Radiolysis via radioactivity is not responsible for rapid methane oxidation in subterranean air

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Abstract

Atmospheric methane is rapidly lost when it enters humid subterranean critical and vadose zones (e.g., air in soils and caves). Because methane is a source of carbon and energy, it can be consumed by methanotrophic methane-oxidizing bacteria. As an additional subterranean sink, it has been hypothesized that methane is oxidized by natural radioactivity-induced radiolysis that produces energetic ions and radicals, which then trigger abiotic oxidation and consumption of methane within a few hours. Using controlled laboratory experiments, we tested whether radiolysis could rapidly oxidize methane in sealed air with different relative humidities while being exposed to elevated levels of radiation (more than 535 kBq m<sup>-3</sup>) from radon isotopes <sup>222</sup>Rn and <sup>220</sup>Rn (i.e., thoron). We found no evidence that radiolysis contributed to methane oxidation. In contrast, we observed the rapid loss of methane when moist soil was added to the same apparatus in the absence of elevated radon abundance. Together, our findings are consistent with the view that methane oxidizing bacteria are responsible for the widespread observations of methane depletion in subterranean environments. Further studies are needed on the ability of microbes to consume trace amounts of methane in poorly ventilated caves, even though the trophic and energetic benefits become marginal at very low partial pressures of methane.

Introduction

Energetic radiation generates ions and radicals in fluids via radiolysis that can trigger subsequent chemical reactions [1], including the oxidation of organics. Radiolysis has likely affected the evolution of early microbial metabolisms and is crucial for powering the deep microbial biosphere [2, 3]. However, few studies have addressed the quantitative importance of radiolysis for contemporary fluxes in the atmosphere and the critical zone, especially in comparison to processes that compete with biologically mediated transformations.
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Materials and methods

The concentration of methane (CH4) in the atmosphere has more than doubled since 1850 to ~1.85 ppmv (i.e., parts per million by volume) and now contributes ~15% of anthropogenic forcing of climate change [4]. The Intergovernmental Panel on Climate Change (IPCC) report [5] includes secondary greenhouse warming effects of CH4 and Arrives at 1 W m⁻² for CH4 relative to 1.7 W m⁻² for CO2, making CH4 the second most important anthropogenic climate forcing agent. In the atmosphere, the removal of CH4 is due primarily to oxidation via photochemically generated tropospheric OH• radicals ([6], and refs. therein). In spite of intense radiation in the atmosphere from sun and space, the residence time of atmospheric CH4 is ~12 years. The second largest sink for atmospheric CH4 is shallow subterranean environments containing aerated soils that are inhabited by CH4 oxidizing bacteria, MOB [4, 7]. MOB are also found in deeper aerated subterranean environments, such as caves in the vadose zone, although their contribution to global CH4 cycling has not been quantified or incorporated into earth system models [4].

A growing number of studies have reported that, throughout the world, concentrations of CH4 are often depleted in the air of caves suggesting that subterranean environments may represent an overlooked sink for atmospheric CH4 (e.g., [8–13]). Based on ventilation rates and CH4 pools, it is estimated CH4 is rapidly consumed in caves on time scales ranging from hours to days [14, 15]. Depletion of CH4 in caves is often attributed to MOB. However, a study from Spanish caves proposed that rapid CH4 oxidation may be attributed to non-biological processes via radiolysis and ionization of subterranean air by natural radioactivity that could lead to the oxidation of CH4 at a sufficiently fast rate to account for appreciable consumption of CH4 [16]. It has been proposed that α-radiation (e.g., from ²²²Rn) can radiolytically ionize, or generate radicals from, atmospheric components (e.g., H₂O) including CH4 [16, 17]. The study by Haynes and Kebarle [16] determined that α-radiation has a slow effect on pure CH4 and mixed hydrocarbon gas in the absence of air, making it difficult to extrapolate results to CH4 in air in the presence of ions and radicals from heteromolecules.

Some studies, however, have raised questions about the relative importance of abiotic CH4 oxidation based on theoretical considerations of kinetics, the inability of α-radiation from metallic uranium and radon to trigger fast oxidation of CH4 [15, 18]. Laboratory and field experiments implicated MOB with the rapid decline in cave CH4 concentrations [18], while isotopically uncharacterized radon was unable to remove CH4 from air in an Australian cave [15]. Studies on radon typically focus on ²²²Rn because its longer half-life of 3.83 days facilitates quantification. No study has yet examined the radiolytic effect on CH4 oxidation of the relatively more energetic decay of ²²⁰Rn (called thoron, with a half-life 55.6 s), particularly in the air close to cave walls and floors where ²²⁰Rn is relatively more abundant. Also, direct experiments linking the constraints of air humidity and natural radiation from specific radon isotopes to CH4 oxidation in air are lacking. The current study fills these gaps with detailed independent experiments in two laboratories using energetically distinct radiation levels from isotopes of radon (²²²Rn and ²²⁰Rn) at different humidities and contrasting the results with CH4-depletion by MOB.
Details of materials and methods are available from protocols.io under http://dx.doi.org/10.17504/protocols.io.s7aehie. We employed two separate, complementary experimental approaches at IU and RHUL. The following two sections offer brief overviews.

**Apparatus at IU for active, time-resolved measurements of gas concentrations with circular flow**

At IU, we constructed an experimental apparatus to assess the loss of CH$_4$ in an active (i.e., with pumping of air) and time-resolved manner with or without added radiation from radon isotopes and their progeny (Fig 1). The use of pumping qualifies this method as active and time-resolved in contrast to passive measurements of radon that integrate over time [19]. Approximately 6 L of air was recirculated in the sealed apparatus that included (i) a glass tube with optional thorium carbonate to generate $^{220}$Rn (also called thoron), and (ii) a glass tube containing uranium ore to generate $^{222}$Rn, with an overlying layer of coconut charcoal to limit the escape of co-produced, short-lived $^{220}$Rn. Blank experiments without elevated radiation identified a reproducible loss of CH$_4$ (likely by diffusion through polymer tubing within the sealed analytical SARAD RTM 2200 instrument) that was subtracted from all other experiments at IU to arrive at net CH$_4$ losses that are due to other factors, such as radiolysis or microbial methanotrophy.

We conducted a number of experiments at IU to assess the importance of $\alpha$-radiation intensity, relative humidity, and the presence or absence of soil on CH$_4$ dynamics. Moisture is critical for the emanation efficiency of radon isotopes from solid sources (i.e., the escape of noble gas radon atoms from the interior of minerals into H$_2$O-containing pore space via recoil subsequent to radioactive decay of parental nuclides; e.g., [20, 21]) and for stabilizing ions and radicals in air. Individual experiments differed in terms of their optional use of elevated humidity, thorium carbonate, and gas flowing through the tube containing uranium ore. The trapped ~6-L volume of air was initially spiked with CH$_4$ from natural gas to ~70 ppmv and with CO$_2$ to ~5,000 ppmv (except for experiments with soils) to distinguish it from room air and to increase the analytical precision during the time-series of measurements that lasted over a few days to weeks. Elevated CO$_2$ concentrations are typical for many cave environments [10].

Most experiments at IU discriminated between $\alpha$-radiation from radon $^{222}$Rn versus thoron $^{220}$Rn. Whereas radon $^{222}$Rn with a half-life of 3.83 days is relatively homogeneously distributed in cave air (also in our apparatus), the much shorter lived thoron $^{220}$Rn with a half-life of only 55.6 s [22] cannot travel far from its parent nuclei residing in minerals [19], thus thoron’s highest concentrations in cave air are near cave walls and the floor. The higher $\alpha$-decay energy of $^{220}$Rn (6.3 MeV) relative to $^{222}$Rn (5.49 MeV) prompted us to design experiments for separate examinations of the ability of both radon isotopes to trigger the oxidation of CH$_4$. The more energetic $\alpha$-decay of thoron $^{220}$Rn should ionize air more efficiently than $^{222}$Rn. Thoron was generated from thorium carbonate that was optionally loaded into a glass tube attached to the round-bottom flask. In other experiments, $^{222}$Rn decay measuring up to 327 kBq m$^{-3}$ was produced in-situ in the glass apparatus by uranium ore chips (Fig 1). Escape of co-produced thoron from ore was reduced by using a layer of coconut charcoal in the upper part of the glass tube as a filter [23]. The resulting adsorption of $^{220}$Rn on charcoal increased the residence time in the glass tube and let $^{220}$Rn decay before it could enter the 5-L glass flask.

We quantified the concentrations of $^{222}$Rn, $^{220}$Rn, CH$_4$ and CO$_2$ during experiments at IU at an air flow rate of ~0.2 L min$^{-1}$ once every hour while operating the diffusion pump in the SARAD RTM 2200. $^{220}$Rn radiation intensity was either measured via $\alpha$-spectroscopy at a faster flow rate of 1 L min$^{-1}$ in 10-min increments ($n \geq 10$) while temporarily operating the
more powerful membrane pump, or values from flow rates $\leq 0.2 \text{ L min}^{-1}$ with the diffusion pump were doubled to adjust for fast $^{222}\text{Rn}$ decay (see S1 File for detailed control experiments and graphed data). Elevated relative humidity fosters the stabilization of ions in air via attachment to clusters of water molecules and may enhance the ability of ions to trigger oxidative degradation of $\text{CH}_4$ (discussed in [10]). Therefore, at IU we recorded humidity in the apparatus along with temperature, air pressure, flow, and battery voltage on an hourly basis. The
accuracy of data from the SARAD RTM 2200 was independently evaluated via direct comparison with a newly manufactured and factory-calibrated Thoron Scout instrument (SARAD GmbH, Dresden, Germany; details available in S1 File).

We conducted a number of experiments at IU to test for the effects of radiation and microbial activity on CH$_4$ dynamics in our experimental apparatus. Multi-day time-series of data were collected in closed-circuit air reflux mode (i) as duplicated blank experiments without added radon or thoron, (ii) with enhanced $^{220}$Rn concentration in dry or moist air, (iii) with enhanced $^{222}$Rn concentration in dry or moist air, and (iv) with jointly enhanced $^{220}$Rn and $^{222}$Rn concentrations in moist air to depict an extreme scenario where cave air had a highly elevated $\alpha$-radiation level. Furthermore, (v) we tested for CH$_4$ oxidation after placing moist soils, which we assumed contained methanotrophic bacteria (MOB), into the 5-L glass flask, without elevated radioactivity. Certain impurities in industrially conditioned natural gas may act as MOB inhibitors, for example acetylene and carbon monoxide (p. 335 in [24]). As a precaution, the CH$_4$ spikes in experiments employing two different soils were derived from gas that was collected from a natural seepage of shale gas in New York State [25]. Natural shale gas is not known to contain acetylene or carbon monoxide.

**Gas-tight terrarium experiments at RHUL**

Experiments at RHUL at atmospheric CH$_4$ abundance used a gas-tight glass terrarium (i.e., an aquarium without water holding a volume of 13.45 L; Fig 2) with a hermetically sealing glass lid. Two air-tight gas ports allowed the withdrawal of 1-L air samples into Tedlar bags without changes in atmospheric pressure. Fragments of uraninite-bearing pitchblende served as a source of radioactivity. An AlphaLab Air Ion Counter with an integrated fan was placed in the terrarium to measure the abundance of ions in air in 30-s intervals. The $\alpha$-radiation was quantified on 1-h intervals with a Canary Pro monitor (Airthings, Oslo, Norway) via $\alpha$-spectrometry. Gas samples in Tedlar bags were analyzed for CH$_4$ mole fractions with a Picarro G1301 CRDS (Cavity Ring-Down Spectrometer, Picarro Inc., Santa Clara, California, USA).

The initial RHUL experiment #1 (Fig 2A) assessed the production of negative ions and the abundance of $^{222}$Rn over ~6 h (i.e., stage 1) without either pitchblende or a beaker with water in the terrarium that had been flushed initially with laboratory air, and subsequently for ~15 h in the presence of pitchblende and a beaker with 130 mL of 38°C warm water in the terrarium (stage 2).

The subsequent RHUL experiment #2 (Fig 2B) in the same terrarium included monitoring of the CH$_4$ mole fraction of laboratory air sealed in the terrarium where pitchblende and a beaker with 130 mL of water (initially at 38°C) had been placed to provide for elevated radioactivity and relative humidity. Elevated relative humidity was needed to simulate cave conditions. The AlphaLab Air Ion Counter failed to provide useful data due to static interference with Tedlar bags. The second experiment lasted for 76 h and 50 min and reached a $^{222}$Rn-based radiation level in excess of 50 kBq m$^{-3}$ after 5 h. Approximate 1-L aliquots of air sampled from the terrarium were analytically compared with aliquots of exterior laboratory air on four occasions.

**Results and discussion**

**Active time-series measurements with circular flow at IU**

Our controlled experiments with and without $^{220}$Rn and/or $^{222}$Rn were designed to directly test whether or not radiation can oxidize CH$_4$ in cave air on ecologically relevant time scales (i.e., hours to days). We relied on comparisons of CH$_4$ inventories in experiments with (i) high radiation intensity from in-situ generated $^{220}$Rn and/or $^{222}$Rn with those from (ii) duplicate
Fig 2. Gas-tight terrarium experiments at Royal Holloway University of London. (a) A hermetically sealed glass terrarium was filled with laboratory air containing atmospheric CH$_4$. A radon monitor provided data on $^{222}$Rn abundance, while an AlphaLab Air Ion Counter measured the concentration of negative ions. After ~6 h into the RHUL experiment #1, the placement of a beaker filled with deionized, warm water elevated the relative humidity to > 85%. At the same time, two fragments of pitchblende (containing uraninite as a radiation source) were placed into the terrarium.
to generate $^{222}\text{Rn}$. Tedlar bags in the terrarium are not shown in the photograph. (b) Diagram of the sampling procedure to collect <1-L aliquots of air from the terrarium in RHUL experiment #2. This experiment lasted for 76 h and 50 min and reached a $^{222}\text{Rn}$-based radiation level in excess of 50 kBq m$^{-3}$ after 5 h. 

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blank experiments with no artificially enhanced radiation to demonstrate the sensitivity of our setup to detect CH$_4$-losses. In addition, we conducted (iii) two experiments with moist soils in the absence of added radon isotopes to assess the potential for environmental microorganisms (i.e., MOB) to remove CH$_4$ as has been demonstrated elsewhere by members of our research team [14, 18]. The comparisons among experiments covered a common range of CH$_4$ concentration and thus only differed in the lengths of their time windows needed to lower the CH$_4$ concentration from the upper to the lower threshold (i.e. yellow rectangle in Fig 3A). The ‘common window’ of CH$_4$ decline for all 11 experiments maximized the data available for comparison.

Multiple trials in our experimental apparatus revealed that CH$_4$ dynamics were unaffected by radiation within the precision of measurements. Repeat blank experiments with dry (experiments #1 and #2) or moist air (experiments #3 and #4) without artificially elevated radon or thoron concentrations resulted in reproducible and systematic small losses of both CH$_4$ and CO$_2$ over time (Fig 3A and 3B; Table 1A). Although radon isotopes, CH$_4$ and CO$_2$ could not diffuse through glass and metal in our apparatus, the SARAD RTM 2200 and its Axetris laser OEM Module LGC F200 methane detector were internally and externally connected to glass and metal components with short segments of various types of clear polymer tubing (Fig 1) that resulted in slow losses via gas diffusion through polymers. The rate of diffusion across a layer of polymer is dependent on the difference in partial pressures between the interior and exterior air, and hence the rates of CH$_4$ and CO$_2$ losses via diffusion over time follow curves that asymptotically approach equilibria (Fig 3F). At a CH$_4$ concentration of ~59 ppmv in the apparatus (i.e., the midpoint of the common CH$_4$ range; Fig 3A) and outside air with ~1.85 ppmv, the mean CH$_4$ diffusive loss from air in the apparatus during blank experiments #1 to #4 consistently amounted to 0.39 ppmv h$^{-1}$ regardless of humidity and small variations in room temperature and air pressure (Table 1A; S1 File). Such a loss of gas over time could theoretically result from a small internal leak in the system. However, the non-parallel pattern of CO$_2$ losses in blank experiments (Fig 3B) is inconsistent with a leak and instead argues for varying diffusivity of the polar molecule CO$_2$ through permeable material at different humidities. The observed degree of CH$_4$ loss from the system was unavoidable and had to be subtracted from the observed bulk CH$_4$ losses in experiments with enhanced radiation and soils to arrive at any specific losses that are due to radioactivity or presumed microbial methanotrophy.

There was a comparable loss of CH$_4$ in recirculating air for all experiments without soil, regardless of the absence or presence of radiation from $^{220}\text{Rn}$, $^{222}\text{Rn}$, or both $^{220}\text{Rn}$ and $^{222}\text{Rn}$, in dry or moist air (Fig 3A). The time needed to cross the ‘common window’ of CH$_4$ decline from 67.2 to 50.9 ppmv was not shorter when radiation from $^{220}\text{Rn}$ and/or $^{222}\text{Rn}$ was added (Table 1A, 1B). The slopes of lines representing CH$_4$ decline within the common window in Fig 3A were not higher for experiments with elevated radiation (mean ~0.38 ppmv h$^{-1}$) than for blank experiments without added radon isotopes (mean ~0.39 ppmv h$^{-1}$; Table 1A and 1B). The mean levels of added radiation from $^{220}\text{Rn}$, and especially the cumulative radiation in experiment #9 from simultaneously added $^{220}\text{Rn}$ and $^{222}\text{Rn}$, ranged between ~50 and 535 kBq m$^{-3}$ after doubling of experimental $^{220}\text{Rn}$ values that were measured at $\leq$0.2 L min$^{-1}$ (Table 1B) and thus always exceeded the radiation levels reported in cave air [26], including the air in all Spanish caves where abiotically driven CH$_4$ oxidation due to radiolysis has been
Radiolysis via radioactivity is not responsible for rapid methane oxidation in subterranean air.
Table 1. Overview on individual experiments performed at Indiana University to constrain the consumption of methane over time.

| Experiment # | Overall duration (h) | Common window (h) | $^{220}$Rn (kBq m$^{-2}$) | $^{222}$Rn (kBq m$^{-2}$) | CH$_4$ loss (ppmv h$^{-1}$) | CO$_2$ loss (ppmv h$^{-1}$) | Corrected temperature ($^\circ$C) | Relative humidity (%) | Pressure (kPa) |
|--------------|---------------------|------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|----------------------|---------------|
| (A) Duplicated blank experiments without added radon or thoron at low or high relative humidity |
| #1, no added radiation, dry | 86 | 42.0 | <0.01$^a$ | <0.01 | 0.39 ± 0.06 | 25.8 ± 14.1 | 23.2 ± 0.9 | 49.7 ± 1.5 | 97.2 ± 0.4 |
| #2, no added radiation, dry | 52 | 42.7 | <0.01$^a$ | <0.01 | 0.39 ± 0.07 | 47.6 ± 21.3 | 22.8 ± 0.4 | 54.7 ± 0.8 | 98.0 ± 0.1 |
| #3, no added radiation, wet | 69 | 42.5 | <0.2$^a$ | <0.4 | 0.39 ± 0.08 | 22.9 ± 23.0 | 23.4 ± 0.7 | 103 ± 2.7$^a$ | 98.1 ± 0.2 |
| #4, no added radiation, wet | 43 | 42.3 | <0.3$^a$ | <0.2 | 0.39 ± 0.07 | n.d. | 25.4 ± 0.7 | 95.3 ± 4.1 | 99.1 ± 0.1 |
| (B) Experiments with enhanced $^{220}$Rn and/or $^{222}$Rn concentrations at low or high relative humidity |
| #5, $^{220}$Rn added, dry | 82 | 42.4 | −50$^a$ | <0.01 | 0.38 ± 0.07 | 18.4 ± 14.2 | 22.9 ± 0.6 | 53.3 ± 2.7 | 98.6 ± 0.2 |
| #6, $^{220}$Rn added, wet | 75 | 41.8 | 143 | <0.01 | 0.39 ± 0.07 | 10.6 ± 15.0 | 22.8 ± 0.7 | 100.4 ± 2.1 | 98.9 ± 0.1 |
| #7, $^{222}$Rn added, dry | 87 | 43.8 | <0.01$^a$ | 153 | 0.37 ± 0.07 | 34.7 ± 35.3 | 24.3 ± 0.8 | 56.3 ± 2.2 | 98.8 ± 0.2 |
| #8, $^{222}$Rn added, wet | 88 | 44.5 | <0.04$^a$ | 216 | 0.37 ± 0.09 | 22.0 ± 29.9 | 25.1 ± 0.9 | 95.5 ± 4.1 | 98.4 ± 0.3 |
| #9, $^{222}$Rn and $^{220}$Rn added, wet | 87 | 43.5 | 208 | 327 | 0.37 ± 0.11 | 10.3 ± 27.9 | 25.8 ± 1.1 | 92.8 ± 3.4 | 98.4 ± 0.2 |
| (C) Experiments with moist soils without added radon or thoron |
| #10, no added radiation, 45 g soil #1 | 456 | 33.8 | <0.03$^a$ | <0.2 | 0.49 ± 0.09 | CO$_2$ was generated | 24.3 ± 0.8 | 100.6 ± 3.9 | 98.6 ± 0.2 |
| #11, no added radiation, 112 g soil #2 | 172 | 34.7 | −0.1$^a$ | −4 | 0.47 ± 0.11 | CO$_2$ was generated | 24.7 ± 0.9 | 97.9 ± 4.3 | 98.8 ± 0.1 |

Analytical data are mean values with standard deviations for the time window when CH$_4$ concentrations declined from 67.2 to 50.9 ppbv in each experiment. This window represents the common range of methane concentrations that is common to all experiments. The length of time needed to deplete methane from the upper to the lower threshold across the common window (i.e., yellow rectangle in Fig 3A) was interpolated from hourly spaced data.

$^a$ Radon radiation values were doubled when measured at flow rates <0.2 L min$^{-1}$ to adjust for fast $^{220}$Rn decay, instead of measurements without doubling of values in 10-min intervals (n ≥ 10) at a flow rate of 1 L min$^{-1}$. See justification in S1 File.

$^\circ$ High values of relative humidity are affected by analytical errors in excess of standard deviation. n.d. = not determined.

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with added radon isotopes (#5 through #9). Thus, in terms of radiation intensity, our experiments represent an extreme test of the radiolysis hypothesis. Only the air in shafts of underground uranium mines has been observed to reach even higher radiation levels of one million or more Bq m\(^{-3}\) [27].

The consistent pattern of CH\(_4\) decline in our experiments without soils can be better appreciated in light of the observed CO\(_2\) dynamics (Fig 3B). CO\(_2\) is more polar than CH\(_4\), can be more easily adsorbed on surfaces, and is more water-soluble and reactive than CH\(_4\). Therefore, it is possible that changes in room temperature (21.1 to 27.5˚C) and atmospheric pressure (96.7 to 99.3 kPa) may have affected adsorption and solubility of CO\(_2\) during our experiments. Moreover, after one week of measurements with a wet paper tissue in the 4-L glass flask without soil, fungi had discolored the paper tissue and metabolically generated CO\(_2\), thus partially stabilizing the CO\(_2\) partial pressure (experiment #6, Fig 3B), apparently without affecting the CH\(_4\) decline (Fig 3A). The paper tissue had been hung by a thread from the central glass stopcock to maximize surface area and to avoid any anoxic microenvironments that could facilitate biological methanogenesis (Fig 1). Subsequent experiments in moist air without soil replaced the wet paper tissue with added deionized water at the bottom of the 4-L glass flask. Experiments with soils initially generated CO\(_2\) via microbial and fungal remineralization of soil organic matter, followed after several days by a decline due to diffusive loss of CO\(_2\).

In the two experiments with moist soils, we documented a CH\(_4\) loss of of ~0.09 ppmv h\(^{-1}\) within the common window of CH\(_4\) concentration decline (Fig 3A), as determined by subtracting the diffusive CH\(_4\) loss in blank experiments from the bulk CH\(_4\) loss in experiments #10 and #11 with soils (Table 1). It is well established that heterogeneously distributed methanotrophic biofilms in the subsurface [28] are capable of scavenging CH\(_4\) from the atmosphere (e.g., [29, 30]). Soil gas can often reach \(^{222}\)Rn radiation levels of many thousand Bq m\(^{-3}\), depending on local geology [31, 32]. If radiolysis would indeed be able to trigger fast oxidative decay of CH\(_4\) in soil gas, such an important CH\(_4\) sink in dry soils without abundant methanotrophic activity would likely have been documented. Also, radiolysis would compete with methanotrophs in moist soils for CH\(_4\) and would have been identified as a factor in soil CH\(_4\) studies.

**Experiments in gas-tight terrarium at RHUL**

The first stage of experiment #1 at RHUL (Figs 2A and 4) established background conditions for the abundance of negative ions (~3800 ions cm\(^{-3}\)) and the concentration of \(^{222}\)Rn (17 to 51 Bq m\(^{-3}\)) in laboratory air at temperatures from 21.4 to 21.7˚C and relative humidities from 26.6 to 29.0%. After the onset of stage 2, the placement of pitchblende and a beaker with 130 mL, 38˚C warm water into the sealed terrarium strongly increased the abundance of negative ions in air (up to ~200,000 ions cm\(^{-3}\)) and the concentration of \(^{222}\)Rn (~118 kBq m\(^{-3}\)). The relative humidity exceeded 85%, and the air temperature intermittently rose by 5˚C. The measurement uncertainty of the Canary Pro radon monitor increased with the \(^{222}\)Rn radiation level (Fig 4). However, the factory-documented uncertainty at the highest measured radiation level and the steadily increasing abundance of negative ions in air suggested that after a run time of ~17 h, the \(^{222}\)Rn-based radiation level exceeded 100 kBq m\(^{-3}\) (Fig 4; data shown in S1 File).

Experiment #2 at RHUL (Fig 2B) used the same sealed terrarium with pitchblende and high humidity to monitor and compare the CH\(_4\) mole fractions in the air of both the terrarium and the outside laboratory air over ~77 h. The Canary Pro radon monitor in the terrarium indicated an increase in \(^{222}\)Rn over time parallel to RHUL experiment #1. After 5 h into RHUL experiment #2, the \(^{222}\)Rn-based radiation in the terrarium was consistently > 50 kBq m\(^{-3}\). Despite high levels of ionization and \(^{222}\)Rn-based radiation in the terrarium, the CH\(_4\) mole
The fraction of 1.9941 ± 0.0036 ppm in terrarium air after being sealed for ~77 h was indistinguishable from the starting value of 1.9971 ± 0.0122 ppm within the uncertainty of measurements (Table 2).

**Synopsis of combined results**

The absence of any experimental evidence for accelerated loss of CH₄ in the presence of elevated radiation makes it highly unlikely that radiation from radon isotopes is important in nature where ²²⁰Rn and ²²²Rn concentrations are typically much lower. Our data indicate that natural radiation in cave air cannot be responsible for the rapid consumption of CH₄ in air on timescales of days, even in caves with high relative humidity. The same conclusion had been reached from earlier laboratory experiments [18] and from observations in Australian cave air [15].

**Table 2. Results of experiment #2 at RHUL to assess the consumption of CH₄ over time in the presence of elevated ²²²Rn concentrations and high relative humidity.**

| Date        | Time | Sample            | CH₄ (ppm) | CH₄ st. dev. (ppm) | H₂O (vol. %) |
|-------------|------|-------------------|----------|-------------------|--------------|
| March 4, 2016 | 11:00 | Laboratory air    | 1.9760   | 0.0006            | 0.85         |
| March 4, 2016 | 11:15 | Initial terrarium air | 1.9971   | 0.0122            | 1.75         |
| March 4, 2016 | 13:15 | Laboratory air    | 1.9616   | 0.0005            | 0.81         |
| March 4, 2016 | 13:15 | Terrarium air     | 1.9873   | 0.0066            | 1.10         |
| March 4, 2016 | 16:00 | Laboratory air    | 1.9643   | 0.0006            | 0.85         |
| March 4, 2016 | 16:00 | Terrarium air     | 1.9818   | 0.0054            | 1.64         |
| March 7, 2016 | 16:05 | Laboratory air    | 1.9693   | 0.0007            | 0.77         |
| March 7, 2016 | 16:05 | Final terrarium air | 1.9941   | 0.0036            | 1.84         |

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Many caves experience seasonally different degrees of venting and even reversals of air flow, which results in differences in air temperature and humidity and is difficult to simulate in laboratory experiments. Still, most cave environments at sufficient distances from cave entrances and vent holes are thermally buffered by surrounding rock and therefore do not express the relatively high diurnal and seasonal temperature and humidity variations as outside environments. Our experiments in laboratories were conducted at relatively constant room temperatures similar to many cave environments. Room temperatures in air-conditioned laboratory buildings are similar to actual temperatures in sub-tropical and tropical caves [14]. The use of water and moist soil in many of our experiments simulated the range of humidity in natural cave air. One possible caveat in terms of dissimilarity between our laboratory settings and actual caves may be the fact that our experiments allowed daylight to reach our experimental setups. However, the amount and timing of indirect light (no direct sunshine) was insufficient to let any photoautotrophs (algae) observably grow in our experiments. A necessary difference between air in our experiments at IU and actual cave air was the presence of traces of CH$_4$. Some CH$_4$ was needed to test for possible radiolytic destruction of CH$_4$. In contrast, most natural cave air is depleted in CH$_4$ relative to outside air. We conclude that the experimental conditions during experiments at IU and RHUL were reasonable approximations to simulate cave conditions. In the open atmosphere, solar radiation is mainly responsible for the generation of OH$^\cdot$ radicals ([6], and refs. therein) that are the longest-lived potential radical reactant with CH$_4$ in air. Subterranean radiolysis by radioactivity involves far more energy than photochemical dissociation of molecules by solar radiation, hence the speciation of resulting ions and radicals is different. A host of highly energetic, short-lived ions and radicals other than OH$^\cdot$ is generated in subterranean air. The first abstraction of an H atom from CH$_4$ requires a far higher activation energy than those of H atoms from methyl CH$_3$ and methylene CH$_2$. We argue that cave environments with elevated radioactivity may host short-lived, yet highly energetic radicals and ions that can supply the needed activation energy for first H-abstraction from CH$_4$ more efficiently than OH$^\cdot$ in the open atmosphere. Thus, the application of kinetic and energetic findings of photochemical CH$_4$ oxidation in the open atmosphere may not be warranted for subterranean environments.

The $\alpha$-radiation level in cave air is typically higher than in the open atmosphere because cave air is relatively close to rock and sediment surfaces with minerals harboring radioactive nuclides. The ionization rate in air via $^{222}$Rn radon decay is larger close to the ground, as reported for a Finnish forest [33], a spa [34], and in houses [35]. The effect is due to (i) strongly elevated radon concentrations in the air in porous, uranium-containing substrates and the rapid dilution of radon above surfaces upon mixing with the open atmosphere, especially during windy conditions. In contrast, cave air far from cave entrances is typically less turbulent and allows for a more even distribution of $^{222}$Rn in cave air. (ii) Short-lived $^{220}$Rn will always exhibit a greater abundance in air close to its parent nuclides in soil, rock, cave walls and floors [19]. Regardless, even exceptionally high combined radiation levels of $^{220}$Rn and $^{222}$Rn provided no evidence for accelerated CH$_4$ oxidation in our experiments.

A plausible reason for slow radiolytic reaction kinetics is the mismatch between the large number of CH$_4$ molecules in 1 m$^3$ of atmosphere containing 1.85 ppmv CH$_4$ at standard conditions (i.e., ~4.55 $\cdot$ 10$^{19}$ molecules CH$_4$) relative to the small number of radon-related nuclear decay events in the same volume of air (e.g., 10 kBq m$^{-3}$ from $^{222}$Rn resulting from the decay of 10,000 atoms of $^{222}$Rn per second). The following simplistic numerical example illustrates the lack of feasibility of radiation-induced rapid oxidation of CH$_4$. If we assume that 1 m$^3$ of atmosphere entering a cave with 10 kBq m$^{-3}$, even if every decay of $^{222}$Rn leads to the oxidation of one molecule CH$_4$, it would require a geologic time period of ~144 million years to oxidize all CH$_4$. In reality, the nuclide-specific radiation from the decay of $^{222}$Rn alone is dwarfed by the...
total radiation from radon, thoron, their radioactive progeny, and any other radioactive nuclides present in a given environment [19]. S1 File offers alternative calculations based on the assumptions that either (i) all energy from α-decay is exclusively invested in radiolytic dissociation of CH$_4$ and results in the oxidation of multiple molecules of CH$_4$ per decay event, or (ii) that only a fraction of the energy from α-decay is dissociating CH$_4$ in the overwhelming presence of other molecules and atoms. The calculated time periods needed to degrade 1.85 ppmv CH$_4$ at a $^{222}$Rn radiation level of 10 kBq m$^{-3}$ range from 45.1 to 153,000 years, respectively. Even the most optimistic assumptions cannot speed up the radiolytic reaction kinetics to consume atmospheric CH$_4$ within hours to days.

We can use the most optimistic scenario for consumption of 1.85 ppmv CH$_4$ during 45.1 years at 10 kBq m$^{-3}$ and calculate a radiation level of ~165 MBq m$^{-3}$ that would be required to perform the same task in 24 h, which would be commensurate with kinetic CH$_4$ observations in caves. Natural radiation levels of a few MBq m$^{-3}$ have been measured in air where $^{222}$Rn emanates through geologic faults from underlying uranium minerals [36]. Radiation levels in the range of MBq m$^{-3}$ have been observed in the air of uranium mines [27]. Still, no location is known to offer values close to the required ~165 MBq m$^{-3}$. We conclude that there is no natural cave environment on earth where the α-radiation level is strong enough to rapidly degrade CH$_4$. The same conclusion was recently described in a study that included arguments based on radiolytic kinetics of ion-induced reactions [15] that complement our calculations using α-decay and activation energy.

Subterranean radiation does not provide a mechanism for a fast-acting sink of atmospheric CH$_4$ that would extend to arid and hyperarid environments, unlike microbial methanotrophy. Our study does not invalidate the geochemical data from previous studies documenting CH$_4$ dynamics in subterranean ecosystems [10]. We do not call into question the fundamental importance of radiolysis of H$_2$O (and other air components) and subsequent redox reactions that are documented in the geologic record (e.g., [37]) or the long-term subterranean radiolytic impact on sedimentary organic matter [1]. However, the exceedingly slow chemical rates of reaction caused by natural rates of radiolysis would likely take years to geologic time periods in cave environments to deplete trace amounts of atmospheric CH$_4$ in cave air. As long as no alternative mechanisms have been identified, microbial methanotrophy serves as the only known fast-acting sink for subterranean CH$_4$ in the critical and vadose zones.

**Conclusions**

Strong radiation from radon isotopes and subsequent radiolysis of air proved unable to rapidly oxidize methane in dry or moist air. In the absence of a feasible alternative methane oxidation mechanism other than microbial methanotrophy, further studies are needed on the ability of microbes to consume trace amounts of methane in poorly ventilated caves, even though the trophic and energetic benefits become marginal at very low partial pressures of methane.

**Supporting information**

S1 File. An Excel file contains a first sheet “read me” with instructions and an overview on additional sheets offering analytical details and radiolysis calculations. (XLSX)

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References

1. Greenwood PF, Shan C, Holman AI, Grice K. The composition and radiolysis impact on aromatic hydrocarbons in sedimentary organic matter from the Mulga Rock (Australia) uranium deposit. Org. Geochem. 2018; 123: 103–112. https://doi.org/10.1016/j.orggeochem.2018.06.013

2. Colwell FS, D’Hondt S. Nature and extent of the deep biosphere, Rev. Mineral. Geochem. 2013; 75: 547–574. http://dx.doi.org/10.2138/rmg.2013.75.17

3. Colman DR, Poudel S, Stamps BW, Boyd ES, Spear JR. The deep, hot biosphere: Twenty-five years of retrospection. PNAS 2017; 114 (27): 6895–6903. https://dx.doi.org/10.1073/pnas.1701266114 PMID: 28674200

4. Xu X, Yuan F, Hanson PJ, Wullschleger SD, Thornton PE, Riley WJ, et al. Reviews and syntheses: Four decades of modeling methane cycling in terrestrial ecosystems. Biogeosciences 2016; 13: 3735–3755. https://dx.doi.org/10.5194/bg-13-3735-2016
5. IPCC. Climate Change 2013: The Physical Science Basis, Figure SPM.5 of the Summary for Policy-makers; 2013. http://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5_SPM_FINAL.pdf (accessed on September 4th, 2018)

6. Prather MJ, Holmes CD. Overexplaining or underexplaining methane's role in climate change. PNAS 2017; 114 (21): 5324–5326. https://dx.doi.org/10.1073/pnas.1704884114 PMID: 28507153

7. Edwards CR, Onstott TC, Miller JM, Wiggins JB, Wang W, Lee CK, et al. Draft genome sequence of uncultured upland soil cluster Gammaproteobacteria gives molecular insights into high-affinity methanotrophy. Genome Announc. 2017; 5: e00047–17. https://doi.org/10.1128/genomeA.00047-17 PMID: 28450499

8. Waring CL, Griffith DWT, Wilson S, Hurry S. Cave atmosphere: A guide to calcification and a methane sink. Geochim. Cosmochim. Acta 2009; 73 (13): A1419–A1419. http://apo.ansto.gov.au/dspace/handle/10238/2461?mode=full (accessed on September 4th, 2018)

9. Mattey DP, Fisher R, Atkinson TC, Latin JP, Durrell R, Ainsworth M, et al. Methane in underground air in Gibraltar karst. Earth Planet. Sci. Lett. 2013; 374: 71–80. http://dx.doi.org/10.1016/j.epsl.2013.05.011

10. Fernandez-Cortes A, Cuevas S, Alvarez-Gallego M, Garcia-Anton E, Pla C, Benavente D, et al. Subterranean atmospheres may act as daily methane sinks. Nat. Commum. 2015; 6: 7003. https://dx.doi.org/10.1038/ncomms8003 PMID: 25912519

11. McDonough LK, Iverach CP, Beckmann S, Manefield M, Rau GC, Baker A, et al. Spatial variability of cave-air carbon dioxide and methane concentrations and isotopic compositions in a semi-arid karst environment. Environ. Earth Sci. 2016; 75: 700. http://dx.doi.org/10.1007/s12665-016-5497-5

12. Webster KD, Mirza A, Deli JM, Sauer PE, Schimmelmann A. Consumption of atmospheric methane in a limestone cave in Indiana, USA. Chem. Geol. 2016; 443: 1–9. https://dx.doi.org/10.1016/j.chemgeo.2016.09.020

13. Webster KD, Drobnia A, Etiope G, Mastalerz M, Sauer PE, Schimmelmann A. Subterranean karst environments as a global sink for atmospheric methane. Earth Planet. Sci. Lett. 2018; 485: 9–18. https://doi.org/10.1016/j.epsl.2017.12.025

14. Nguyễn-Thùy D, Schimmelmann A, Nguyễn-Văn H, Drobnia A, Lennon JT, Та PH, et al. Subterranean microbial oxidation of atmospheric methane in cavernous tropical karst. Chem. Geol. 2017; 466: 229–238. https://doi.org/10.1016/j.chemgeo.2017.06.014

15. Waring CL, Hankin SI, Griffith DWT, Kertesz MA, Kobylski V, Wilson NL, et al. Seasonal total methane depletion in limestone caves. Sci. Rep. 2017; 7: 8314. https://dx.doi.org/10.1038/s41598-017-07769-6 PMID: 28814720

16. Haynes RM, Kebarle P. Mass-spectrometric study of ions at near-atmospheric pressure. III. The alpha radiolysis of methane. J. Chem. Phys. 1966; 45 (11): 3899–3906. https://doi.org/10.1063/1.1727435

17. Rasul G, Prakash GKS, Olah GA. Comparison of structures and energies of CH52+• with CH4+• and their possible role in superacidic methane activation. PNAS 1997; 94 (21): 11159–11162. https://dx.doi.org/10.1073/pnas.94.21.11159 PMID: 11038583

18. Lennon JT, Nguyễn-Thùy D, Pham TM, Drobnia A, Та PH, et al. Microbial contributions to subterranean methane sinks. Geobiology 2017; 15 (2): 254–258. https://dx.doi.org/10.1111/gbi.12214 PMID: 27671735

19. Meisenberg O, Mishra R, Joshi M, Gierl S, Rout R, Guo L, et al. Radon and thoron inhalation doses in dwellings with earthen architecture: Comparison of measurement methods. Sci. Total Environ. 2017; 579: 1855–1862. http://dx.doi.org/10.1016/j.scitotenv.2016.11.170 PMID: 27939079

20. Markkanen M, Arvela H. Radon emanation from soils. Radiat. Prot. Dosimetry 1992; 45 (1–4), 269–272. https://doi.org/10.1093/oxfordjournals.rpd.a081541

21. Morawska L, Phillips CR. Dependence of the radon emanation coefficient on radium distribution and internal structure of the material. Geochim. Cosmochim. Acta 1993; 57 (8): 1783–1797. https://doi.org/10.1016/0016-7037(93)90113-B

22. Hursh JB. Thoron half-life. J. Inorg. Nucl. Chem. 1966; 28 (12): 2771–2776. https://doi.org/10.1016/0022-1902(66)80001-5

23. Wang J, Meisenberg O, Chen Y, Karg E, Tschiersch J. Mitigation of radon and thoron decay products by filtration. Sci. Total Environ. 2011; 409 (19): 3613–3619. https://doi.org/10.1016/j.scitotenv.2011.06.030 PMID: 21767867

24. Oremland RS, Capone DG. Use of “specific” inhibitors in biogeochemistry and microbial ecology. In: Marshall KC, editor. Advances in Microbial Ecology 10 (ch. 8), Plenum Publishing Corporation; 1988. p. 335. https://doi.org/10.1007/978-1-4684-5409-3_8
25. Farhan Ul Haque M, Crombie AT, Ensminger SA, Baciu C, Murrell JC. Facultative methanotrophs are abundant at terrestrial natural gas seeps. Microbiome 2018; 6: 118. https://doi.org/10.1186/s40168-018-0500-x PMID: 29954460

26. Cigna AA. Radon in caves. Int. J. Speleol. 2005; 34 (1–2): 1–18. http://scholarcommons.usf.edu/cgi/viewcontent.cgi?article=1203&context=ijs (accessed on September 4th, 2018)

27. Wismut GmbH and MECSEK-ÖKO. Annual Report 2010 on the Cooperation between Wismut GmbH and MECSEK-ÖKO. 2011; p. 24–26. https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=3&ved=2ahUKEwjm7rrq5JrdAhWF34MKHScrBTQQFjACegQICBAC&url=http%3A%2F%2Fgov.pecs.hu%2Fdownload%2Findex.php%3Fid%3D309232&usg=AOvVaw0u7IRhg7ZYyU2tGyshAXy (accessed on September 4th, 2018)

28. Yan Z, Liu C, Liu Y, Bailey VL. Multiscale investigation on biofilm distribution and its impact on macroscopic biogeochemical reaction rates. Water Resour. Res. 2017; 53 (11): 8698–8714. https://dx.doi.org/10.1002/2017WR020570

29. Mancinelli RL. The regulation of methane oxidation in soil. Annu. Rev. Microbiol. 1995; 49: 581–605. https://doi.org/10.1146/annurev.mi.49.100195.003053 PMID: 8561473

30. Conrad R. Microbial ecology of methanogens and methanotrophs. Adv. Agron. 2007; 96: 1–63. https://doi.org/10.1016/S0065-2113(07)96005-8

31. Lindmark A, Rosen B. Radon in soil gas—Exhalation tests and in situ measurements. Sci. Total Environ. 1985; 45: 397–404. https://doi.org/10.1016/0048-9697(85)90243-8 PMID: 4081740

32. Papastefanou C. Measuring radon in soil gas and groundwaters: a review. Annals Geophys. 2007; 50 (4): 569–578. http://www.annalsofgeophysics.eu/index.php/annals/article/download/3070/3113 (accessed on September 4th, 2018)

33. Tammet H, Hörrak U, Laakso L, Kulmala M. Factors of air ion balance in a coniferous forest according to measurements in Hyytiälä, Finland. Atmos. Chem. Phys. 2006; 6: 3377–3390. https://doi.org/10.5194/acp-6-3377-2006

34. Cosma C, Suciu I, Jäntsch L, Bolboacă SD. Ion-molecule reactions and chemical composition of emanated from Herculean Spa geothermal sources. Int. J. Mol. Sci. 2008; 9 (6): 1024–1033. https://dx.doi.org/10.3390/ijms9061024 PMID: 19325844

35. Kolarz PM, Filipović DM, Marinković BP. Daily variations of indoor air-ion and radon concentrations. Appl. Radiat. Isot. 2009; 67 (11): 2062–2067. https://doi.org/10.1016/j.apradiso.2009.07.023 PMID: 19700332

36. Seyis C, İnan S, Streil T. Ground and indoor radon measurements in a geothermal area. Acta Geophys. 2010; 58 (5): 939–946. https://link.springer.com/article/10.2478/s11600-010-0012-y

37. Lefticariu L, Pratt LA, LaVerne JA, Schimmelmann A. Anoxic pyrite oxidation by water radiolysis products—A potential source of biosustaining energy. Earth Planet. Sci. Lett. 2010; 292 (1–2): 57–67. https://dx.doi.org/10.1016/j.epsl.2010.01.020