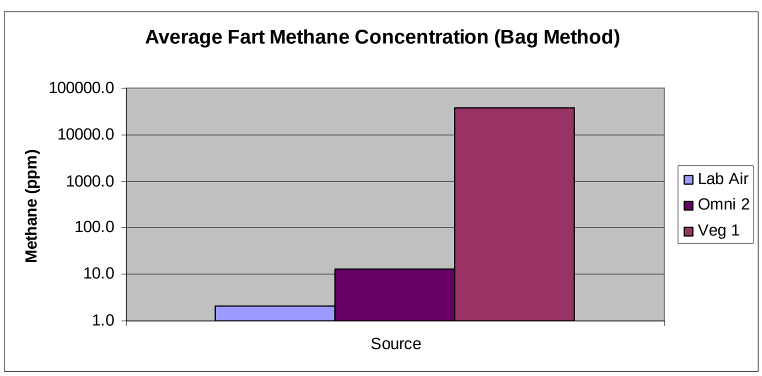

Figure 4: Average Fart Methane Concentration (Bag Method)

The concentration of the vegetarian colonic gas samples shows that they could be a source of contamination. Figure 4 shows that the bag method was possibly better than the bottle method. This is because the bag allows collection of more gas before it is dispersed in the air.

The data also suggests that vegetarians produce more methane than omnivores. This is probably true because they eat more fruits and vegetables such as beans, broccoli, cabbage, brussels sprouts, artichokes, asparagus, pears, apples, and peaches that produce gas. Many of these foods are a good source of carbon for the specialized bacteria that produce methane in the colon.

The samples that had a high enough methane concentration to measure isotopes were all emitted by a vegetarian. As expected the results fall in the biogenic range with $\delta^{13}C$ values ranging between -66.7 and -72.9 ‰ (Figure 5).

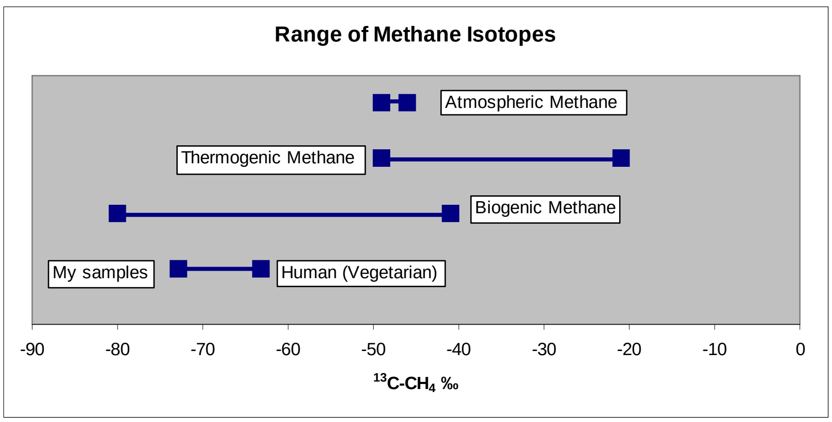

Figure 5: Sources of Methane and Isotope Values

Conclusion:

Dr. Mattey measured $\delta^{13}C$ methane as light as -53 ‰ in the caves he is studying. Cave air methane should be heavier (more positive) than background atmosphere (-49 to -45 ‰) because of microbial oxidation. Microbes "eat" away at the lighter carbon, making the isotope ratio less negative. The isotope data from this study shows that it would be possible for human flatulence to contaminate samples during collection.

I have provided Dr. Mattey with data to help answer his question. He has actually changed the way he collects samples to make sure there is no chance of human contamination.

More importantly, the analysis of methane isotopes provides us with information about changes in the atmosphere and about sources of methane. This is important because methane is an extremely effective green-house gas. Methane concentration and isotope data allows us to better understand the past climate and potential changes in the future.

Future possibilities for the current research include collecting a larger number of samples from a larger test group. To better test the effects of diet it would be necessary to control or record the diets of all the subjects. The methane signature will be affected by the amount of C3 or C4 plant material in the diet. It would be interesting to test because C3 plants (rice, wheat, soybeans, potatoes) would produce methane with less ^{13}C or more negative isotope ratios. C4 plants (corn, or corn-fed beef) would result in methane with more ^{13}C or more positive isotope ratios.

In order to collect highly concentrated samples, that can be easily analyzed, all samples should be collected using the bag method. Lower concentration samples could also be measured using an isotope ratio mass spectrometer that allows you to concentrate the sample.

Acknowledgments:

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APPENDIX A

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