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Characterization and microbial mitigation of fugitive methane emissions from oil and gas wells: Example from Indiana, USA

Yidong Yin [a,*], Maria Mastalerz [b], Jay T. Lennon [c], Agnieszka Drobniak [b], Arndt Schimmelmann [a]

[a] Department of Earth and Atmospheric Sciences, Indiana University, 1001 E. 10th St., Bloomington, IN, 47405, USA
[b] Indiana Geological and Water Survey, 611 N. Walnut Grove Ave., Bloomington, IN, 47405, USA
[c] Department of Biology, Indiana University, 1001 E. 3rd St., Bloomington, IN, 47405, USA

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ABSTRACT

Hydrocarbon gas emissions from active, inactive, and improperly sealed or abandoned oil/gas wells significantly contribute to anthropogenically emitted greenhouse gases, predominantly in the form of methane (CH_4). We explored the extent of hydrocarbon gas emissions from 20 active, inactive, plugged and abandoned oil/gas wells in Indiana (USA), where it is estimated that there are more than 80,000 well sites throughout the state. After this initial survey, using a static flux tent, we quantified fugitive CH_4 emissions from an active gas well to approximately 2 L h^{-1}. To evaluate the potential for microbial mitigation of hydrocarbon emissions to the atmosphere, we conducted laboratory microcosm experiments to quantify the CH_4 oxidizing potential of soils collected from sites with varying distances to the leaking gas well. Soils in close proximity to the well (0.5 m) efficiently consumed nearly all (97%) of the added CH_4, while only 14% of added CH_4 was consumed by soils that were more distant from the well (20 m). These results suggest that fugitive CH_4 emissions enrich methanotrophic bacteria in soils immediately adjacent to the well. Consistent with this view, we found that prolonged exposure of soils to elevated concentrations of CH_4 enhanced the methanotrophic activity. Together, these findings prompted us to design a "methanotrophic soil mound" to assess the feasibility of mitigating point sources of CH_4 by harnessing the natural methanotrophic capacity of soil microbial communities. We found that a methanotrophic soil mound from a landfill could sustainably mitigate the CH_4 emission from the artificial source, providing a promising low-cost solution to ameliorate fugitive CH_4 emissions from abandoned oil and gas wells to the atmosphere. The effectiveness of microbe-based remediation is limited in cold climates and arid environments.

1. Introduction

A major contributing factor to global climate change is the increased supply of greenhouse gases, especially carbon dioxide (CO_2) and methane (CH_4), to the atmosphere, which is associated in part with the processing and combustion of fossil fuels (e.g., coal, oil, natural gas). CH_4 ranks as the third most important atmospheric greenhouse gas contributing to global warming after water vapor and CO_2 and currently accounts for 15–20% of global warming (Shindell et al., 2009; Van Amstel, 2012; Uhlig et al., 2018). However, on a molar level, the radiative forcing potential of CH_4 is 34 and 86 times more potent than that of CO_2 on 100-year and 20-year time horizons, respectively (Peischl et al., 2015; Etminan et al., 2016). The global CH_4 concentration in the troposphere has increased ~2.5–3.0 fold since the preindustrial era (Keppler et al., 2006; Hendrick et al., 2016). Global atmospheric CH_4 concentrations have increased rapidly since 2014 and recently reached an all-time high (Deaton, 2020; NOAA, 2020). Activities associated with the oil and gas industry are largely responsible for the recent global rise in CH_4 emissions (NASA, 2018).

Fugitive CH_4 emissions to the atmosphere result from the oil and natural gas industrial supply chain. For example, CH_4 is released from a range of processes including exploration, drilling and completion, extraction, processing, storage and distribution of oil and natural gas, routine operation of venting and transport installations, and improper sealing and abandonment of oil/gas wells (Van Amstel, 2012; Etiope et al., 2013; Karion et al., 2013; Vielstädte et al., 2015; Hendry et al., 2016; Kang et al., 2016; Laurenzi et al., 2016; Townsend-Small et al., 2016; Schout et al., 2019). Although with large uncertainty, CH_4 flux

* Corresponding author.
E-mail addresses: yid_yin@alumni.iu.edu (Y. Yin), mmastale@indiana.edu (M. Mastalerz), lennonj@indiana.edu (J.T. Lennon), agdrobni@indiana.edu (A. Drobniak), aschimme@indiana.edu (A. Schimmelmann).

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from oil/natural gas extraction and processing amounted to 79 Tg yr^{-1} in 2003–2012 and is considered the second largest source of the total anthropogenic CH_4 emission flux of 352 Tg yr^{-1} (Saunois et al., 2016, Table S1). Owing to CH_4's tenfold shorter residence time in the atmosphere than CO_2, the mitigation of anthropogenic CH_4 emissions would be effective and beneficial to limit near-term global warming (Dlugokencky et al., 2011; Howarth et al., 2011; Alvarez et al., 2018). Therefore, it is imperative to identify and reduce industrial CH_4 emissions to mitigate climate change and limit global warming.

CH_4 can be aerobically metabolized and oxidized to CO_2 by CH_4-oxidizing microbes (methanotrophs). Methanotrophs use CH_4 as their sole carbon and energy source (Iverach et al., 2017). Methanotrophic bacteria inhabit soils in forests, grasslands, heathlands, tundras, and deserts, as well as subterranean environments such as caves, serving as the only significant biological sinks for atmospheric CH_4 (Roslev et al., 1997; Henckel et al., 2000; Van Amstel, 2012; Lennon et al., 2017; Ni and Groffman, 2018; Webster et al., 2018; Zhou et al., 2018). Soils can act as a net sink of CH_4 with an estimated uptake flux of 28–38 Tg yr^{-1} in 2003–2012, which accounts for 5–7% of the total CH_4 sink (Saunois et al., 2016). As such, methanotrophs play an important role in modulating the global CH_4 budget and mitigating global warming. Slowly leaking CH_4 from natural seepages is known to be partly consumed by methanotrophs in soils around those seepages before it can reach the atmosphere (Henckel et al., 2000; Farhan UI Haque et al., 2018; Schimmelmann et al., 2018). Methanotrophic bacteria with high activity may have established themselves in soils over and near CH_4 seepages with a high and continuous supply of CH_4 (Kallistova et al., 2005). Therefore, soils enriched in methanotrophs above and near hydrocarbon seepages have a potential to mitigate hydrocarbon gas emissions from leaking oil/gas wells. For example, methanotrophic bacteria in the soil in termite mounds can oxidize 20–80% of termite-produced CH_4 before its emission to the atmosphere (Nauer et al., 2018).

According to the Petroleum Database Management System (PDMS) of the Indiana Geological and Water Survey (IGWS), there are more than 80,000 active, inactive, temporarily abandoned and permanently plugged oil and gas wells in the state of Indiana (USA) alone. Most oil and gas wells in Indiana and many other states in the USA predate legal and environmental requirements or even registration with state authorities (e.g., permitting by state geological surveys). The extent of fugitive hydrocarbon emissions from oil/gas wells to the atmosphere has not been as well studied in Indiana as it has been in other states in the USA (Pétron et al., 2014; Kang et al., 2014, 2016; Riddick et al., 2019). With this large number of oil and gas wells in Indiana, there were three major objectives of this study. First, we assessed the extent of fugitive CH_4 emissions from Indiana oil/gas wells. We selected 20 active or abandoned oil/gas wells across Indiana and quantified the fugitive CH_4 emission from an active gas well (IGS ID 125487) near Bloomington, Indiana using a static flux tent (see Kang et al., 2014). Second, we quantified and compared the methanotrophic activities of soils in the vicinity of an active gas well. Third, we evaluated the feasibility of methanotrophic soil mounds inoculated with methanotrophs from a landfill to mitigate CH_4 emissions above leaking oil/gas wells.

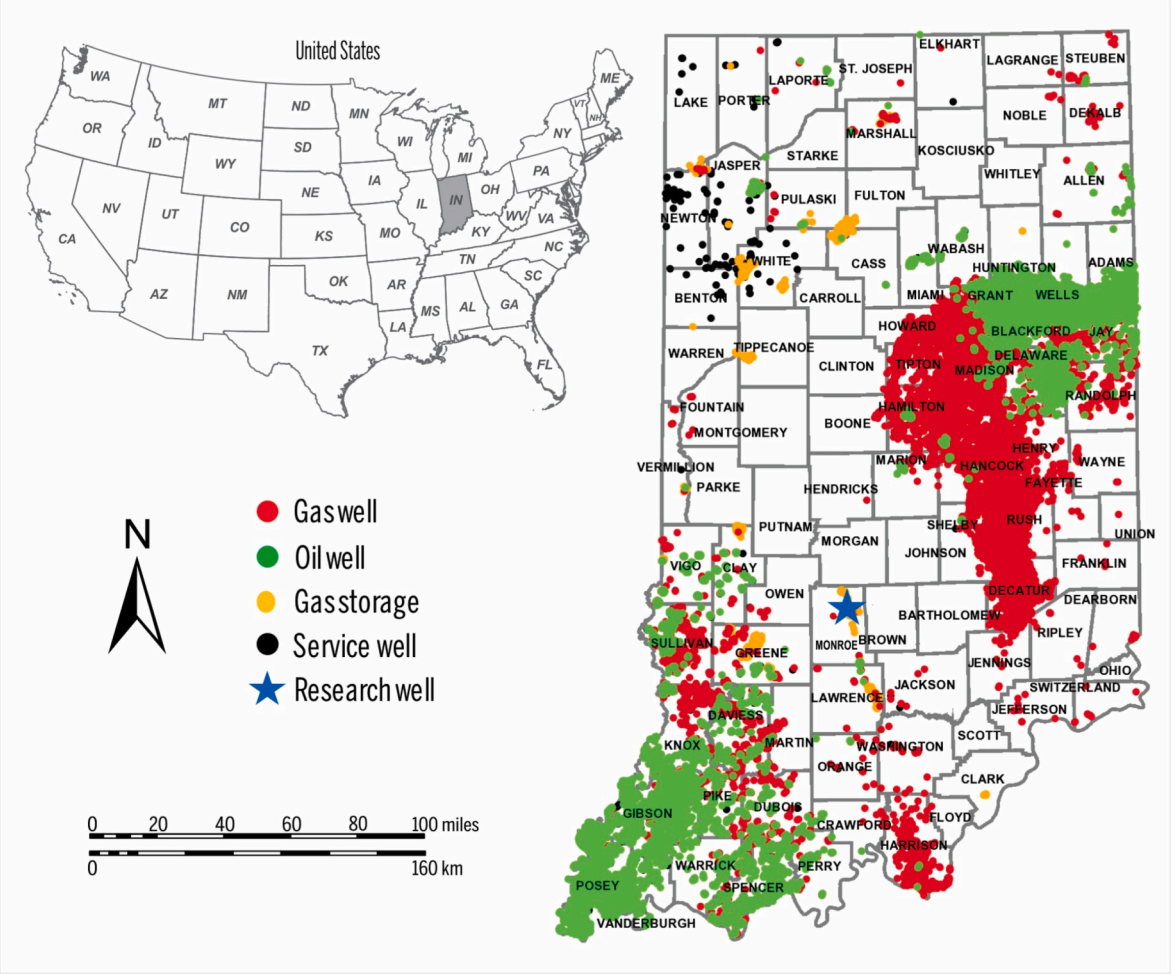

Fig. 1. Distribution of oil/gas wells in Indiana from the Petroleum Database Management System (PDMS) of the Indiana Geological and Water Survey (IGWS). Leaking active gas well IGS ID 125487 north of Bloomington in Monroe County is marked by a blue star. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

CH_4-emitting landfills contain soils exhibiting strong, yet patchy methanotrophy (Kallistova et al., 2005).

2. Methodology

2.1. Research area

The Petroleum Database Management System (PDMS) of the IGWS has a record of 83,798 oil/gas wells in Indiana, 12,736 of which are active wells (Fig. 1). The well records of the Indiana Department of Natural Resources indicate 233 inactive, 513 orphaned, 18,550 plugged and abandoned, and 45,707 temporarily plugged oil/gas wells in Indiana. We investigated 20 active, temporarily deactivated or plugged-abandoned oil/gas wells across Monroe, Daviess and Sullivan counties in Indiana (Table 1). The selected wells are located in well known oil and gas fields in Indiana, had reliable location information in the database, and could be accessed from nearby roads.

We used a Fisher M-97 metal detector (Escondido, California) to locate remaining metal pieces of abandoned oil/gas wells on and below ground. However, locating abandoned wells in the field proved to be exceedingly difficult when well fittings were deeply buried and precise locations were not known. Plowing of fields and regrowth in forests have concealed many former well locations beyond recognition. Current technology presents challenges when locating leaking abandoned wells. However, we can expect that future remote sensing technologies, probably in connection with drones, will improve our ability to economically and efficiently detect CH_4 point sources in the field. Geochemical tracers in streams may point to leaking gas wells (Grieve et al., 2018). Instead of selecting an abandoned well, we chose a leaking active gas well (IGS ID 125487) north of Bloomington in Monroe County as a site for quantifying fugitive CH_4 emission and testing for methanotrophic activity (i.e. the extent of microbial CH_4 oxidation) in surrounding soils. The well has been producing natural gas from the Ordovician Black River Formation and serves as an observation well above a natural gas storage reservoir since 1975.

Table 1
Details of 20 investigated oil/gas wells across Indiana.

Well No.	IGS ID	County	Symbol[a]	Reported depth (m)	CH_4 in surrounding air (ppm by vol.)
1	125,457	Monroe	GSG	250.5	1.9–2.1
2	125,486	Monroe	OBG	217.0	1.1–1.8
3	125,487	Monroe	OBS	640.7	1.8–12.9
4	125,523	Monroe	DRY	211.5	1.2–2.0
5	125,466	Monroe	OBS	281.3	2.4–2.8
6	125,468	Monroe	DRY	251.2	2.6
7	101,606	Daviess	OIL	204.5	1.4
8	101,607	Daviess	WIO	320.0	1.4–1.5
9	101,668	Daviess	OIL	198.7	1.9
10	162,349	Daviess	OIL	187.5	~25
11	160,310	Daviess	OIL	581.9	1.8
12	101,602	Daviess	WIO	320.0	1.9–2.4
13	101,605	Daviess	OIL	320.0	2.5
14	120,316	Sullivan	OIL	72.5	>96.5 [b]
15	120,267	Sullivan	OIL	74.4	0
16	163,253	Sullivan	GAS	65.5	0
17	unknown	Sullivan	GAS	unknown	4.0
18	163,228	Sullivan	GAS	64.6	0
19	165,127	Sullivan	GAS	224.6	0
20	unknown	Sullivan	AGAS	unknown	0

[a] Acronyms are defined by the Petroleum Database Management System of the Indiana Geological and Water Survey: "GSG" = gas well to gas storage, "OBG" = gas well to observation well, "OBS" = observation well, "DRY" = dry hole, "OIL" = oil well, "WIO" = oil well to water injection, "GAS" = gas well, "AGAS" = abandoned gas well.

[b] CH_4 concentration in air exceeded 96.5 ppm.

2.2. Quantification of CH_4 emissions

The active gas well (IGS ID 125487) north of Bloomington expressed leakage through above-ground fittings rather than through a CH_4 leak along an imperfectly cemented well string below surface. We measured CH_4 emission using a static flux tent. We constructed a polyethylene foil tent to completely enclose all above-ground fittings of the gas well (Fig. 2A). The tent had a triangular cross section of ca. 0.12 m^2 and a length of 6.0 m. The bottom of the polyethylene tent was ballasted by stones to seal against the ground around the perimeter of the tent. A 12-V DC fan was operated within the tent to generate turbulence and homogenize the CH_4 concentration in tent air. Prior to measuring, the air in the tent was vented by flapping one section of the tent, followed by re-ballasting the base of the tent. The air from within the tent was sampled through a Tygon® tube into a membrane pump in a SARAD RTM 2200 instrument (SARAD GmbH, Dresden, Germany) and CH_4 concentrations were determined over time with an Axetris Laser OEM Module LGC F200 CH_4 detector (Kagiswil, Switzerland). The maximum and minimum CH_4 concentrations that could be measured with this instrument were 96.5, 0.1 ppm (i.e. parts per million) by volume, respectively. We detected significant CH_4 emissions only between metal pipes and fittings at the two distal ends of the well structure (Fig. 2A). The southern end had the strongest CH_4 leakage. To differentiate between the CH_4 emissions from the two ends, we built two separate smaller polyethylene foil tents to enclose individual ends. Fig. 2B shows the tent enclosing the southern strong leak.

CH_4 emissions were quantified under different weather conditions (i.e. air temperature, air pressure, humidity). We recorded the relative humidity and air pressure with a SARAD RTM 2200 instrument along with air temperature using a portable Garmin 64st GPS (B&H, New York, NY). The CH_4 concentration in each tent increased linearly over time within the range of our measurements (0–96.5 ppm by volume). The CH_4 emission rate in the tents was derived using the following formula:

$$R = k\ V\ 3.6 \quad (1)$$

where R is the CH_4 emission rate (L h^{-1}), k is the slope of CH_4 concentration change over time in the tent (mL m^{-3} s^{-1}), and V is the volume of the polyethylene tent (m^3).

2.3. Microcosm experiments

Laboratory microcosm experiments were conducted to assess the CH_4 oxidation rates of soil samples from underneath and near the fittings of the leaky gas well. We collected soil from the surface of the ground directly underneath the fittings of the leaky well and 20 m away from the well (i.e. control soil) to evaluate their comparative methanotrophic activities. Soils were stored at 4 °C until their deployment in triplicate microcosm experiments in pre-annealed and butyl septum-stoppered 70-mL glass culture bottles in contact with a CH_4-enhanced standard atmosphere in the headspace of each bottle. CH_4 from a natural gas outlet in the laboratory was collected using a glass syringe (BD, Franklin Lakes, New Jersey) and injected into the headspace of each culture bottle immediately prior to septum-sealing at ambient atmospheric pressure, thus increasing the CH_4 partial pressure in the headspace of each experiment. Initial and remaining CH_4 concentrations over time in headspace gases of culture bottles were quantified using a SARAD RTM 2200 instrument with an Axetris CH_4 detector. For each measurement, an aliquot of 1 mL of headspace air was sampled each time from the bottles using a 1-mL BD syringe and injected into the inlet of the SARAD instrument to determine the CH_4 concentration. 1-mL of room air was injected into the bottles before each sampling to keep the air pressure constant in culture bottles. Experiments in bottles without soil and with dry soil proved that diffusional loss of CH_4 through septa and repeated sampling of 1-mL aliquots did not significantly affect the measurements.

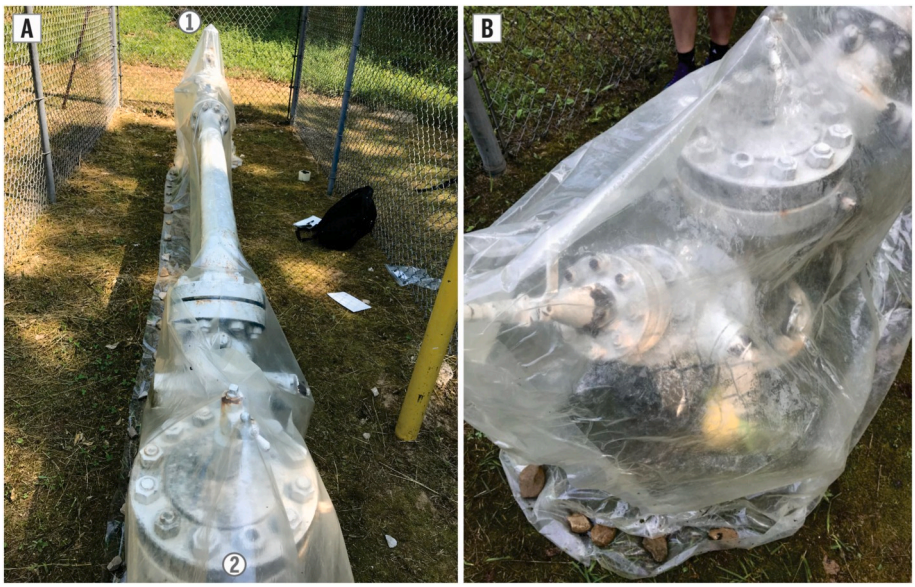

Fig. 2. A: Initial long polyethylene tent enclosing all fittings of the leaky gas well (IGS ID 125487) north of Bloomington, Indiana. 1 – northern end, 2 – southern end; B: Polyethylene tent enclosing the strongly leaking southern end of the gas well.

To test whether prolonged exposure of soils from a leaking well to elevated concentrations of CH_4 enhances the activity of methanotrophs in soils, we exposed control soil samples to an elevated CH_4 concentration in culture bottles for one month and then measured their methanotrophic activities in triplicate to test whether the microbes were conditioned and became more effective at oxidizing CH_4. In addition, the effect of soil moisture on methanotrophic activity of soils was tested. We homogenized soil samples collected adjacent to the leaky well and subdivided the soil into multiple aliquots. The original moisture content was 32 wt % (determined by drying a pre-weighed aliquot for 48 h and reweighing). Multiple aliquots of the soil were prepared as a series of soil samples with moisture contents of 0, 16, 24, 32, 40, 48, and 64 wt % water, followed by deployment in triplicate microcosm experiments and determination of their methanotrophic activities at room temperature, i.e. 20.5 °C (see Table 2).

2.4. Artificial soil mound experiments

We experimentally tested the feasibility of "methanotrophic soil mounds" over CH_4 seeps to reduce CH_4 emissions into the atmosphere. A CH_4 seep was simulated in the laboratory by placing the end of a Teflon™ capillary tubing with a regulated flow of 99.7 vol % pure CH_4 (Scientific Specialties, Hanover, Maryland) at the bottom of a polyethylene bucket without lid that was positioned in a 0.903 × 0.462 × 0.358 m plexiglass terrarium with lid (Fig. 3A). Regulated by a control valve (Fig. 3B), the CH_4 flow first passed through a bubble counter made of glass before being directed into the capillary. The CH_4 flux of the artificial CH_4 seep at the bottom of the bucket was linearly related to the number of gas bubbles per minute (linear regression $y = 12.39\ x$, where y is the flux in mL h^{-1} and x is the number of bubbles per minute; Fig. 1S). The CH_4 inflow rate from the Teflon™ capillary was set at 74 mL h^{-1} (i.e. approx. 6 bubbles min^{-1}) for all soil mound experiments and kept constant for days to weeks. The end of the Teflon™ capillary at the bottom of the bucket was first covered with a highly permeable layer of small rocks with an average diameter of ca. 3 cm and a rock layer with a height of ca. 10 cm. The rock mound was covered by a layer of soil with a thickness of ca. 5 cm. The soil was either derived from 20 m away from the leaky gas well north of Bloomington, Indiana (Fig. 3C) or from a solid waste landfill enriched in methanotrophic bacteria in Bloomington (39.28° N, 86.47° W). The base diameter of the circular mound in the bucket was 0.26 m. A low-velocity AC fan was used to homogenize the CH_4 concentration inside of the terrarium. At time zero of each CH_4 measurement, the terrarium air with a volume of 149.4 L was exchanged with room air at an ambient CH_4 concentration of ca. 2 ppm by volume. After sealing the perimeter of the terrarium's lid with tape, and leaving a small vent at the cable/tube feedthrough to prevent overpressure, air from the inside of the terrarium was admitted through a Tygon® tube into a SARAD RTM 2200 instrument with an Axetris CH_4 detector. The CH_4 concentration was recorded every minute until it reached the maximum value that could be measured with our instrument (96.5 ppm by volume). The methanotrophic activity of the soil mound was proportional to the amount of time needed to reach 96.5 ppm by volume of CH_4 in terrarium air. We then used the amount of time needed to reach 96.5 ppm by volume CH_4 as a proxy for the CH_4 oxidation rate of the soil mound.

To test whether prolonged exposure of a soil mound to enhanced levels of CH_4 increases methanotrophic activity through conditioning of methanotrophs, we built a mound in a bucket using control soil from 20 m away from the leaky gas well north of Bloomington and placed the open bucket into the semi-closed terrarium (Fig. 3D). The air in the terrarium was enriched with CH_4 to 85 ppm by volume at room temperature (20.5 °C) for eight days, after placing a Teflon™ capillary tubing with a flow of CH_4 in the terrarium. The CH_4 flow and the partial closure of the terrarium lid were simultaneously adjusted to keep the CH_4 concentration in terrarium air at 85 ppm, as monitored by the SARAD instrument. The methanotrophic activity of the soil mound was assessed in the terrarium at the onset of the experiment (i.e. day zero), after 1 day, and after 8 days. The evaporative loss of water from the soil was compensated by intermittent addition of deionized water to maintain the weight of the bucket containing the soil mound, which therefore kept the soil moisture constant at ca. 20 wt % during the experimental

Table 2
Initial setups of microcosm experiments in 70-mL culture bottles.

Experiment	Soil used	Soil mass (g)	Added CH_4 (mL)
#1	Well soil[a], Control soil[b]	4.0	0.5
#2	Control soil[b]	15	1.5
#3	Control soil[b]	4.0	0.5
#4	Well soil[a]	2.7	2.0

[a] Soil from directly underneath the fittings of the leaky gas well.
[b] Soil from a distance of 20 m from the leaky gas well.

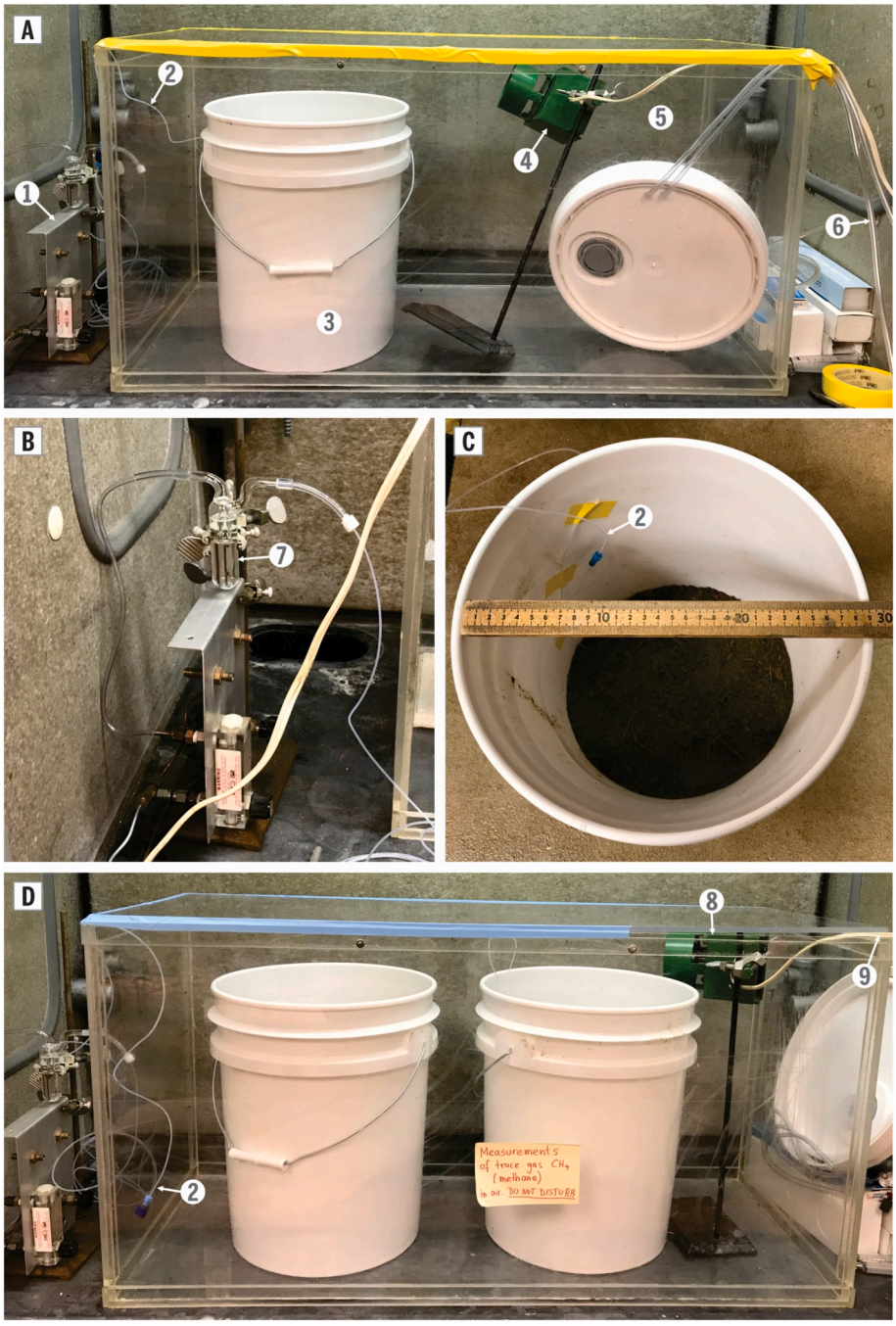

Fig. 3. A: Soil mound experiment in a terrarium. Control unit (1) regulating the CH_4 flow to the Teflon™ capillary (2). A bucket (3) holds the mound. A low-velocity AC fan (4) homogenized the air in the terrarium (5). Air from the terrarium is sampled through Tygon® tubing (6); B: CH_4 control unit featuring a bubble counter (7). C: Mound in bucket covered with soil. The Teflon™ capillary (2) directs the flow of CH_4 to the bottom of the bucket, below the mound; D: Experiment for prolonged exposure of soils in buckets to 85-ppm CH_4 in the terrarium. The Teflon™ capillary (2) directs a slow flow of CH_4 into the terrarium, while the lid of the terrarium has a gap (8) on the right side, kept open by the power cable of the AC fan (9). The regulated balance of CH_4 supply and leakage keeps the CH_4 concentration in the terrarium at 85 ppm.

sequence.

3. Results and discussion

3.1. CH_4 emissions from Indiana oil/gas wells

3.1.1. Field investigation

Among 20 active, temporarily deactivated or plugged-abandoned oil/gas wells we investigated in Indiana, 11 wells had a CH_4 concentration in ambient air surrounding their well fittings at or below the typical ambient environmental CH_4 concentration (ca. 2 ppm), indicating that these wells have no significant CH_4 leaks. The measured CH_4 concentration in air next to the fittings of the 20 investigated wells and their basic parameter information are listed in Table 1. We note that leakage from oil and gas wells can be episodic and that single measurements of atmospheric CH_4 concentrations in the vicinity of wells do not provide conclusive evidence for either the absence or the absolute flux of CH_4 over time.

Our initial field work focused on abandoned wells and their locations as reported in official records. The following description offers examples of problems encountered during our field survey. The exact location of abandoned well IGS ID 125523 could not be located in the field, in part owing to unrelated metallic covers on the ground over water-filled concrete pipes that interfered with our ability to use a metal detector for identifying the well's precise location. However, the location was known with sufficient precision to warrant measurements of CH_4 in air surrounding the suspected location. Some abandoned wells like IGS ID 125468 were located within forests where newly grown trees and abundant metallic debris prevented the identification of the original well sites. Abandoned wells IGS ID 101602 and IGS ID 101605 gave no

above-ground indication of their former existence and atmospheric CH_4 measurements in the area failed to detect any positive anomaly, suggesting that any buried well fittings had been plugged properly. Vigorous CH_4 bubbling on the surface of a pond indicated the site of a leaking, abandoned, and submerged well near active well IGS ID 120316. Based on the intensity of bubbling on the surface of the pond, the gas flux was estimated to 0.2 L min^{-1}.

It was far easier to find properly documented active wells and test them for emissions of fugitive gas. Well IGS ID 120316 is an active oil well with surrounding CH_4 concentration in air exceeding 96.5 ppm (i.e. exceeding the measurement range of our portable SARAD RTM 2200 analytical equipment) while other nearby active oil/gas wells within the same county (e.g., wells IGS IDs 120,267, 163,253, 163,228, and 165,127) had no measured significant CH_4 emissions.

3.1.2. *Fugitive CH_4 flux from the active gas well*

CH_4 concentrations in tents enclosing the leaky gas well (IGS ID 125487) north of Bloomington initially increased linearly over the first 5 min of measurements and were within the range of low CH_4 concentrations that we could quantify with the SARAD RTM 2200. Sniffing gas from various fittings and along the soil surface with a plastic hose attached to the SARAD RTM 2200 proved effective to locate point sources. We found no evidence for CH_4 migration through the soil to the atmosphere. Using the long tent covering the entire well (Fig. 2A) at an air temperature of 24.5 °C, air pressure 99.7 kPa, and 44% relative air humidity on June 9, 2018, we calculated the CH_4 emission rate at the southern stronger leak as ~1.4 L h^{-1} using formula (1) (based on three measurements: k = 0.51, 0.58, 0.49 mL m^{-3} s^{-1}; V = 0.72 m^3), and the CH_4 emission rate at the northern weaker leak as ~0.14 L h^{-1} (k = 0.05 mL m^{-3} s^{-1}; V = 0.72 m^3) (Fig. 4A, C). Using the smaller tents enclosing parts of the well at an air temperature of 22.6 °C, air pressure 99.3 kPa, and 76% relative air humidity on June 16, 2018, the average CH_4 emission rate from the southern stronger leak was calculated to ~1.7 L h^{-1} (based on three measurements: k = 1.62, 1.32, 1.37 mL m^{-3} s^{-1}; V = 0.34 m^3), and the CH_4 emission rate from the northern weaker leak as ~0.04 L h^{-1} (k = 0.026 mL m^{-3} s^{-1}; V = 0.38 m^3) (Fig. 4B and C). The CH_4 flux from the northern weaker leak was one to two orders of magnitude lower than that from the southern stronger leak rendering the northern leak's contribution to the well's overall fugitive CH_4 flux negligible. We derived an average fugitive CH_4 flux from the leaky gas well of ~1.6 L h^{-1} based on all six measurements at the southern stronger leak in both long and small tents.

We note that there is a discrepancy between the calculated fugitive CH_4 fluxes at the southern stronger leak from measurements in the long and small tents, i.e. ~1.4 *versus* ~1.7 L h^{-1}, respectively. The CH_4 concentration in the air in the long tent was not homogeneous during measurements because the DC fan was not strong enough. A heterogeneous CH_4 concentration in the tent likely affected the calculated fugitive CH_4 flux in the long tent. We hypothesize that the calculated fugitive CH_4 flux from the long-tent measurement was biased towards a smaller value relative to that from the small-tent measurement.

There might also be a case that the contrasting measurements in different tents on separate days portray a real difference in fugitive fluxes. Both measurements were conducted under similar air temperature and pressure conditions, in calm weather at wind speeds of less than 1 m s^{-1}, but the relative humidity in air differed between 44% and 76% during the long-tent and small-tent measurements, respectively. It seems unrealistic that the moisture content in the external air can impact the fugitive CH_4 flux through leaks in metal fittings when the seeping gas from the pressurized underground reservoir maintains constant relative humidity in the leak. Instead, we speculate that the underground reservoir of natural gas expressed different gas pressures over time, or that the control valves of the well were set for different delivery pressures resulting in changing gas pressures at the leak. Higher gas pressure would exacerbate the rate of fugitive CH_4 loss.

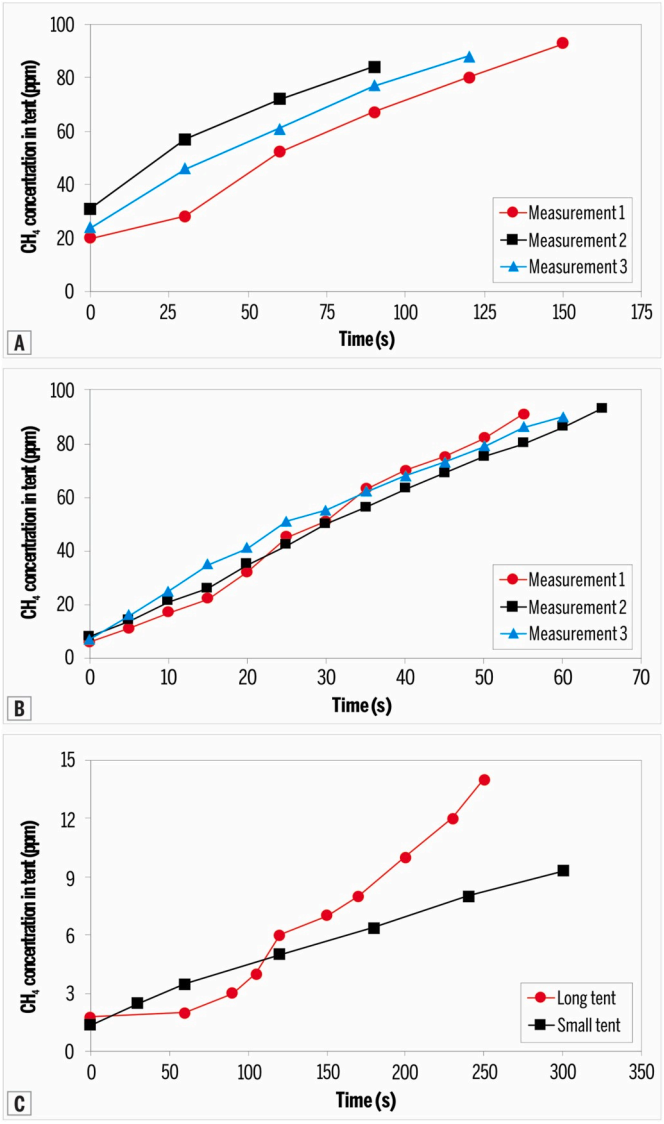

Fig. 4. A: CH_4 concentrations over time of three series of measurements at the leaky gas well (IGS ID 125487) north of Bloomington, Indiana near the southern stronger leak after closure of the long tent; B: CH_4 concentrations over time of three series of measurements at the leaky well north of Bloomington near the southern stronger leak after closure of the small tent; C: CH_4 concentrations over time of two series of measurements at the leaky well north of Bloomington near the northern weaker leak after closure of the long and small tents. The precision of each measurement is 0.5 ppm.

3.2. *Microcosm experiments with soils in culture bottles*

The comparative methanotrophic activities of soils from directly underneath, and 20 m away from the fittings of the leaky gas well IGS ID 125487 discussed in the previous section were evaluated in microcosm experiments. The initial experimental setup used aliquots of 4.0 g soil and 0.5 mL CH_4 in the air headspace of 70-mL glass culture bottles, resulting in ~7400 ppm of initial CH_4 in headspace gas. Soil from directly underneath the fittings of the leaky well consumed 96.9% of the initial CH_4 after 138 h, while the microcosm experiments with no soil and 4.0 g of control soil from 20 m away from the well consumed only 13.3 and 14.4%, respectively (Fig. 5A). The minor initial CH_4 loss in the microcosm experiments with no soil may be attributed to the dissolution of CH_4 into the butyl septa of culture bottles and repeated sampling of headspace gases for CH_4 measurements. The overall data suggest that soils closer to leaky wells exhibit higher methanotrophic activity. We

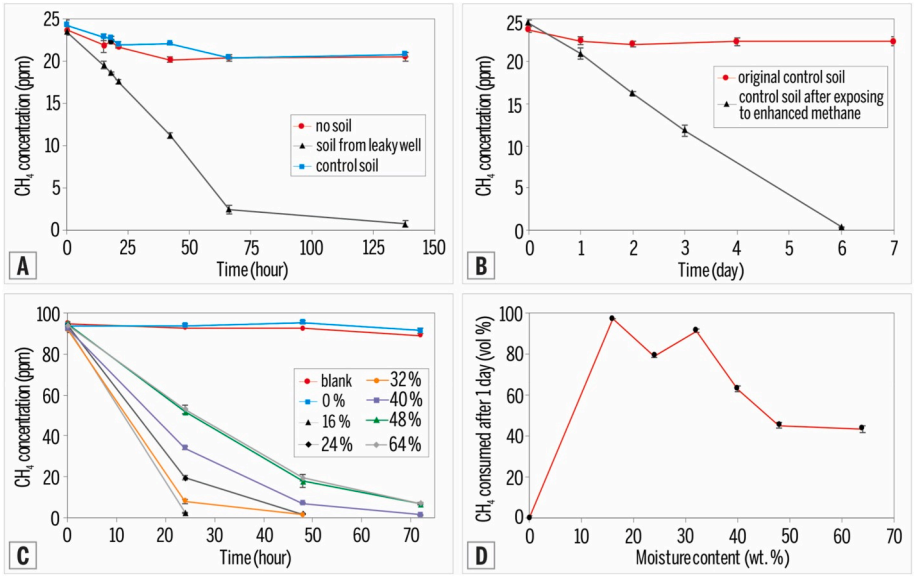

Fig. 5. A: CH_4 concentration over time in the air headspace of microcosm experiments with no soil, with soil from underneath the fittings of the leaky gas well (IGS ID 125487) north of Bloomington, Indiana, and with control soil from a distance of 20 m from the well head. Vertical error bars indicate the standard deviation of triplicate microcosm experiments. The average standard deviations of CH_4 concentrations of experiments with no soil, soil from the leaky well, and with control soil are ±0.51, 0.40, 0.44 ppm by volume, respectively; B: CH_4 concentration over time in the air headspace of microcosm experiments with (1) original control soil from a distance of 20 m from the head of the leaky well north of Bloomington and (2) another aliquot of control soil after one month of exposure to elevated concentrations of CH_4. The average standard deviations of CH_4 concentrations of experiments with original soil and exposed soil are ±0.22, 0.41 ppm by volume, respectively; C: Contrasting declining CH_4 concentration in the air headspace of microcosm experiments with soils containing different amounts of moisture (0, 16, 24, 32, 40, 48, 64 wt % water). 'Blank' denotes experiments with no soil. The average standard deviations of CH_4 concentrations of experiments with moisture contents of 0, 16, 24, 32, 40, 48, 64 wt % water are ±0.94, 0.61, 0.51, 0.48, 1.12, 0.60, 0.68 ppm by volume, respectively; D: Percentage of CH_4 consumed after 1 day in the air headspace of microcosm experiments *versus* soil moisture content. The standard deviations of CH_4 percentages consumed in experiments with moisture contents of 0, 16, 24, 32, 40, 48, 64 wt % water are ±0.96, 0.13, 1.02, 0.89, 1.32, 1.42, 1.66 vol %, respectively.

further tested the methanotrophic activities of the original control soil from a distance of 20 m away from the leaky well and another 15-g aliquot of control soil after continuous exposure to an elevated concentration of CH_4 (1.5 mL CH_4 in the air headspace of a 70-mL culture bottle) at room temperature (20.5 °C) for one month (Experiment #2 in Table 2). The starting conditions for each experiment were 4.0 g soil and 0.5 mL CH_4 in the air headspace of a culture bottle. The pre-exposed soil consumed 98.4% of the initial CH_4 after 6 days, while the same amount of original soil consumed only 5.7% after 7 days (Fig. 5B). This indicates that the methanotrophic consortium of microbes in the control soil had strongly enhanced its methanotrophic potential during pre-exposure to elevated CH_4 concentrations. Differences in CH_4 oxidation could reflect an increase in the total abundance or composition of methanotrophic bacteria. It is also possible that exposure of soils to elevated CH_4 "wakes up" metabolically inactive methanotrophic bacteria that persist over time in a dormant state (Lennon and Jones, 2011).

We conducted a series of microcosm experiments in triplicate to evaluate soil methanotrophic activity as a function of moisture content, where we used (1) aliquots of 2.7 g of dry soil from underneath the fittings of the leaky well with added water to achieve soil moisture levels of 0, 16, 24, 32, 40, 48, 64 wt % water and (2) 2.0 mL CH_4 in the air headspace of each 70-mL culture bottle. The amount of oxygen in the headspace of each culture bottle was large enough to prevent anoxic conditions in the bottle. The CH_4 was completely consumed after only one day by the soil with 16 wt % moisture. The CH_4 was consumed after two days by the soils with 32 wt % and 24 wt % water, after three days by the soil with 40 wt % water, and was essentially unchanged after three days in contact with dry soil (0 wt % water; Fig. 5C). Fig. 5D ranks the various experiments in terms of decreasing CH_4 loss after 1 day in the order 16 > 32 > 24 > 40 > 48 ≈ 64% > 0 wt % water. These results suggest that the type of soil used in our experiments required an optimal soil moisture content of about 16 wt % to express maximum soil methanotrophic activity under the chosen environmental conditions. Sufficient soil moisture is required for all microbial biochemical activities, but an overabundance of water causes flooding of pore spaces in soil and restricts gas transport of CH_4 and O_2 from the air into soil. Such conditions not only impede methanotrophy (Mills et al., 2013), but can even create anoxic conditions leading methanogens to produce CH_4, such as in wetlands. In turn, completely dry soils trigger dormancy of methanotrophs, which may represent normal conditions of soils during drought.

3.3. *Evaluation of methanotrophic efficiency of experimental soil mound over artificial seep emitting pure CH_4*

In theory, the 149.4 L of air in the closed plexiglass terrarium containing a soil mound in an open bucket require ca. 12 min of a CH_4 influx of 74 mL h^{-1} through the Teflon™ capillary to elevate the ambient CH_4 concentration of ca. 2 ppm to a maximum measurable CH_4 concentration of 96.5 ppm (i.e. the upper threshold of CH_4 quantification for our analytical instrument). A longer time needed to reach 96.5 ppm CH_4 in terrarium air indicated a higher CH_4 oxidation rate in the soil mound. In practice, the time needed to reach 96.5 ppm CH_4 in the terrarium with either no mound, with control soil from 20 m away from the leaky well, or with soil from a Bloomington landfill was 14, 19 and 38 min, respectively (Fig. 6A). This indicates that the methanotrophic activity of landfill soil increases the mound's effectiveness at mitigating CH_4 emissions. The kinetics of experiments without soil were 2 min slower than the theoretical time, which may be due to minor exchange of terrarium air with room air through small gaps between the terrarium lid and side walls during experiments, for example at locations where tubing and cables had to enter the terrarium. Pre-conditioning of methanotrophic microbial consortia in control soil from 20 m away from the leaky well for 0, 1, or 8 days at 85 ppm of CH_4 in the terrarium yielded response times of 17, 21 and 34 min to reach 96.5 ppm CH_4, respectively (Fig. 6B). Based on these findings, we conclude that the

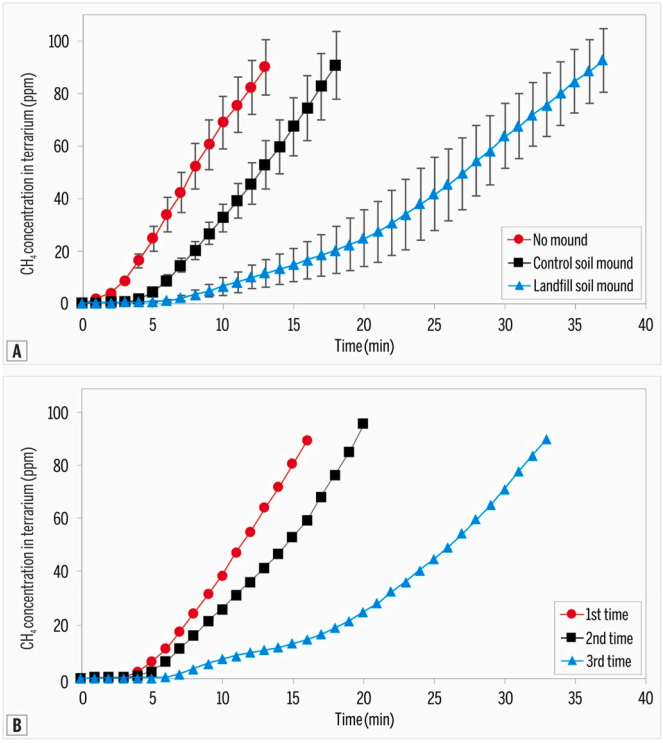

Fig. 6. A: Change of CH_4 concentration over time in the closed terrarium (1) with no mound, (2) with control soil from 20 m away from the leaky gas well (IGS ID 125487) north of Bloomington, Indiana, and (3) with soil mound covered with Bloomington landfill soil. Vertical error bars indicate standard deviations of triplicate mound experiments. The average standard deviations of CH_4 concentrations of experiments (1), (2), (3) are ±5.2, 6.4, 6.0 ppm by volume, respectively; B: Changes in CH_4 concentration in the closed terrarium containing a mound covered with control soil from near the leaky well north of Bloomington. The mound had been pre-conditioned during exposure to 85 ppm of CH_4 since September 10th, 2018. Three duplicate series of measurements of methanotrophic effectiveness were performed on September 10th (first, i.e. prior to pre-conditioning), September 11th (second, after one day of pre-conditioning), and September 18th, 2018 (third, after 8 days of pre-conditioning).

activity of methanotrophs in soil mounds can be enhanced during exposure to elevated CH_4 concentrations.

3.4. Mitigation strategy

Results of the artificial soil mound experiments support the technical feasibility of soil mounds with high methanotrophic activity to mitigate fugitive hydrocarbon gas emissions from leaky oil/gas wells into the atmosphere. Soils with high methanotrophic activity can be found above and near CH_4 seepages (e.g., landfills, leaky oil/gas wells) and can be used to inoculate newly established soil mounds. Shading of established soil mounds over CH_4 seepages by trees and bushes can avoid summer temperature extremes and mitigate excessive evapotranspiration and drying of soil. Seeping CH_4 should first encounter a highly permeable mound of rocks or pebbles before it slowly diffuses through a sufficiently thick layer of methanotrophic topsoil, thus avoiding 'fast tracks' that would limit the residence time of hydrocarbons in the soil. Engineered methanotrophic soil mounds over hydrocarbon seeps may offer a cost-effective, self-sustaining, and optically pleasing solution to mitigate some of the fugitive hydrocarbon emissions from abandoned gas wells. Using methanotrophic activity data from the experimental soil mound in a plexiglass enclosure with a soil cover from the solid waste landfill north of Bloomington at room temperature (20.5 °C), we extrapolate from the surface area and CH_4 oxidation rate of the experimental mound that ca. 2.3 m^3 of CH_4 can be microbially oxidized daily by a larger soil mound with a surface area of 100 m^2. Approximately 1.6 m^2 of the landfill soil with a thickness of 5 cm would be theoretically needed to eliminate CH_4 emissions from the leaky gas well north of Bloomington with a CH_4 leakage of 1.55 L h^{-1}. Although a 5 cm thin soil horizon would be sufficient, for practical purposes, a landfill soil layer with a thickness of at least 20 cm would be desired to prevent soil drying out too fast in summer and eroding away during severe weather events (e.g., thunderstorms). The efficiency of methanotrophy in soils further depends on water chemistry, porosity, and permeability of soil, all of which can be adjusted by suitable additions and conditioning. The landfill cover soil should be amended by adding biochar produced at 400 °C, which can increase its CH_4 oxidation capacity (Huang et al., 2019; Wu et al., 2020). Grass cover or an additional top layer of gravel would stabilize the soil containing methanotrophs. Microbial oxidation of CH_4 generates moisture that helps sustaining methanotrophy.

4. Conclusions

Plugged and abandoned oil/gas wells in Indiana often have no above-ground indication of their former existence (e.g., intact wellhead) and their methane emissions cannot be easily detected as positive anomalies in the field. A statistically relevant survey of fugitive emissions from plugged and abandoned oil/gas wells in Indiana would require time and resources far in excess of the constraints of the present work. The average fugitive methane flux from an active leaky gas well north of Bloomington, Indiana was 1.55 L/h measured within the time interval from June 9 to June 16, 2018. Microcosm experiments in stoppered glass bottles suggest that soils closer to leaky oil/gas wells exhibit higher methanotrophic activity. The methanotrophic potential of microbes in soils can be enhanced by pre-exposure to elevated concentrations of methane. Soil from underneath the fittings of the leaky gas well north of Bloomington experiences maximum methanotrophic activity at a soil moisture content of about 16 wt %. Dry soil has essentially zero methanotrophic activity.

Microbial uptake of CH_4 in an experimental 'methanotrophic mound' covered with a layer of soil from a landfill north of Bloomington, Indiana reduced the CH_4 emissions from an artificial methane seep underneath the mound, thus supporting the concept of engineered soil mounds with high methanotrophic activity above hydrocarbon gas seeps for cost-effective and sustainable mitigation of fugitive hydrocarbon emissions to the atmosphere. Our results suggest that the CH_4 emissions from the leaky gas well north of Bloomington can theoretically be eliminated by a ca. 1.6 m^2 large mound covered with a layer of Bloomington landfill soil.

Because of the abundance of oil and gas wells in Indiana and documented significant contributions of oil and gas well CH_4 emissions in other states, the CH_4 emission rates of plugged and abandoned oil/gas wells in Indiana need to be evaluated in future studies to estimate the total fugitive CH_4 flux and to plan mitigation strategies.

Data availability

Datasets related to this article can be found at https://dx.doi.org/10.17632/79ww92z4z6.1, an open-source online data repository hosted at Mendeley Data.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2020.104619.

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