Subterranean karst environments as a global sink for atmospheric methane

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ABSTRACT

The air in subterranean karst cavities is often depleted in methane (CH_4) relative to the atmosphere. Karst is considered a potential sink for the atmospheric greenhouse gas CH_4 because its subsurface drainage networks and solution-enlarged fractures facilitate atmospheric exchange. Karst landscapes cover about 14% of earth's continental surface, but observations of CH_4 concentrations in cave air are limited to localized studies in Gibraltar, Spain, Indiana (USA), Vietnam, Australia, and by incomplete isotopic data. To test if karst is acting as a global CH_4 sink, we measured the CH_4 concentrations, $\delta^{13}C_{CH_4}$, and $\delta^2H_{CH_4}$ values of cave air from 33 caves in the USA and three caves in New Zealand. We also measured CO_2 concentrations, $\delta^{13}C_{CO_2}$, and radon (Rn) concentrations to support CH_4 data interpretation by assessing cave air residence times and mixing processes. Among these caves, 35 exhibited subatmospheric CH_4 concentrations in at least one location compared to their local atmospheric backgrounds. CH_4 concentrations, $\delta^{13}C_{CH_4}$, and $\delta^2H_{CH_4}$ values suggest that microbial methanotrophy within caves is the primary CH_4 consumption mechanism. Only 5 locations from 3 caves showed elevated CH_4 concentrations compared to the atmospheric background and could be ascribed to local CH_4 sources from sewage and outgassing swamp water. Several associated $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values point to carbonate reduction and acetate fermentation as biochemical pathways of limited methanogenesis in karst environments and suggest that these pathways occur in the environment over large spatial scales. Our data show that karst environments function as a global CH_4 sink.

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1. Introduction

Atmospheric methane (CH_4) is a greenhouse gas and its concentration is increasing in the atmosphere (Dlugokencky et al., 2011; Sussmann et al., 2012; Ciais et al., 2013). The present globally averaged CH_4 concentration is 1.87 ppmv which is 2.5 times higher than preindustrial levels (Nisbet et al., 2016). The increase in atmospheric CH_4 is due to an imbalance between CH_4 sources and sinks. Anthropogenic and natural sources combine to contribute about 680 Tg a^{-1} of CH_4 to the atmosphere while reactions with hydroxyl ($\cdot$OH) and chlorine radicals in the troposphere

and stratosphere remove about 600 Tg a^{-1} (Kirschke et al., 2013). Methanotrophic consumption in soils, the next largest sink, removes 30 Tg a^{-1} (Kirschke et al., 2013). Despite improvements in estimating individual sources and sinks of atmospheric CH_4, the associated errors remain large (Kirschke et al., 2013). Recent studies suggest that caves may act as an additional CH_4 sink (Mattey et al., 2013; Fernandez-Cortes et al., 2015; McDonough et al., 2016; Webster et al., 2016; Lennon et al., 2017).

Caves and associated karst landscapes may be an important overlooked sink for atmospheric CH_4 because they are estimated to cover as much as 10 to 20% of the continental surface with more precise estimates suggesting about 13.8% (Palmer, 1991; Ford and Williams, 2007). Karst landscapes are frequently associated with the chemical dissolution of limestones, but can form in any soluble rock body. The resulting caves, solution-enlarged fractures, and internal drainage networks that function to trans-

port mass from high elevations to low elevations also allow for subsurface-surface atmospheric exchange (Kowalczk and Froelich, 2010; Garcia-Anton et al., 2014). The total volume and surface area of karst conduits able to interact with the atmosphere is unknown, in part due to small fractures and the difficulty of imaging the subsurface with geophysical methods. Karst caves, due to their accessibility, provide opportunities for non-invasive, *in-situ* analyses and sampling.

Cave and karst landscapes form in two common ways, each of which influences karst's capacity to act as a CH_4 sink. Epigenic karst forms through the interaction of limestone with carbonic acid derived from the dissolution of atmospheric and soil CO_2 into surface waters. By contrast, hypogenic caves form when corrosive water from deep sources migrates into and dissolves limestone bedrock. Epigenic caves are more widespread, and atmospheric to subatmospheric CH_4 concentrations of 1.8 ppmv to <0.1 ppmv have been observed in these settings (Mattey et al., 2013; Fernandez-Cortes et al., 2015; McDonough et al., 2016; Webster et al., 2016; Lennon et al., 2017). For comparison, in some hypogenic caves elevated CH_4 concentrations from 2 ppmv to 1% have been observed in association with CH_4-rich springs or seeps related to fluid migration from deep hydrocarbon-bearing sedimentary rocks, i.e. seepage processes that are widespread on Earth (Sarbu et al., 1996; Hutchens et al., 2004; Jones et al., 2012; Webster et al., 2017). The dominance of epigenic karst suggests these regions are functioning as a CH_4 sink at the global scale, but more observations are needed.

Different hypotheses have been put forward to explain the low CH_4 concentrations observed in epigenic cave air. The combination of subatmospheric CH_4 concentrations and the stable carbon isotopic ratio of CH_4 in the air of caves in Gibraltar led to the hypothesis that microorganisms were responsible for the removal of CH_4 (Mattey et al., 2013). In turn, low CH_4 concentrations in Spanish caves, in the presumed absence of CH_4-consuming (methanotrophic) bacteria, led to the hypothesis that CH_4 oxidation was induced by ions and ·OH generated by the radioactive decay of radon and daughter nuclides (Fernandez-Cortes et al., 2015). Since these initial observations, datasets from caves in Australia, the USA, and Vietnam have pointed towards methanotrophic CH_4 oxidation (McDonough et al., 2016; Webster et al., 2016; Lennon et al., 2017; Waring et al., 2017).

The chemical composition of cave air results from the mixing of the atmosphere and air from the overlying soils and epikarst. These processes should also influence the CH_4 concentrations of cave air. Previous studies have shown that CH_4 concentrations have been inversely correlated with CO_2 concentrations in cave air (Mattey et al., 2013; Ferndandez-Cortes et al., 2015; McDonough et al., 2016; Webster et al., 2016). Cave air CO_2 concentrations are positively correlated with radon (Rn) concentrations and Rn is known to track cave air residence time (Cunningham and LaRock, 1991; Batiot-Guilhe et al., 2007; Kowalczk and Froelich, 2010; Mattey et al., 2010; Gregorič et al., 2011, 2014). Additionally, the stable C isotope composition of CO_2 ($\delta^{13}C_{CO_2}$), can track the sources of CO_2 in the environment. For example, $\delta^{13}C_{CO_2}$ values of $-24‰$ are associated with soil CO_2, while atmospheric CO_2 has $\delta^{13}C_{CO_2}$ values ranging from $-8.5‰$ to $-10‰$ (Amundson et al., 1998; Keeling et al., 2010; Peyraube et al., 2013). Thus CO_2, Rn, and $\delta^{13}C_{CO_2}$ in cave air can help determine the influence of cave air mixing processes on CH_4.

The stable C and H isotope compositions of CH_4 ($\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$) also provide tools for understanding the sources and sinks of CH_4 in caves because different CH_4 sources are associated with characteristic $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values. For example, CH_4 produced from carbonate reduction has $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values that range from -112 to $-60‰$ VPDB and from -350 to $-100‰$ VSMOW respectively (Whiticar, 1999). Atmospheric CH_4

has $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values around -47.5 and $-100‰$ (Miller et al., 2002; Townsend-Small et al., 2012). The $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values of CH_4 can also be altered through secondary processes such as oxidation and mixing. The oxidation pathways of CH_4 by methanotrophs or the ·OH have fractionation factors that cause the residual CH_4 to show increases in $\delta^2H_{CH_4}$ values of 8.5‰ for every 1‰ increase in $\delta^{13}C_{CH_4}$ value and increases in $\delta^2H_{CH_4}$ values of 72‰ for every 1‰ increase in $\delta^{13}C_{CH_4}$ value, respectively (Feisthauer et al., 2011; Saueressig et al., 2001). Mixing between two different CH_4 sources creates a linear trend between the two members. Thus, measuring the $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ of cave air should allow for the determination of cave air CH_4 sources.

The objective of the present work is to extend the karst CH_4 dataset and test the hypothesis that karst systems act as a CH_4 sink on a global scale. To this aim, we studied CH_4 concentrations, $\delta^{13}C_{CH_4}$, and $\delta^2H_{CH_4}$ in cave air from 33 epigenic caves in the USA and three epigenic caves in New Zealand. CO_2, $\delta^{13}C_{CO_2}$, and Rn were also measured to support CH_4 data interpretation *via* assessing cave air residence times and mixing processes. Data analysis is focused on determining CH_4 concentrations, origin, mixing processes and isotopic fractionations.

2. Methods

2.1. Sampling and analyses

Air samples from the study caves were collected over a timespan of roughly four years (Fig. 1; Table 1). Study caves fell into three broad groups, those from the Appalachian fold and thrust belt (16); those in gently warped intracratonic basins of the USA (17); and those from the North Island of New Zealand (3). Cave air was sampled using *in-situ* and discrete methods. *In-situ* CH_4, CO_2, and Rn abundance analyses were carried out using a suite of instruments (Table 2). Discrete samples of cave air were collected in pre-evacuated 50-mL serum vials, in 1 to 3-L Tedlar® bags, or in 4-L glass bottles. CH_4 and CO_2 concentrations of discrete samples were measured *via* gas chromatography.

We assessed cave air mixing processes through a variety of techniques. A qualitative estimate on cave air residence time was obtained by comparing CH_4 to CO_2 concentrations at individual locations in each cave. Additionally, we measured the Rn concentrations of caves 32 through 36 to assess the relationship between cave air residence time, CH_4 concentrations, and CO_2 concentrations. $\delta^{13}C_{CO_2}$ data were used to assess the sources of CO_2 and thus of air entering the caves. We also assessed the distance from each sampling location to cave entrances as another tool to understand cave air mixing processes.

CH_4 and CO_2 concentrations from discrete air samples were measured at Indiana University using a Varian 450 gas chromatograph (GC) (Varian – Agilent Technologies, Palo Alto, California). The GC was fitted with a flame ionization detector (FID) for CH_4 and a thermal conductivity detector (TCD) for CO_2. Standard gas mixtures from Air Liquide America Specialty Gasses LLC (Plumsteadville, Pennsylvania) were used for 3-point calibration curves to convert signals measured on the GC to concentrations. CH_4 standards measured on the GC had errors of ± 5 to $\pm 14\%$ of the reported concentrations. CH_4 concentrations are reported with the uncertainty associated with the standard curve unless the calculated uncertainty was ≤ 0.1 ppmv. Samples with calculated uncertainties ≤ 0.1 ppmv were assigned uncertainties of 0.1 ppmv based on replicate measurements. The uncertainty associated with standard curves for CO_2 concentrations varied from $<\pm 1$ to 5%. CO_2 concentrations were assigned uncertainties based on their associated standard curve.

The stable carbon isotope ratios of CH_4 and CO_2 and hydrogen stable isotope ratios of CH_4 were measured on a ThermoFinnigan