Consumption of atmospheric methane in a limestone cave in Indiana, USA

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ABSTRACT

Recent observations suggest that karst landscapes may be an unaccounted sink for atmospheric CH_4, but questions remain about the processes contributing to sub-atmospheric CH_4 mole fractions in caves. The CH_4 dynamics associated with karst environments were studied over 18 months at 6 locations in Buckner Cave, Southern Indiana by measuring the mole fractions and stable isotopic composition of CH_4 and carbon dioxide (CO_2). CO_2 mole fractions were used to infer seasonal changes in airflow. Samples were obtained on a monthly basis. CH_4 mole fractions ranged from 1.9 ± 0.1 ppm near the cave entrance to 0.1 ± 0.1 ppm in the more remote parts of the cave. The carbon and hydrogen stable isotopic compositions of CH_4 in the cave ranged from -58.7 to $+7$ ‰ (VPDB) and -170 to $+10$ ‰ (VSMOW), respectively. The isotopic data suggest that the CH_4 dynamics of Buckner Cave can be described by a seasonally variable mixing system in which atmospheric CH_4 enters primarily through the main entrance and is subsequently consumed by methanotrophs. Additionally, at least two smaller CH_4 sources are evident when air has been stagnant. The results suggest that subterranean karst cavities are an important sink for atmospheric CH_4.

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1. Introduction

The rapidly increasing abundance of atmospheric methane (CH_4), a greenhouse gas, has been linked to anthropogenic activity (Craig and Chou, 1982; U.S. EPA, 2010; Ciais et al., 2013). Accurate climate forecasting requires a detailed understanding of CH_4 sources and sinks affecting atmospheric abundances. Despite progress quantifying CH_4 sources and sinks, the uncertainties of individual sources and sinks remain large (Kirschke et al., 2013). Major CH_4 sources to the atmosphere include natural sources such as wetlands, freshwaters, and geologic emissions (seepage), as well as anthropogenic sources such as agriculture and fossil fuel use (Ciais et al., 2013). The major sink of atmospheric CH_4 is oxidation by the hydroxyl radical (•OH) which accounts for 90 % of the total losses, whereas oxidation by CH_4 consuming (methanotrophic) microorganisms in soils is the next largest sink and accounts for about 2 % of the losses (Naik et al., 2013; Dlugokencky et al., 2011). The advective flow of air through porous rock units, including karst, causes the atmosphere to interact with the subsurface which, if oxidizing agents are present, would aid in the removal of CH_4 from the atmosphere.

Karst landforms cover 10–20 % of the continental surface (Palmer, 1991), and result from the interaction between soluble rock units and water. Mature karst landscapes exhibit solution-enlarged fractures, caves, and internal drainage networks which also provide conduits for atmospheric exchange (Atkinson et al., 1983; Gregorič et al., 2014). The surface area of the conduits capable of interacting with the atmosphere is unknown, in part because much of the surface area occurs in fractures that are too small for easy exploration (Curl, 1966). Despite the fact that some subsurface karst environments are inaccessible, the accessibility of caves provides a way to assess atmospheric exchange with the subsurface.

Limestone caves form as acidic water dissolves carbonate bedrock. Two common types are (1) epigenic caves, which form as meteoric water enriched in carbonic acid dissolves limestone, and (2) hypogenic caves, which form where deep-sourced waters, usually with sulfuric acid, migrate upwards. The different chemistry of the fluids entering these two types of caves also influences the paths of dissolved ions and gases, including CH_4, into the cave. Subterranean measurements of CH_4 mole fractions in karst air come from caves formed or forming from carbonic acid (epigenic speleogenesis) and those currently undergoing sulfuric acid speleogenesis (hypogenic). Epigenic caves dominate the total land area represented by karst and the CH_4 dynamics of these caves are more representative of the typical biogeochemical conditions present in karst. CH_4 mole fractions in the air of epigenic caves in Gibraltar, Spain, and Australia (Mattey et al., 2013; Fernandez-Cortes et al., 2015; McDonough et al., 2016) are generally below that of the atmospheric background of 1.8 ppm (ppm, parts per million, is used to abbreviate µmol mol^{-1}, dry air mole fraction) (Dlugokencky et al., 2003;

Adushkin and Kudryavtsev, 2010; Dlugokencky et al., 2011). The observations of sub-atmospheric CH_4 mole fractions in caves and karst have led to suggestions that they are functioning as CH_4 sinks, however questions regarding the processes contributing to low CH_4 mole fractions in caves remain. In contrast, CH_4 mole fractions in the air of caves undergoing sulfuric acid speleogenesis have ranged from 3 ppm to 1 % by volume and have been reported from only three locations (Sarbu et al., 1996; Hutchens et al., 2004; Engel et al., 2004; Jones et al., 2012). These mole fractions are higher than the atmospheric background.

The sub-atmospheric CH_4 mole fractions observed in the systems in Gibraltar Spain, and Australia were proposed to have been caused by different mechanisms. The mechanism put forward to explain low CH_4 mole fractions in the Gibraltar cave relied on increases in $\delta^{13}C_{CH_4}$ values that coincided with decreasing CH_4 mole fractions. These data fit a Rayleigh distillation model caused by methanotrophy (i.e., CH_4 being consumed by microorganisms, Mattey et al., 2013). This hypothesis is supported by the observation of methanotrophs in other epigenic cave systems (Pašić et al., 2010; Porca et al., 2012; Ortiz et al., 2013; McDonough et al., 2016). In contrast, the low CH_4 mole fractions observed in the air of Spanish caves were hypothesized to have been caused by radical reactions with CH_4 that were initiated by the radioactive decay of radon (Fernandez-Cortes et al., 2015).

The stable isotopic ratios of ^{13}C to ^{12}C and of ^2H to ^1H in CH_4 are known to reflect the process by which the CH_4 was generated, and may help determine the sources and sinks of CH_4 in caves. Atmospheric CH_4 has $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values near -47 ‰ and -100 ‰, respectively (Miller et al., 2002; Townsend-Small et al., 2012). Microorganisms produce CH_4 through two major pathways, carbonate reduction and acetoclastic methanogenesis; the CH_4 produced by both of these pathways is enriched in light isotopologues (Whiticar, 1999). CH_4 generated from carbonate reduction is characterized by $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values from -110 to -60 ‰ and -250 to -100 ‰, respectively (Whiticar, 1999; Tazaz et al., 2013). In contrast, CH_4 generated from acetate fermentation has a narrow range of $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values encompassing values from -65 to -48 ‰ and -370 to -260 ‰, respectively (Whiticar, 1999).

The stable isotopic ratios of ^{13}C to ^{12}C and of ^2H to ^1H in CH_4 are also known to reflect process, such as oxidation, that affect CH_4 after it has formed. CH_4 oxidation by •OH causes the residual $\delta^2H_{CH_4}$ value to increase by 72 ‰ for every 1 ‰ increase in $\delta^{13}C_{CH_4}$ values (Saueressig et al., 2001). Methanotrophy, in contrast, imparts an increase in the $\delta^2H_{CH_4}$ value of 8.5 ‰ for every 1 ‰ increase in $\delta^{13}C_{CH_4}$ values (Feisthauer et al., 2011). These differences in the kinetic isotope fractionation factors associated with CH_4 oxidation can help assess the oxidation process present in δ^2H-$\delta^{13}C$ space. Thus, the $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values may help determine the sources and sinks of CH_4 in caves.

We studied the carbon and hydrogen stable isotopic compositions and mole fractions of CH_4 and carbon dioxide (CO_2) in Buckner Cave, Southern Indiana to better characterize the CH_4 dynamics of epigenic karst landscapes. We hypothesized that if CH_4 in caves has an atmospheric source and cave processes decrease CH_4 mole fractions in cave air, then CH_4 should become more depleted as the distance from the cave entrance increases. We also asked, what are the biogeochemical processes that govern the mole fractions and stable isotopic composition of CH_4 in karst cavities? Our work presents time-series data over 18 months and the first measurements of the ratio of deuterium to hydrogen (^2H/^1H) in CH_4 from caves. Additionally we present a high resolution temporal study of a daily change in CH_4 mole fractions in Buckner Cave. Our work shows that the stable isotopic composition of CH_4 in Buckner Cave can be described by methanotrophic CH_4 oxidation as well as CH_4 production from at least two different biogeochemical pathways.

2. Geological setting

Buckner Cave is located within the Crawford Upland physiographic province of Southern Indiana (Fig. 1). The rock outcrops at the surface in the Crawford Upland consist of the interbedded sandstones and limestones of the Stephensport and West Baden groups (Conner, 1987; Lakey and Krothe, 1996). These rocks are resistant to erosion and cause an increase in topographic relief. Surface erosion by streams locally exposes the underlying limestones of the Blue River Group i.e. the Paoli Formation, the Saint Louis Formation, and the Saint Genevieve Formation. Buckner Cave is hosted in rocks of the Blue River Group, and is primarily hosted in the Saint Genevieve Fm., but the highest sections of the cave are located in the Paoli Limestone (Conner, 1987). The total vertical relief of Buckner Cave is 36.6 m with the lowest room having an elevation of 215.5 m a.s.l. (elevation at surface 259 m) and the highest room having an elevation of 252.1 m a.s.l (elevation at surface 255 m).

Buckner Cave has been managed by the Richard Blenz Nature Conservancy since 2005. Buckner Cave is a wild cave and is visited by about 6 people per week. There is one natural entrance to Buckner Cave (Fig. 2). A second entrance (Bull's Eye Pit) was blasted in 1992 to provide access for rescue purposes. This entrance has been closed, and is thought to be air tight. Air flow in Buckner Cave is also thought to be connected to the nearby Queen Blair Cave, which is lower in elevation than Buckner Cave, based on air tracer experiments (DesMarais, 1971). Additionally, fractures in the limestone may allow for exchange with the atmosphere. The average air temperature of Buckner Cave is 12.8 °C.

Buckner Cave is a branchwork cave with some anastomosing passages (Palmer, 1991). Some of the cave passages exhibit features indicative of formation by vadose processes while others appear to have formed by phreatic processes. Buckner Cave has two small drainages that eventually outflow at Big Blair Spring (DesMarais, 1981) (Fig. 2).

3. Methods

3.1. Air sampling

Air sampling was carried out in two discrete sampling campaigns. A preliminary study determined seasonal patterns of CO_2 mole fractions in Buckner Cave by measuring monthly CO_2 mole fractions at six locations from August 2010 through July 2012 to (Fig. 2). Sampling locations were selected based on their intersections with other passages, their distance from the main entrance, and their elevation. Distance to the main entrance was defined as the distance along the shortest passageway from a sampling location in Buckner Cave to the main entrance and was measured using the map of Buckner Cave shown in Fig. 2. CO_2 mole fractions were measured in-situ with a portable gas monitor (Gasman – Crowcon Detection Instruments Ltd., Erlanger, Kentucky, USA; range 0–50,000 ppm; uncertainty, ± 100 ppm). Daily high and low temperatures and total precipitation were measured at the Monroe County Airport approximately 5 km northwest of Buckner Cave (NCEI Asheville, NC). Data from this early part of the study indicate two distinct seasons of airflow for Buckner Cave (Fig. 3). We defined summer airflow to encompass periods when CO_2 mole fractions were above 2000 ppm. Data from this study also indicated that air exchange through the sealed Bull's Eye Pit entrance was not a major influence on airflow in Buckner Cave.

In the second, more detailed part of the study from July 2013 to March 2015, samples from sites 1 through 5 were collected monthly and analyzed for the mole fractions and isotopic compositions of CH_4 and CO_2 in Buckner Cave (Fig. 2). Air sampling occurred during evenings from 6 to 8 pm. Air from sampling locations was collected in Tedlar® bags using 60 mL or 140 mL syringes via three way valves. Each Tedlar® bag was flushed three times with 60 or 140 mL of air and was emptied before collecting the final air sample of ~550 to 650 mL. Samples were acquired in less than a minute.

An experiment to capture a daily change in the CH_4 mole fraction of Buckner Cave air took place September 29, 2014. The high and low atmospheric temperatures on the 29th were 27.8 and 10.0 °C,