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Examples of the fluid-escape features related to lower water levels in the Lake Powell near Hite, Utah. The mud volcanoes range from being extensive (left, with 1.7-m-tall individual) to relatively small in size, such as the bubbling volcano on the right (frog is approximately 5 cm).

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Methane Emissions from Muds During Low Water-Level Stages of Lake Powell, Southern Utah, USA

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ABSTRACT

The Glen Canyon Dam, along the Colorado River in Page, Arizona, was completed in 1963, creating the Lake Powell reservoir which spans the Arizona-Utah border. The water levels of Lake Powell peaked in 1983 and have declined since, releasing overlying pressure on the underlying sediment. In general, water levels experience seasonal highs and lows, with punctuated periods of considerable and steady decreases (1987 to 1993, 1999 to 2005, and 2011 to 2014) and less dramatic recoveries (1993 to 1999 and 2005 to 2011). This release of overpressure coupled with increasing pore pressures due to biological methane production has created mud volcanoes, structures along the shoreline made of cavities that allow fluid and gas to rise to the surface and escape. Although these sedimentary structures have been assessed using geophysical techniques and excavation to characterize their morphologies and fracture propagation, limited chemical data has been reported on the inputs and products of these gas- and fluid-escape features.

This research investigates the relative proportions of methane (CH₄), carbon dioxide (CO₂), and air (unseparated nitrogen [N₂] and oxygen [O₂]) gas released, the variability of these proportions through time, and how these gases formed in the subsurface. The field site is along the Lake Powell near Hite, Utah.

Three gas samples were collected from mud volcanoes along the delta in July 2014, whereas 21 samples were collected in July 2015 and were analyzed via gas chromatography (GC). The GC analyses from 2014 and 2015 have a mean CH₄ concentration of 81.47 ± 9.29 percent of volume (% v/v) and 32.40 ± 15.31% v/v, respectively. In May 2016, 50 samples from 25 vents were collected and analyzed via GC for bulk composition, and 11 of which were analyzed by isotope ratio mass spectrometry (IRMS) for carbon and hydrogen isotope content of CH₄. The 2016 GC analysis detected average relative concentrations for CH₄, CO₂, and air of 74.51 ± 14.08% v/v, 2.82 ± 3.76% v/v, and 22.67 ± 14.28% v/v, respectively. Gas compositions from individual vents varied over the three-day sampling timeframe in the summer of 2016 including CH₄ decreases of up to 66% v/v and increases of up to 38% v/v. IRMS signatures of samples collected in 2016 indicate the gasses are in part generated during microbial respiration through hydrogenotrophic and acetoclastic methane production.

Citation for this article.
INTRODUCTION

Methane Generation in Lacustrine Settings

Mud volcanoes, pockmarks, water-filled craters (salses), and sedimentary deformation features in lacustrine settings can serve as natural gas seeps and can provide insight on mechanisms behind hydrocarbon and greenhouse gas generation and expulsion (Dlugokencky and others, 1995; Judd, 2005; Forster and others, 2007; Etiope and others, 2009; Bussmann and others, 2011). For example, up to 40 to 60 million tons (40–60 teragrams) of methane (CH\textsubscript{4}) are released annually via geological sources including mud volcanoes (Etiope, 2004), and 70 L/min of CH\textsubscript{4} has been estimated to vent from the Dashgil mud volcano along the coast of Azerbaijan alone (Kopf and others, 2010). More specifically, terrestrial and marine mud volcanoes are recognized as significant sources of CH\textsubscript{4} that may be of either biogenic, thermogenic, or a combination of both origins (Hovland and others, 1997; Tinivella and Giustiniani, 2012). One primary source of CH\textsubscript{4} is the respiration of microorganisms such as those prevalent in lacustrine settings, wetlands, rice paddies, and landfills among other natural and anthropogenic sources (Chanton and others, 2005). Large reservoir systems created by dams are also sites of significant biogenic CH\textsubscript{4} production and decreasing overlying pressure from the lowering water table (Netoff and others, 2010; Livingston and others, 2014, 2015; Sherrod and others, 2016; Miller and others, 2018). These studies identify algal blooms and the organic-rich clays as substrates to sustain methanogens (CH\textsubscript{4}-producing microorganisms). For example, the organic-rich clay layer described in Miller and others (2018) contained mm thick zones of fine, macerated plant materials and stem fragments decomposed, in part by microorganisms. This layer underlies heterolithic layers containing gas-filled cavities and ranges in depths from 0 to 6 m due to fluid migration and subsequent sediment mobilization.

These prior studies have discussed the origins and evolution of the Lake Powell gas seeps from primarily physical observations. For the first time, here we document the chemical signature of these gases through relative hydrocarbon compositions, then relate isotopic composition to the biogenic mechanisms for methanogenesis, and finally consider potential biological, hydrological, and chemical controls on CH\textsubscript{4} production in discussing future field measurements.

Geologic Setting of the Lake Powell Delta

Lake Powell is a reservoir located on the Utah-Arizona border and results from the 1963 completion of the Glen Canyon Dam near Page, Arizona (figure 1). Water levels experience seasonal highs and lows, with punctuated periods of considerable and steady decreases (1987 to 1993, 1999 to 2005, and 2011 to 2014) and less dramatic recoveries (1993 to 1999 and 2005 to 2011) (figure 2; U.S. Bureau of Reclamation, 2017). Such drastic water level fluctuations trigger undercutting erosion of canyon walls, subaqueous gravity flows, and up to one-hundred-fold increases in sediment accumulation (Pratson and others, 2008; Anderson and others, 2010). Over the three-year sampling period presented here (July 2014, July 2015, and May 2016), water levels were approximately 1100 m above sea level in 2014 and 2015, and 1097 m high during the 2016 period (figure 2). Overall, the reservoir has been gradually decreasing since the 1127 m full pool high in 1983.

Lake Powell, in the study area, is underlain by the Cedar Mesa Sandstone, a confined aquifer sealed by Lake Powell muds. The uppermost 2 m of the delta consists of clays, silts, and fine sands (Willis, 2012). Notable soft-sediment deformation, gas- and fluid-escape features including domes, pockmarks, craters, salses, sediment-filled craters, mud and sand volcanoes, dike systems, and sub-centimeter gas bubble cavities are recognized at Hite (Netoff and others, 2010; Livingston and others, 2014, 2015; Sherrod and others, 2016; Miller and others, 2018). These soft-sediment deformation
structures (SSDS) are non-seismic in origin as the region has only experienced two earthquakes since 1850, both under 3.5 magnitude, and are well below the 5.5 magnitude threshold for liquefaction and fluidization (Allen, 1986; Obermeier, 1996; Galli, 2000; Anderson and others, 2010; University of Utah Seismograph Stations, 2020). Decreasing overlying water pressure and increasing underlying pore water and gas pressures are the primary triggers for the Lake Powell SSDS (Netoff and others, 2010; Livingston and others, 2014, 2015; Sherrod and others, 2016; Miller and others, 2018).

These prior studies have attributed \( \text{CH}_4 \) production to decaying organic matter in the subsurface and from algal blooms. In particular, macerated plant material in a mm-thick clay-rich, laterally extensive layer has been identified and is a likely source of organics on which methanogens can feed (Sherrod and others, 2016; Miller and others, 2018).

**Methanogenic Pathways**

Lacustrine greenhouse gases can be produced through various mechanisms. The following processes,
hydrogenotrophic production and acetoclastic production, are the focus of this study as they are most relevant to the Lake Powell delta system. These two mechanisms are mediated by the amount of substrates and hydrogen available to the methanogens as well as the amount of sulfate-reducing bacteria present. In this study, we use the ratios of carbon (\(^{12}\text{C}\) versus \(^{13}\text{C}\)) and hydrogen (\(^{1}\text{H}\) versus \(^{2}\text{H}\)—also known as deuterium, D) measured in mud volcano CH\(_{4}\) to interpret the methanogenic processes responsible for the gas ebullition. Further details regarding the isotopic characterization can be found in appendix A, but provided here are general descriptions of methanogenic and thermogenic processes sourced from Whiticar and others (1986) and Whiticar (1999).

The first process described here, hydrogenotrophic production, is characterized by the following reaction:

\[
\text{CO}_2 + 8 \text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\]

It is the most predominant process of biogenic gas production and the main source of CH\(_{4}\) in marine/saline settings. However, it may occur in freshwater settings when acetate sources are exhausted, and methanogens require a new substrate. Hydrogenotrophic production is often the secondary means of microbial CH\(_{4}\) generation in freshwater environments, but will predominate when acetate pools, such as those necessary for certain acetoclastic formation, are exhausted. At this point, the microorganisms switch to reducing the bicarbonate with hydrogen.

The second process described is acetoclastic production. Upon the breakdown of organic matter, acetate (CH\(_3\text{COOH}\)) is generated and subsequently converted to CH\(_{4}\) in the respiration processes of microorganisms (Whiticar and others, 1986):

\[
\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2
\]

This is the dominant means of biogenic gas production in freshwater environments (Whiticar and others, 1986). The carbon dioxide (CO\(_2\)) produced through this fermentation can subsequently serve as a reactant in hydrogenotrophic production (above) when the acetate source is depleted (Whiticar, 1999). Sulfate-reducing bacteria will (chemically) reduce the acetate otherwise used in fermentation with a greater energy yield, and therefore can limit the amount of fermentation and subsequently the amount of hydrogenotrophic production. In sulfate-rich marine settings, sulfate-reducing bacteria out-compete methanogens for acetate, mitigating acetate fermentation (Chanton and others, 2005). Therefore, acetate fermentation tends to be more characteristic of the freshwater rhizosphere than marine.

Finally, thermogenic CH\(_{4}\) occurs when organic matter is broken down by elevated temperatures (> 100°C) and pressures. Although Lake Powell is located within the Kaiparowits Basin, which has been assessed to contain gas (National Assessment of Oil and Gas, 2012), we will...
discuss why this is an unlikely mechanism for gas generation along the delta.

**MATERIALS AND METHODS**

**Gas Collection**

Samples were collected during the field seasons of July 2014 and 2015, and in May 2016. The 2014 and 2015 samples were collected during lake level highs for each season (between 1100 and 1102 m above sea level) whereas the 2016 samples were collected during lake level lows (about 1095 m above sea level, figure 2). The majority of samples reported here were collected in 2016 from 25 vents (figure 3). Fifty of the samples collected in 2016 were analyzed via gas chromatography (GC) for bulk composition, and 11 samples with elevated percent volumes of CH₄ were selected for isotope ratio mass spectrometry (IRMS) of carbon and hydrogen isotope content of the CH₄.

Gas samples were collected by filling a 20-mL headspace vial (Restek) with liquid from within a mud volcano or the Colorado River (depending on the sampling site) then inverted for sampling. A small plastic funnel was immersed in the sampling site with the stem inserted into the mouth of the headspace vial. Gas bubbles were directed into the headspace vial using the funnel until the vial was approximately 4/5 full of gas (1/5 lake water). The vial was capped under water with a PTFE/Silicone septum lined cap (Restek), sealed with Parafilm and maintained in an upside-down position until analysis with the 1/5 water content preventing gas escape. At least 20 volcanoes were sampled once on a single day, whereas three volcanoes were sampled over a two-day period, and six volcanoes were sampled over a three-day period. Samples for the 2016 season were refrigerated until September, when chromatography tests were completed. Remaining gas from the 2016 season continued to be refrigerated until April of 2017 when isotopic analyses were completed. The authors did not conduct tests to determine whether biological activity altered relative gas compositions during storage.

**Gas Chromatography**

Gas standards and samples collected in 2014 and 2015 were analyzed using a Hewlett-Packard 5890 gas chromatograph equipped with a packed, 2.4-m-long by 0.3 cm (8-ft-long by 1/8 in) O.D., 80/100 mesh Poropak Q column and a thermal conductivity detector. Gas mixtures were prepared in 20-mL headspace vials over water to mimic the conditions of the samples. A gas-tight syringe was used to transfer aliquots of gas to water-filled, inverted 20-mL headspace vials leaving 4 mL of water remaining in the vials. Vials were capped underwater and remained upside-down until analysis.

Gas standards and samples from 2016 were analyzed using an Agilent 7890 gas chromatograph equipped with G1888 automated headspace sampler (Agilent Technologies). A 200°C injector operating at a 20:1 split ratio was connected to a 30 mm by 0.53 mm Carboxen 1006 PLOT column (Supelco) to separate the gas components. Thermal conductivity and flame ionization detectors were used in series to quantify and confirm chromatographic peak identities (see appendix B for headspace sampler and chromatograph operating conditions).

**Isotope Ratio Mass Spectrometry**

Isotopic compositions of carbon and hydrogen in CH₄ can be used to identify the processes behind the CH₄ generation (Whiticar and others, 1986). Details on the theory behind carbon to hydrogen isotopic ratios can be found in appendix A. Eleven samples from 2016 were favorably selected for IRMS analyses if they had relatively higher quantities of CH₄ (as detected with the gas chromatography) and if the samples were in a set of multiples taken from the same volcano (appendix C). For IRMS, samples were separated and analyzed using an Agilent GC combustion unit (either HP 6890 or HP 6890/7890 gas chromatography) joined with a mass spectrometer (either to ThermoFinnigan Delta Plus Advantage or Thermo Scientific Delta V Plus) in continuous flow mode. Peak detection and quantification were completed in Finnigan’s Isodat software. Hydrocarbon components were isolated in the GC unit and were introduced into a combustion furnace to produce CO₂ which was sent to the mass spectrometer for isotopic analyses of ¹³C. Liquid nitrogen was used to remove air and enrich concentrations of hydrocarbons. For the
deuterium analysis, gas was channeled through a pyrolysis furnace to permute CH$_4$ to H$_2$ and carbon, upon which the H$_2$ entered the mass spectrometer. Each sequence began with reference gases, and 10% of the analyses were check standards.

**ANALYTICAL RESULTS**

**Gas Chromatography**

All GC values are noted in percent of volume of specific gas to total sample volume when denoted with “v/v” unless otherwise specified. The average percent volume of CH$_4$ for each of the three years, 2014, 2015, and 2016, is 81.47% v/v with a ± 9.29% v/v standard deviation, 32.40 ± 15.31% v/v, and 74.51 ± 14.08% v/v, respectively (figure 4, tables C1 to C3 in appendix C). The average CH$_4$ composition of the 50 gas samples collected in 2016 is approximately 7% v/v lower than the average concentration of CH$_4$ in gas samples previously collected from the marina during the 2014 field season (Livingston and others, 2014) and is about 42%

![Field photographs during May 2016. (a) Salse near the edge of Lake Powell with high effusive rates disrupting the water surface. Individual is 1.7 m tall. (b) Mud volcano with gas effusion. The individual is 1.7 m tall. (c) Salse with slow effusing gas emission. The card (bottom left) is 15 cm long. (d) Field scientist (1.75 m tall in prone position) sampling a salse. Note the shore of the Lake Powell in the background.]
v/v greater than the average CH$_4$ collected in 2015.

Although sample sizes (n) vary from year to year, the following data sets convey the variation in gas content between samples between and from the same field seasons. For example, although at 81.47% v/v, the 2014 sampling year had the greatest CH$_4$ on average, the 2016 sampling year includes CH$_4$ compositions ranging from 25.31% v/v to 93.34% v/v. Overall, the 2015 sampling year had the least amount of CH$_4$ on average, and also yielded the lowest minimum and maximum concentrations of CH$_4$ (0.00% v/v minimum and 45.50% v/v maximum). For each sampling year, of the three gases tested, CO$_2$ yields the lowest percent content on average, and for each year, when compared to CH$_4$ and air (unseparated nitrogen [N$_2$] and oxygen [O$_2$]), CO$_2$ also yields the lowest minimum and maximum percent content (tables C2 and C3 in appendix C; figure 4).

Of the 2016 data, chromatographic analyses yielded an average concentration of 74.51 ± 14.08% v/v CH$_4$, 2.82 ± 3.76% v/v CO$_2$, and 22.67 ± 14.28% v/v air (tables C1 and C3 in appendix C). The CH$_4$, CO$_2$, and air concentrations ranged from 25.31 to 93.34% v/v, 0.00 to 23.58% v/v, and 5.28 to 74.69% v/v, respectively.

Four volcanoes (16-1, 16-3, 16-5, 16-10) were sampled over the course of two days, whereas six volcanoes (16-7, 16-12, 16-17, 16-20, 16-25, 16-27) were sampled over a three-day timespan (figure 5). For the following fluctuation calculations, duplicates taken from the same volcano in the same day were averaged to a single measurement for that day (tables C3 and C4 in appendix C; figure 5). For example, all four CH$_4$ measurements collected at volcano 16-20 on the third day (samples 16-20C1 to 16-20C3, and 16-20C5) were averaged to represent a single measurement at volcano 16-20 on day three. Daily fluctuations were calculated using the averaged measurements. In 2016, there was a mean increase of 6.08% v/v in CH$_4$ from the first to second day and a 24.68% v/v decrease from the second to third day while the CO$_2$ content showed a 0.89% v/v increase between the first two days of sampling and a 0.5% v/v decrease from the second to third day. The average variation from day to day was a 5.46% v/v decrease in CH$_4$ and a 0.37% v/v increase in CO$_2$ (table C4 in appendix C).

Geographically, there is a cluster of eight volcanoes, a single volcano to the north (16-1), and a single volcano to the south (16-10). Changes in relative CH$_4$ concentration range from extremely low variation of only 2% v/v increases (volcano 16-17), to great variations of up to 38% v/v increases (volcano 16-5) and 66% v/v decreases (volcano 16-7) across multiple days. Several volcanoes within the southern end of the cluster (volcanoes 16-3, 16-5, 16-7, 16-20, 16-27) exhibited increases...
in CH₄ from day one to day two while 16-12 and 16-7 had steady CH₄ fluxes, and only 16-25 observed a decrease. Two volcanoes, 16-7 and 16-12, are proximal to one another and both exhibited decreases in CH₄ from 80% v/v or more down to less than 40% v/v between the second and third day. Volcano 16-20 also shows a decrease from day two to three, but not as severe (about a 35% v/v fall). Vent 16-10 to the south exhibits a slight increase from day one to day two while vent 16-1 in the north shows the opposite trend.

**Isotope Ratio Mass Spectrometry**

All IRMS results are detailed in table D1 in appendix D. When plotted on a carbon-deuterium (CD) CH₄ source discrimination diagram (figure 6; Whiticar, 1999), δ¹³C and δD CH₄ signatures of all but two samples lie within the ranges characteristic of bacterially produced CH₄ (regions 1 and 2 in figure 6) (>-100 to about -45 δ¹³C‰ PDB, and about -400 to -150 δ¹⁵D‰ SMOW). This excludes the possibilities of geothermal or hydrothermal (region 5), abiogenic or mantle (region 6), or artificial (region 7), production of these gases.

**DISCUSSION**

**Gas Chromatography Compositions**

Flux measurements are commonly used to assess CH₄ and CO₂ emissions with production mechanisms. Although gas fluxes were not collected from the Lake Powell gas seeps, relative magnitudes of CH₄, CO₂, and air should be considered during future flux measurements from vents along the delta near Hite. For this study, temporal changes in relative lacustrine CH₄ content are discussed across a short-term (within a three-day time frame) and long-term period (beyond a three-day time frame) below. Sampling of the following would be useful in understanding controls on temporal correlations with methanogenesis in the Lake Powell delta: (1) seasonal flux sampling throughout the year and over a longer period of time, (2) soil and water temperatures, (3) soil and root redox potentials, and (4) identification
Figure 6. δ¹³C versus δD diagram used for classification of natural gas (adapted from Whiticar, 1999). Higher values of δ¹³C and δD will plot closer to zero than lower values. The isotopic signatures follow more closely the oxidation trend as emphasized with the single-headed arrow and the region outlined with a dashed border.

1) Bacterial: Hydrogenotrophic (Carbonate Reduction)
2) Bacterial: Acetoclastic (Methyl Type Fermentation)
3) Bacterial: Mixed
4) Thermogenic
5) Geothermal or Hydrothermal Crystalline
6) Abiogenic or Mantle
7) Artificial

Samples reported in this study
Shift due to substrate depletion
Predicted methane oxidation shift as applied to IRMS samples
and quantification of vegetation and organic sources among the sampled vents.

**Short-Term Changes in Relative Methane Content**

Short-term, specifically diurnal fluxes in CH$_4$ ebullition have been attributed to acute water depth fluctuations and water circulation, soil redox potentials, and vegetation. These variables are explored in context of the ten mud volcanoes sampled for relative CH$_4$ content over multiple days in 2016.

In the instance of water depth fluctuation, Sebacher and others (1986) found an increase in methanogenic CH$_4$ fluxes of about 300 mg m$^{-2}$ d$^{-1}$ with increasing water depth of about 45 cm in Alaskan bogs, fens, and marshes. Among other variables including water temperature and permafrost depth, water level held the strongest correlation to fluxes in their study. Moore and Roulet (1993) synthesized aerobic and anaerobic peat columns in the laboratory using bog, fen, and swamp soils. They observed that CH$_4$ fluxes increased with initially falling water levels (0 to 20 cm depth) and then a decrease in fluxes upon further falling water levels (20 to 50 cm depth). The authors concluded that there is a strong but complex relationship between water table fluctuations and CH$_4$ outgassing.

Similarly to Moore and Roulet (1993), if there is a relationship between the Lake Powell delta water table level and relative CH$_4$ content variations from day to day, then it may be complex and vary to some degree from volcano to volcano. During the most recent sampling period (2016), water levels increased daily between 17 and 19 cm (U.S. Bureau of Reclamation, 2017). Yet upon steady water level increase, relative CH$_4$ content experienced an average 6.08% v/v increase from sampling day one to day two, and on average a 24.68% v/v decrease from day two to three (table C4 in appendix C). Variations in water levels could impact certain gas fluxes in volcanoes more than others. Changes in water levels will impact a greater volume of pores in spatially larger volcanoes and impart a more extensive impact on gas fluxes. Additionally, volcanoes that experience more extreme or frequent episodes of wetting and drying may exhibit different patterns of gas production. Therefore in order to better understand how water levels are affecting day-to-day CH$_4$ release from volcanoes along Lake Powell, it would be beneficial to measure not only the CH$_4$ flux, but also overall water levels and water levels local to each gas seep.

Water circulation has also been shown to impact short-term CH$_4$ production in settings similar to the Lake Powell delta. Effects of water circulation were observed when Podgrajsek and others (2014) found that the greatest CH$_4$ generation of a freshwater lake (38 km$^2$ area and 1.3 average depth) occurred in the morning (average of about 10 nmol m$^{-2}$s$^{-1}$ and outliers of over 100 nmol m$^{-2}$s$^{-1}$) and lowest in the evenings (average of about 5 nmol m$^{-2}$s$^{-1}$ and outliers of less than 30 nmol m$^{-2}$s$^{-1}$). They consider that water-side convection is one mechanism of transporting CH$_4$ from various depths in the water column to the surface. In measuring convection, they installed a 6-m-high monitoring tower, which may not be feasible along the clay and mud-rich Lake Powell delta. To investigate the impact of water circulation on short-term changes in relative CH$_4$ concentrations, an alternative approach to measuring water circulation measurements might be necessary.

Duan and others (2005) found pronounced variations in CH$_4$ ebullition fluxes correlated with the predominant vegetation (*Phragmites australis* and *Potamogeton pectinatus*) but no direct correlation with mean water level (about 46 cm depth versus about 83 cm depth) in Wuliangsu Lake of Inner Mongolia. However, they noted that water level will determine the type of vegetation which thrives and indirectly CH$_4$ generation as well. Their study also showed that increased diurnal CH$_4$ fluxes were correlated with increasing photosynthetically active radiation (PAR) in reeds and more so than in pondweeds. Coupling PAR measurements with surrounding vegetation and daily flux measurements of the Lake Powell volcanoes would be useful in understanding the effects of low versus high photosynthetic activity along the delta on CH$_4$ generation.

Prior studies show that redox potentials of plant roots and soils have also been correlated with daily changes in CH$_4$ production. Chen and others (2010) found CH$_4$ fluxes in a ponded system of up to 15 mg CH$_4$ m$^{-2}$ hr$^{-1}$ with flux increases of about 10 mg CH$_4$ m$^{-2}$ hr$^{-1}$ in a six-hour period. These diurnal variations were significantly correlated with paralleled soil redox
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Flux and redox potential measurements at each volcano could also be useful in determining to what extent these influence short term CH₄ generation.

Long-Term Fluctuations in Methane Content from 2014 to 2016

The influencing factors on long-term changes in methanogenic production discussed here are temperature and precipitation as previous studies show these factors vary between seasons and impact methanogenesis in similar freshwater systems. For example, Pugh and others (2018) showed that average monthly CH₄ fluxes were strongly correlated with air temperatures. In their study, CH₄ fluxes increased from near-zero fluxes in winter and up to 39 mg C m⁻² day⁻¹ in summer months. Schulz and Conrad (1996) demonstrated that after including a chloroform inhibitor, a temperature increase of 16°C resulted in ten times more methanogenesis over a six-day-long incubation period. With a 25 to 32 day incubation and a sampling time frame of less than two weeks, Schulz and others (1997) showed that CH₄ production rates peaked around 35°C (in a comparison to temperatures ranging from 0 to 50°C). Chanton and others (2005) showed that elevated temperatures in the summer result in sulfate depletion and more availability of acetate to methanogens. Alternatively, Rask and others (2002) demonstrated with 300 days’ worth of data, that temperature had variable influence on CH₄ fluctuations depending on the location (flark, string, deep bay or shallow bay) in their freshwater system.

Although we did not sample for temperature or precipitation variables, we relate relative CH₄ concentrations to regional temperature and precipitation and discuss below how these would impact gas ebullition along the Lake Powell delta. The average temperatures of July 2014 and 2015 were similar (23.27°C and 21.69°C, respectively), while the average temperature of May 2016 was lower at 12.5°C (U.S. Climate Data, 2020). If temperature is a predominant predictor of CH₄ ebullition along the Lake Powell delta, one might suspect the July 2014 and 2015 CH₄ relative concentrations to be more similar and deviate from the 2016 data; however, this trend is not observed in the data. Future work measuring gas fluxes, air temperature, and temperature of water pooled in each volcano throughout longer term sampling could allow us to constrain the correlation between heat energy and CH₄ production in this system.

Precipitation and wetting may be one explanation for the variation in CH₄ between sampling seasons. Estop-Aragones and others (2016) conducted a year-long study on 15 bogs in Europe focusing on an initial wet period, a prolonged dry period (when the water table decreased over 35 cm), and a rewetting episode (when the water table increased 30 cm). They observed a peak in CH₄ fluxes during the early dry period (520.7 mg C·CH₄ m⁻²·d⁻¹) yet continued drying decreased fluxes through time (down to 14.5 mg C·CH₄ m⁻²·d⁻¹). Upon rewetting, CH₄ fluxes increased once more, but not to the point of early dry period fluxes. Similar trends (sharp peaks at the beginning of drought conditions and slow recovery of CH₄ emissions) were found in gully-mires over a six-year period (Hughes and others, 1999) and a 10-week period (Dowrick and others, 2006). Drought conditions (lasting two weeks) in the Auchencorth Moss peatland of Scotland also resulted in delayed increase in CH₄ flux and subsequent dramatic decrease without rebounding to original fluxes (Dinsmore and others, 2009). The Lake Powell delta experienced slightly less precipitation (on average 3.48 and 2.16 cm precipitation, respectively) and elevated CH₄ concentrations (greater than 70% v/v) in both the July 2014 and May 2016 sampling months while the month of July 2015 experienced slightly greater precipitation (5.23 cm) and experienced the lowest average CH₄ concentrations (less than 35% v/v). Lake Powell temperature and precipitation data were sourced from usclimate.data.com.

Isotope Ratio Mass Spectrometry Compositions

In this study, we use the ratios of carbon (¹²C versus ¹³C) and hydrogen (¹H versus ²H—also known as deuterium, D) measured in mud volcano CH₄ to interpret the methanogenic processes responsible for the gas ebullition. Upon plotting %o δ¹³C and %o δD against one
another, nine of the eleven CH₄ samples lie within the “mixed” methanogenic region (region 3 of figure 6). Region 1 is denoted with signatures of bacterial hydrogenotrophic production (carbonate reduction) and region 2 is denoted with bacterial acetoclastic production (methyl-type fermentation) signatures (Whiticar and others, 1986; Whiticar, 1999). The isotopic signatures of this study fall relatively well within the freshwater sediment range (-65 to -50‰ δ¹³C and -400 to -250‰ δD) described in Whiticar and others [1986]).

The Δ δD/Δ δ¹³C value (the slope of the line when plotting δD versus δ¹³C) of our samples is 4.81, R = 0.8344, which lies within the range (2.5 to 13.5 Δ δD/Δ δ¹³C) associated with methanotrophic activity in Chanton and others (2005). In addition to the physical water datum discussed above, water chemistry such as sulfate, acetate, and organic content measurements would offer additional insight into gas generation within the Lake Powell delta mud volcanoes. The impacts of these chemical variables are discussed in more detail below in context of specific methanogenic pathways.

Isotopic signatures within the “mixed” region of the δ¹³C and δD plot may result from one or both of two scenarios. Scenario one is that separate pools of gas (some derived from acetoclastic production and others from hydrogenotrophic production) are initially generated in isolation and are later transported and converge during migration. Scenario two is that the CH₄ source itself is shifting either spatially or temporally.

For example, CH₄ of isolated sources may have been mixed due to migration or diffusion of gas (Whiticar, 1999). Decreasing surface water levels of Lake Powell contribute to depressurizing of pore fluids and gases, allowing trapped CH₄ from separate subsurface sources (with varying initial substrates and isotopic signatures) to migrate upwards through the sediment as gas bubbles. This proposed mechanism would parallel previously reported evidence of gas release and upward migration by pressurization (Netoff and others, 2010; Livingston and others, 2014, 2015; Sherrod and others, 2016; Miller and others, 2018).

In this instance, the isotopic composition of the original substrate may shift the signatures of the produced CH₄. For example, if a precursor substrate had both ¹³CH₃OOH and ¹²CH₃OOH acetate, the substrate will more easily diffuse the lighter compound with lesser mass, than the former acetic acid molecule. This will result in a greater amount of bacterial ¹²CH₄ generated and very little bacterial ¹³CH₄ created. As ¹³C is left behind in the original substrate, the next generation of bacterial CH₄ will be more enriched in ¹³C than the first, and so on (Whiticar, 1999; Chanton and others, 2005). This transition would result in differences in the amount of δ¹³C generated (Whiticar, 1999).

Additionally, a change in substrate composition and methanogenesis is often observed with increasing depth. For example, Hornibrook and others (1997) showed that acetate fermentation processes predominated in shallow organic-rich soils, while in deeper (greater than 45 cm depth), older, less reactive peat, CO₂ reduction predominated. Similar observations have been previously reported in the literature (Hornibrook and others, 1997, 2000a, 2000b; Chasar and others, 2000a, 2000b). This transition will result in decreasing δ¹³C (of CH₄) signatures with depth similar to the decrease in the 11 samples presented here. Quality of the substrate throughout the delta could impact the scarcity of nutrients and mechanism of methanogenesis.

However, should these be the only processes taking place, the carbon isotopic signatures alone would exhibit a wide range and result in a linear shift (figure 6: “shift due to substrate depletion”) (Whiticar, 1999). These two processes alone do not account for the wider range in δD. Increasing δ¹³C and δD of isotopic signatures, which results in a “sympathetic” trend (linear and trending from lesser to greater signatures of both isotopes), is often the result of oxidizing methanotrophic bacteria (Chanton and others, 2005). This aerobic oxidation often occurs during bacterial CH₄ consumption in freshwater settings at the anoxic/oxic interface (Whiticar, 1999) which lies in the top several centimeters of lake sediments. Similar oxidation and subsequent δD/δ¹³C trends have been observed in landfill soils, wetlands, and laboratories incubation studies (Chanton and others, 2005).

Thermogenic sources tend to have greater δ¹³C signatures than biogenic sources, and will have further increased δ¹³C signatures with greater maturity (Whiticar, 1999), supporting the conclusion that the Lake Powell delta gas seeps are not related to thermogenic activity.
CONCLUSIONS

• This is the first reporting of CH₄, CO₂, and air (N₂+O₂) compositions as well as CH₄ isotope signatures of samples collected over a multiple day and multiple year period at Lake Powell, Hite, Utah. Average relative concentrations of CH₄, CO₂, and air released from the Lake Powell gas volcanoes in the spring of 2016 ranged from 74.51 ± 14.08% v/v, 2.82 ± 3.76% v/v, and 22.67 ± 14.28% v/v, and ranged from 25.36 to 93.34% v/v, 0.00 to 23.58% v/v, and 5.28 to 74.69% v/v.

• Gas chromatography data show changes in relative CH₄ concentrations ranging from extremely low variations of only 2% v/v increases, to greater variations of up to 38% v/v increases and 66% v/v decreases across multiple days. Acute water depth fluctuations and water circulation, soil redox potentials, and vegetation have been shown to result in short-term changes in CH₄ ebullition rates in the literature, but more work must be done to understand the extent to which these factors influence CH₄ production along the Lake Powell delta.

• Carbon and hydrogen isotopes from 11 samples with the greatest concentrations of CH₄ were analyzed using IRMS. The δ¹³C and δD signatures of these samples support that the CH₄ ebullition along the Lake Powell delta is biogenic and may source from a mixture of acetoclastic production and hydrogenotrophic production. This mixture may be the result of two possible mixing mechanisms. First, there may exist isolated CH₄ generation (of either predominantly acetoclastic production or predominantly hydrogenotrophic production), subsequent upward migration during pore depressurization, and finally mixing. Alternatively, original CH₄ sources are shifting from fermentation to reduction. Alternatively, original CH₄ sources are shifting from fermentation to reduction, resulting in a mixed isotopic signature. Isotopic signatures may potentially result from original substrates becoming depleted in lighter isotopes (¹²C), and heavier isotopes (¹³C) are subsequently used in bacterial respiration as well as CH₄ oxidation. Additionally, if methanogenesis occurs in an organic-rich zone and shifts to a depleted zone, the process may shift from fermentation to reduction.

• Future field work should include measuring CH₄ concentrations through time to calculate and relate fluxes to literature values. Additional biological, hydrological, and chemical measurements within and around gas-producing volcanoes are necessary to further constrain impacts on biological CH₄ production along the delta. Additional data must be gleaned to constrain long-term (seasonal and annual) changes in CH₄ ebullition and potential influences. Two possible controls on CH₄ production are temperature and wetting of the delta subsurface. Measurements of soil and water temperature, observations of water table fluctuations, and monitoring of wetting within and surrounding the mud volcanoes are necessary to better understand controls on CH₄ production.

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