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Core Ideas

- Vadose zone CH_4 migration was densely monitored during a controlled-release scenario.
- Soil moisture strongly influenced vadose zone CH_4 fate and CH_4 oxidation.
- Soil CH_4 fate appears primarily controlled by biological CH_4 oxidation.

Methane Transport during a Controlled Release in the Vadose Zone

Mark Felice,* Nick de Sieyes, Juan Peng, Radomir Schmidt, Maya Buelow, Parisa Jourabchi, Kate Scow, and Douglas Mackay

Shallow, small-rate releases of ethanol-blended fuels from underground storage tanks (USTs) may be quite common and result in subsurface CH_4 generation. However, vadose zone transport of CH_4 generated from these fuel releases is poorly understood, despite the potential to promote vapor intrusion or create explosion hazards. In this study, we simulated shallow CH_4 generation with a controlled subsurface CH_4 release from July 2014 to February 2015 to characterize subsurface CH_4 migration and surface emissions and to determine environmental controls on CH_4 fate and transport. July 2014 through November 2014 was an extended period of drought followed by precipitation during December 2014. Throughout the experiment, under varied CH_4 injection rates, CH_4 formed a radially symmetrical plume around the injection point. Surface efflux during the drought period of the experiment was relatively high and stable, with approximately 10 to 11 and 34 to 52% of injected CH_4 reaching the ground surface during the low- and high-rate injections, respectively. Following the period of precipitation and increased soil moisture, efflux dropped and stabilized at approximately 1% of injected CH_4, even as soil moisture began to decrease again. Tracer and inhibitor experiments and estimates of soil diffusivity suggest that microbial CH_4 oxidation was responsible for the observed drop in efflux. The decrease in efflux only after soil moisture increased suggests a strong environmental control over the transport and oxidation of vadose zone CH_4.

Abbreviations: BGS, below ground surface; DFE, difluoroethane; PVC, polyvinyl chloride; TDR, time domain reflectometry; UST, underground storage tank.

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Despite concerns about CH_4 generation at petroleum-hydrocarbon-contaminated sites (Jewell and Wilson, 2011; Ma et al., 2014; Rasa et al., 2013; Sihota et al., 2013; Spalding et al., 2011; Wilson et al., 2012), many aspects of CH_4 transport in vadose zone soils are poorly understood, particularly in the case of small-rate, shallow gasoline vapor releases. While increased regulation of underground storage tank (UST) construction and installation has resulted in fewer large releases of liquid fuel, small-rate gasoline vapor releases still occur and often go undetected and overlooked due to their smaller release rates. The result is a limited understanding of the environmental and health risks associated with small-rate releases of these fuels and their degradation products, such as CH_4.

Large crude oil and fuel releases to groundwater are well studied, but these differ substantially from small-rate shallow fuel vapor releases. Small-rate shallow fuel vapor releases present a potential point source of CH_4 generation in the vadose zone just below the ground surface, in contrast to more commonly studied scenarios where CH_4 is generated in groundwater contaminant plumes. Small-rate fuel vapor releases may be quite common. For example, a survey of California USTs found that >60% of surveyed tanks were leaking fuel at rates undetectable by the leak detection technology at that time (highest rates ranged from 7.6×10^{-4} to 1.5 L d^{-1} of liquid fuel, with others were at or below 7.6×10^{-4} L d^{-1}) (Young and Golding, 2002). In these cases, leaks typically occur due to pressure fluctuations during fuel dispensing or tank refilling, and occur at fittings on the top of the UST, often at fill-vent risers. This places the leaks at very shallow depth, approximately 1 m below the ground surface (Young and Golding, 2002).

Methane generation may occur anywhere that organic compounds are degraded under anaerobic conditions and frequently occurs at fuel-contaminated sites due to high C inputs from fuel. Fuel stored in USTs is frequently biofuel, which can be up to 95% ethanol or gasoline blended with ethanol (10–85%). Ethanol is a highly labile C source that can be rapidly degraded, depleting O_2 and exacerbating the generation of CH_4 (Ma et al., 2013; Powers et al., 2001).

Methane may have several negative health and safety impacts at the local scale: the generated CH_4 may (i) pose an asphyxiation or explosion hazard under a limited set of circumstances if it becomes trapped and accumulates to sufficient concentration in a structure or enclosed space overlying the contaminated zone (Jewell and Wilson, 2011; Ma et al., 2014; Nelson et al., 2010; Sihota et al., 2013; Wilson et al., 2012), (ii) increase the risk of vapor intrusion by creating pressure gradients that drive advective transport of toxic fuel constituents (Ma et al., 2014; Sihota et al., 2013; Wilson et al., 2012), and (iii) create higher O_2 demand that will deplete O_2 otherwise available for degradation of fuel constituents (Jewell and Wilson, 2011; Ma et al., 2012, 2014; Sihota et al., 2013; Wilson et al., 2012). These effects may be exacerbated by the shallow depth of small-rate vapor releases, which allows less residence time for the degradation of CH_4 or volatile organic compounds during migration to surface or subsurface structures. Numerical model simulations of vapor intrusion from a benzene source below a basement or slab-on-grade building have identified depth as one important factor in controlling benzene vapor intrusion risk (Abreu and Johnson, 2006). In addition to the potential negative health and safety impacts, CH_4 is a potent greenhouse gas contributing to climate change, with a global warming potential approximately 28 times higher than CO_2, and trailing only CO_2 in radiative forcing (IPCC, 2013).

Methane transport through the vadose zone occurs by advection and/or diffusion in the vapor phase, attenuated by processes that transfer mass from vapor to other phases or that degrade CH_4. For small-rate fuel releases, it is likely that diffusion is the dominant gas transport mechanism (Johnson et al., 2006; Lundegard and Johnson, 2006; Ma et al., 2014; Sihota et al., 2013). Soil physical properties such as porosity and moisture status strongly influence diffusive transport processes but also influence biological CH_4 oxidation, an important control on CH_4 fate (Gebert et al., 2011).

Methane-oxidizing bacteria (methanotrophs) are ubiquitous in soils and can oxidize CH_4 to CO_2. However, CH_4 oxidation kinetics are influenced by the microbial communities present (Aronson et al., 2013) and their interaction with environmental factors, such as soil moisture (Bender and Conrad, 1995; Gulledge and Schimel, 1998; van den Pol-van Dasselaar et al., 1998), soil structure (Hütsch, 1998), and soil N levels (Maxfield et al., 2008; Seghers et al., 2003). Because methanotrophs rely on gas transport to supply their C source, they are particularly sensitive to changes in soil moisture and soil structure, with a lower optimum soil moisture content than many other bacteria, also preferring coarser textured and higher porosity soils (Boeckx et al., 1997; Dörr et al., 1993; Gebert et al., 2011). Given the effect of soil physical properties and methanotroph community structure, CH_4 oxidation efficiency varies widely, with soils in some studies showing almost no CH_4 attenuation while others show complete oxidation of CH_4 prior to reaching the ground surface (Börjesson et al., 2007; Chanton et al., 2009; Le Mer and Roger, 2001; Sass et al., 1992). For example, a review of landfill CH_4 emission studies reported that, on average, studies found that 36% of the CH_4 produced was oxidized before reaching the atmosphere, but values varied from net CH_4 consumption to no CH_4 oxidation (Chanton et al., 2009). A study measuring CH_4 emissions and production in rice (*Oryza sativa* L.) paddies found that an average of 73% of CH_4 produced was oxidized, but again, the numbers were highly variable, ranging from 0 to >90% (Sass et al., 1992).

A better understanding of CH_4 fate and transport in the shallow vadose zone is essential for assessing the risk posed by CH_4 associated with shallow small-rate ethanol-blended fuel releases. A number of studies have addressed shallow subsurface transport of CH_4 originating from leaking natural gas lines (Okamoto and Gomi, 2011; Yan et al., 2015). However, these experiments simulated significantly higher CH_4 release rates than expected CH_4 generation rates at small-rate ethanol-blended fuel releases, and very few studies have examined the impact of soil and environmental properties on CH_4 fate and transport at the field scale under controlled conditions, which is a unique opportunity afforded by our study. The objectives of this study were to: (i) characterize subsurface CH_4 migration and transformation from a controlled field release at shallow depths, including the areal extent of the CH_4 plume; (ii) measure the lag time for CH_4 oxidation to begin; (iii) determine the fraction of subsurface CH_4 reaching the atmosphere; and (iv) measure seasonal variability and identify environmental controls of CH_4 migration. We hypothesized that biological CH_4 oxidation would begin within several days of introducing CH_4 to the soil and that this biological activity would limit the efflux of CH_4 to the atmosphere. We also hypothesized that CH_4 migration would be tied to soil moisture, with decreased efflux during wet periods.

Materials and Methods
Site Characterization

The CH_4 injection experiment was conducted at a field site located in the Putah Creek Riparian Reserve, approximately 2.25 km south of the University of California campus at Davis. The soil is mapped as riverwash (Soil Survey Staff, 2017), with a measured texture of silt loam in the upper 0.25 m of soil and from approximately 0.95 to 1.5 m below ground surface (BGS), the maximum depth of monitoring. The texture is silt from approximately 0.25 to 0.95 m BGS. Weighted averages ± standard deviations for solid density, bulk density, and porosity are 2.66 ± 0.04 g cm^{-3}, 1.38 ± 0.14 g cm^{-3}, and 0.48 ± 0.05, respectively. See Supplemental Material for complete site characterization.

Experimental Methods

Injection and Monitoring Network

As shown in Fig. 1, during the experiment, the site was instrumented with an array of narrow-diameter, custom-built, stainless steel drive points installed at 0.5, 1.0, and 1.5 m BGS to allow gas injection and sampling of soil gas, and an array of polyvinyl chloride (PVC) collars for the measurement of surface gas efflux with a portable gas analyzer described below. The site was also instrumented with temperature sensors installed at regular depth intervals throughout the soil profile (details below).

Gas Injection

Gas was injected in the center of the monitoring network at the 1-m depth. The injection initially alternated between 1000 mL d^{-1} of a mix of 25% CH_4 and 75% Ne and 1000 mL d^{-1} of pure CH_4 to observe CH_4 transport under different injection rates. The Ne was initially included as a conservative tracer but was found to be below method detection limits in soil gas and surface efflux when injected at the rates described above. The experiment also included periods during which 1,1-difluoroethane (1,1-DFE) was injected as a conservative tracer or ethene was injected as a methanotroph inhibitor to help identify the role of biological CH_4 oxidation. Injection periods are summarized in Table 1. The 25 and 100% CH_4 injections are equivalent to the CH_4 generated from the degradation of 3.8×10^{-3} and 1.5×10^{-2} L d^{-1}, respectively, of liquid E10 gasoline blend releases, assuming complete conversion of all ethanol to CH_4. Typical low-rate fuel releases documented in a field survey of California USTs fell between 7.6×10^{-4} and 1.5 L d^{-1} (Young and Golding, 2002).

Soil Sampling

Cores extending to 1.5 m BGS were collected throughout the experiment for moisture content analysis. Pre-release samples were also used for bulk density measurements. The pre-release cores were collected volumetrically by driving a 1.7-cm i.d. and1.9-cm o.d. aluminum tube into the soil at 7.5-cm intervals, except for the first interval, which was 3.8 cm. To reduce compaction and improve recovery, a pilot hole for the aluminum tube was produced using a hand auger for samples taken below 26.3 cm. The tubing was trimmed to remove soil from the overlying layers that may have contaminated the sample. Subsequent samples not used for bulk density analysis were collected directly with a 5-cm-diameter auger. All samples were sealed in plastic bags and placed on ice, then stored at 4°C until further processing. Throughout the experiment, sampling events included samples collected adjacent to the injection point and in randomly selected background locations outside of the area with detectable soil gas CH_4 and CH_4 efflux. On the final two sampling events (16–17 Dec. 2014 and 28 Jan. 2015), a transect was sampled including four points extending from directly adjacent to the injection point to approximately 2.4 m distal to the injection point.

Soil Analysis

Soils collected during soil sampling events were analyzed for particle size distribution, mineral density, bulk density, organic C content, and moisture retention characteristics. A Beckman Coulter LS 230 laser diffraction particle size analyzer was used to analyze the distribution of particle sizes from Core B11, the closest core to the experimental plot. The top 1.5 m of the core was subsampled in triplicate at 9-cm intervals. Each triplicate subsample was then itself analyzed in triplicate, and the results for all runs of all replicates were averaged for analysis.

Organic C content and moisture retention curves for soils sampled at three depths between the surface and 1.5 m were analyzed by the University of California–Davis Analytical Laboratory using loss-on-ignition (Nelson and Sommers, 1996, p. 1004) and pressure plate (10, 33, 100, 500, 1000, and 1500 kPa; Klute, 1986) methods, respectively.

Efflux Monitoring

Real-time surficial monitoring of CO_2 and CH_4 efflux was conducted using a LI-COR LI-8100A automated soil CO_2 flux system (LI-COR Biosciences) connected to a Los Gatos Research Ultraportable Greenhouse Gas Analyzer. Efflux monitoring
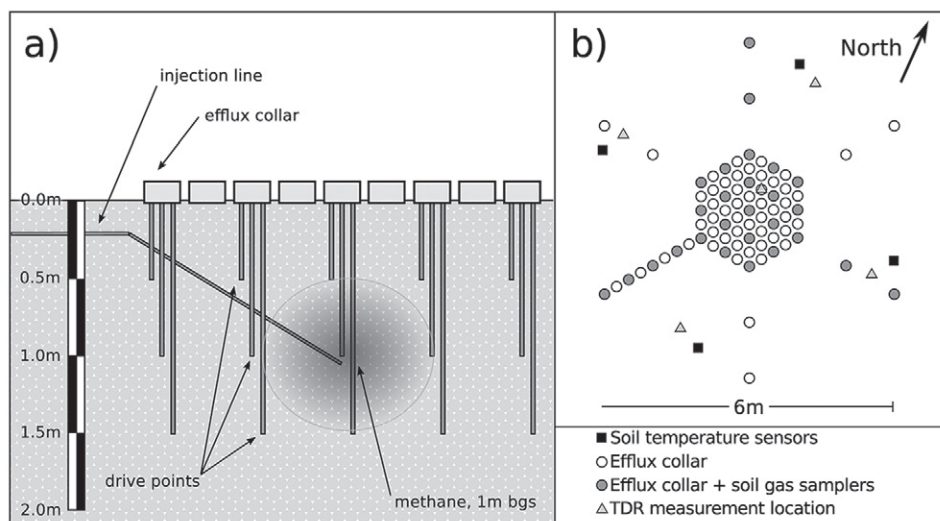

Fig. 1. (a) Vertical cross-section and (b) plan view schematics of the CH_4 injection and monitoring network.

locations were established using a grid of concentric hexagonal rings centered on the ground surface directly above the gas release location and extending out to a radius of 104 cm, as depicted in Fig. 1. A less dense array of collars was installed along the 60° "arms" of the network outside of the densely monitored central zone.

Soil Gas Monitoring

Custom soil gas samplers were manufactured from 6.4-mm o.d. 316 stainless steel straight tubing. The ends were sealed with stainless screw nails, and side ports were drilled into a vertical groove approximately 2 cm from the sealed end to minimize clogging during installation. At all locations, clusters of samplers were hammered by hand to depths of approximately 0.5, 1.0, and 1.5 m BGS; the locations of all clusters are shown in Fig. 1. At the release point, additional points were installed to approximately 0.25 and 1.75 m BGS. An additional drive point for releasing gas into the subsurface was driven diagonally to 1.0 m BGS directly below the central efflux collar. The tops of all drive points were finished with gas-tight polypropylene valves and stainless steel quick-connect fittings.

The sampling of drive points was conducted using a custom hand vacuum pump system (see the Supplemental Material). This hand pump system was used to purge 80 mL of gas, equivalent to more than three sampler volumes, from each sampler. During sampling, needled inlets and outlets were inserted through the septa on a 20-mL sample vial, and the gas flow from the sampler was routed through the inlet–outlet, thereby purging the vial with soil gas. Once 80 mL of soil gas had been purged through the vial, the inlet and outlet needles were removed and the soil gas sample was labeled, stored in the dark, and returned to the laboratory for analysis.

Samples were run on an Agilent 6890N gas chromatograph outfitted with an Agilent CP7429 column and both a thermal conductivity detector (TCD) and a flame ionization detector (FID) connected to an Agilent 7694 headspace autosampler (Agilent Technologies). Concentrations of O$_2$, N$_2$, Ne, and CO$_2$ were analyzed using the TCD, while ethene, 1,1-DFE, and CH$_4$ were analyzed using the FID. The detection limits for O$_2$, CO$_2$, ethene, 1,1-DFE, and CH$_4$ were 1.5, 0.0075, 0.00098, 0.00050, and 0.00016%, respectively.

Temperature Monitoring

Soil temperature was logged using five strings of iButton temperature loggers (Maxim Integrated) installed into PVC casings installed at the site (Fig. 1b). Temperature sensors in the four strings at the perimeter of the site were spaced at 34, 64, 94, 156, and 224 cm BGS. Temperature sensors in the string near the center of the site were spaced at 17, 37, 56, 79, 99, 119, 140, 161, 180, 200, 221, and 230 cm BGS.

Moisture Monitoring

Moisture content was determined gravimetrically for all depths sampled during soil sampling events throughout the duration of the experiment by loss of moisture after oven drying 5- to 15-g subsamples of soil for at least 48 h. Starting in September 2014, the moisture content of surficial sediments to 0.1 m BGS was analyzed in the field every 4 d using a hand-held GS3 time-domain reflectometry (TDR) probe with a ProCheck handheld reader (Decagon Devices). For the TDR measurements, a custom calibration curve of probe response vs. soil moisture content was created using site sediments, pursuant to manufacturer instructions. Surface soil measurements were made routinely at one location inside the central efflux monitoring network and four locations adjacent to temperature loggers (Fig. 1b).

◆ Results

Soil Moisture and Precipitation

No precipitation fell from the beginning of the experiment (July 2014) until 24 Sept. 2014 (Fig. 2), during which time soil moisture at 2 cm decreased (Fig. 3). At 100 and 145 cm, soil moisture increased from April to June 2014 and decreased in September. Precipitation intensity and frequency increased significantly and peaked from the end of November until the end of December, which was accompanied by increases in soil moisture. Moisture at 2 cm was temporally coupled with precipitation, peaking in December as precipitation peaked. Changes in moisture at depth were delayed relative to precipitation events, with moisture at 100 and 145 cm peaking at the end of the experiment in February 2015.
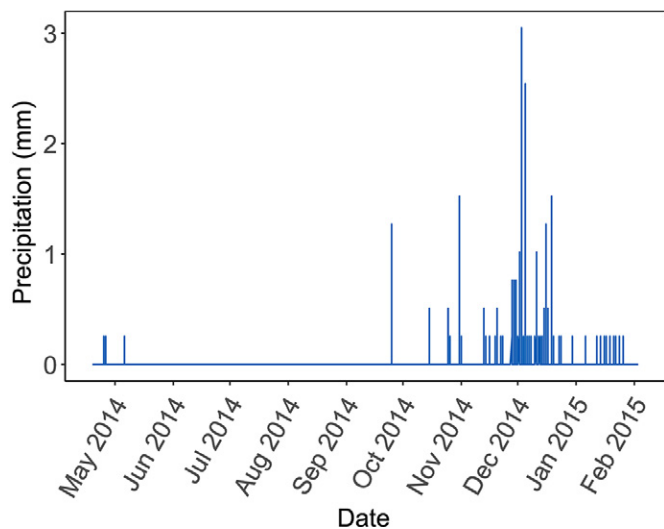
Fig. 2. Precipitation events between the first pre-experimental soil sampling (9 Apr. 2014) and conclusion of the final 100% CH$_4$ injection (3 Feb. 2015). Data were obtained from the weather station at the Campbell Tract, Davis, CA, approximately 5.2 km (3.2) miles northwest of the experiment site.
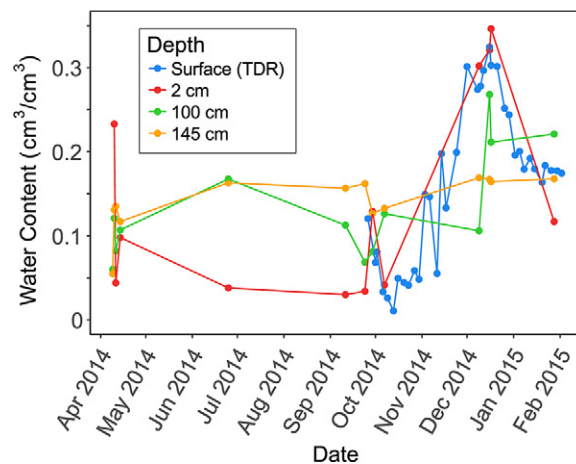

Fig. 3. Volumetric soil water content measured between the first pre-experimental soil sampling (9 Apr. 2014) and conclusion of the final 100% CH$_4$ injection (3 Feb. 2015). Water content at 2, 100, and 145 cm was determined by oven drying. Water content at the soil surface was determined from the average time domain reflectometry (TDR) probe reading from five sampling locations.

Minimum, maximum, and average soil moisture content at these depths are shown in Table 2. Monitoring of surficial soils by TDR probe began in September 2014 and showed similar trends to the soil sampling (Fig. 3).

Soil Gas: Methane

At monitoring points located away from the injection point, elevated CH$_4$ was detected in the soil gas shortly after the start of injection and responded rapidly to changes in injection rate (Fig. 4). This implies that CH$_4$ migration was very rapid. The highest CH$_4$ concentrations were measured at the injection point, with concentrations decreasing radially. Methane was regularly present at low concentrations above the method detection limit as far as 3 m from the injection point. Soil gas profiles from the low- and high-rate injection periods are shown in Fig. 5.

Methane concentrations appeared to be stable during the first 25 and 100% CH$_4$ injection periods (Fig. 4). Methane concentrations were also stable during the second 25% injection period. The average CH$_4$ concentration at the injection point was 0.024 ± 0.003 and 0.032 ± 0.005% during the two 25% CH$_4$ injection periods, and 0.012 ± 0.013 and 0.19 ± 0.019% during the 100% CH$_4$ injection periods. Based on average soil gas CH$_4$ concentrations from each injection period, the fourfold higher injection rate

initially resulted in a 2.9- to 7.3-fold increase in vapor concentrations above and below the injection point. The greatest vapor concentration increases occurred at the 0.25- and 1-m depths.

While soil gas CH$_4$ concentrations remained relatively stable throughout most of the experiment, they began to change in November 2014 during the final 100% CH$_4$ injection period. The trends in soil gas CH$_4$ concentration varied depending on depth and lateral distance from the injection point. All sampling locations distal to the injection point showed a similar temporal pattern, where concentrations increased and peaked in early December 2014 followed by declining concentrations until the end of the experiment. The change in surface moisture content (TDR) also peaked in early December and then declined until the end of the experiment (Fig. 3). However, at the injection point, soil gas CH$_4$ concentrations rose steadily until the end of the experiment,

Table 2. Range in volumetric soil moisture content measured at various depths during the experiment. Moisture content was measured by oven drying.

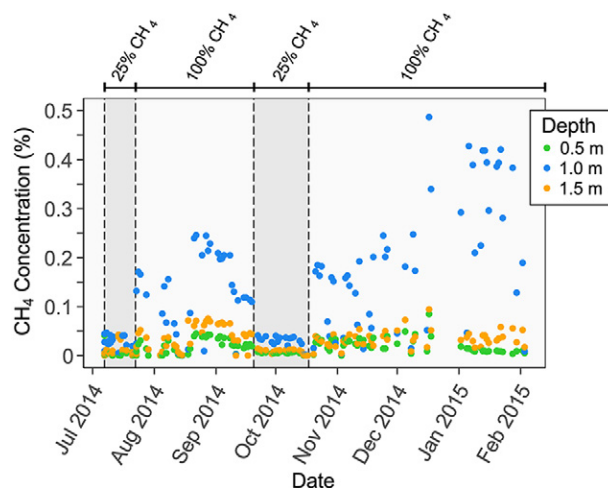| Depth	Min.	Max.	Avg.
cm		%	
2	2.8	36.0	13.3
100	5.2	27.5	14.3
145	5.5	18.3	14.8

Fig. 4. Subsurface CH$_4$ concentrations at the central monitoring point (Ring 0,0) throughout the CH$_4$ injection experiment (7 July 2014–3 Feb. 2015).
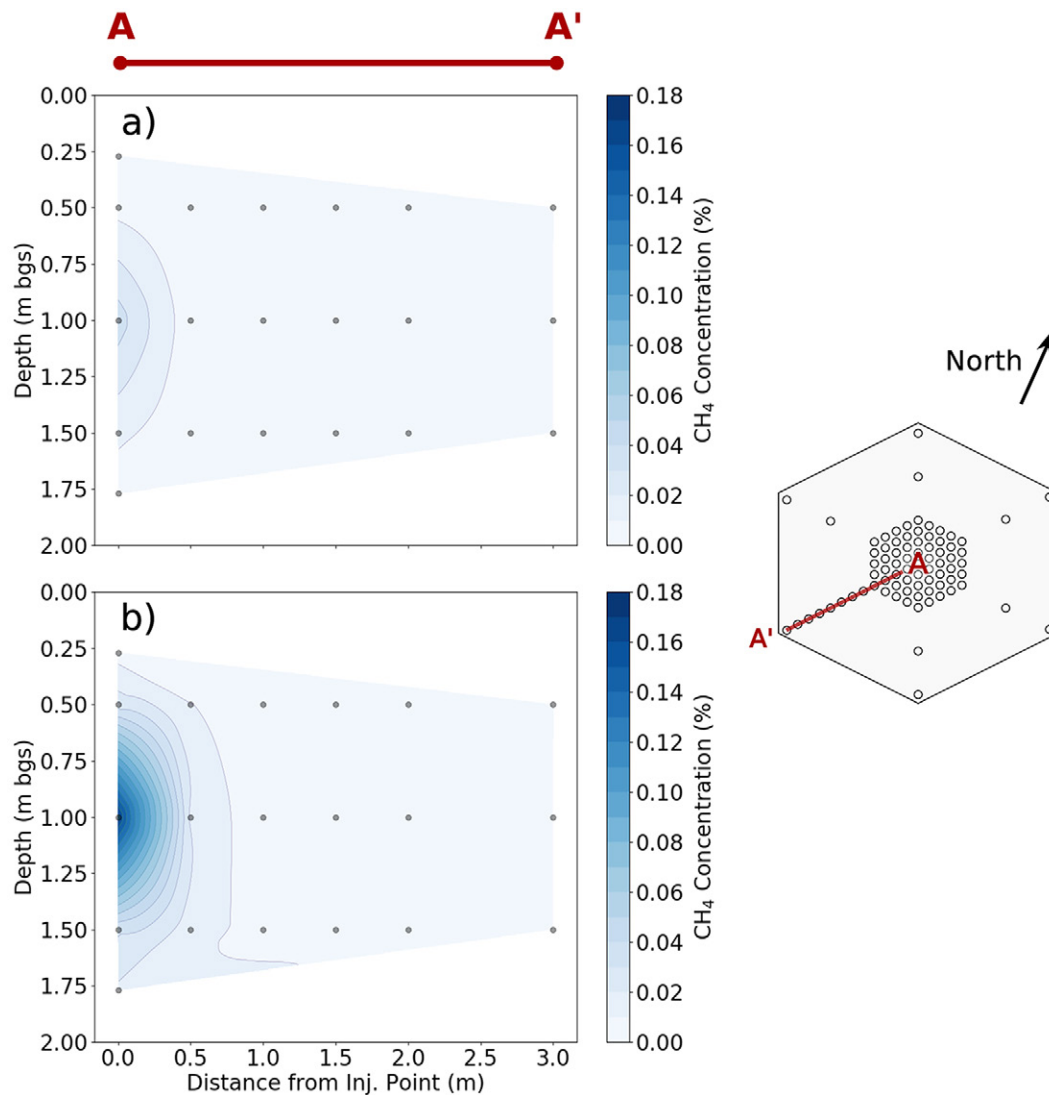
Fig. 5. Soil gas profiles during the second (a) 25% (8 Oct. 2017) and (b) 100% (23 Oct. 2017) CH$_4$ injection periods. Circles represent sampling points. Interpolations estimated by Delauney triangulation.

even as soil moisture began to decline (Fig. 4). During this period, the cross-sectional area of the plume increased.

Efflux

Prior to CH$_4$ injection, CH$_4$ efflux ranged from −0.0008 to 0.0006 µmol m^{-2} s^{-1} (−0.0003 µmol m^{-2} s^{-1} average), indicating some net CH$_4$ emission from the soil to the atmosphere, but more frequently net movement of CH$_4$ from the atmosphere to the soil (Fig. 6). There was no clear pattern in the distribution of CH$_4$ efflux during this period. Methane was detected at the surface as far as 1 m from the injection point (the most distal monitoring point during the initial injection) within 1 d of beginning injection and reached steady state within 3 d of beginning injection or changing the injection mix (Fig. 7). Sitewide CH$_4$ efflux reflected the injection rate or mix, averaging 0.0018 and 0.0015 µmol m^{-2} s^{-1} during the first and second 25% CH$_4$ injection periods, respectively, and 0.0060 and 0.0065 µmol m^{-2} s^{-1} during the first and second 100% CH$_4$ injection periods. The

fraction of injected CH$_4$ reaching the surface as efflux was also correlated to the injection rate. An average of 11 ± 1 and 10 ± 1% of the injected CH$_4$ was detected as efflux during the two 25% CH$_4$ injection periods, while 52 ± 6 and 34 ± 6% was detected during the two 100% CH$_4$ injection periods. However, the fraction of efflux declined throughout the final 100% CH$_4$ injection period from >50% to <2%.

Methane efflux was highest directly above the injection point, with rates decreasing radially (Fig. 6). Very low positive CH$_4$ efflux was periodically detected at 3 m from the injection point throughout most of the experiment, but efflux at these 3-m monitoring points fluctuated between low-magnitude positive and negative values. The areal extent of positive CH$_4$ efflux remained consistent throughout most of the final 100% CH$_4$ injection period, extending to the outer monitoring points approximately 1.5 m from the injection point. However, CH$_4$ efflux decreased dramatically at the end of the injection period in January 2015, with positive CH$_4$ efflux detected to approximately 0.5 m from the injection point
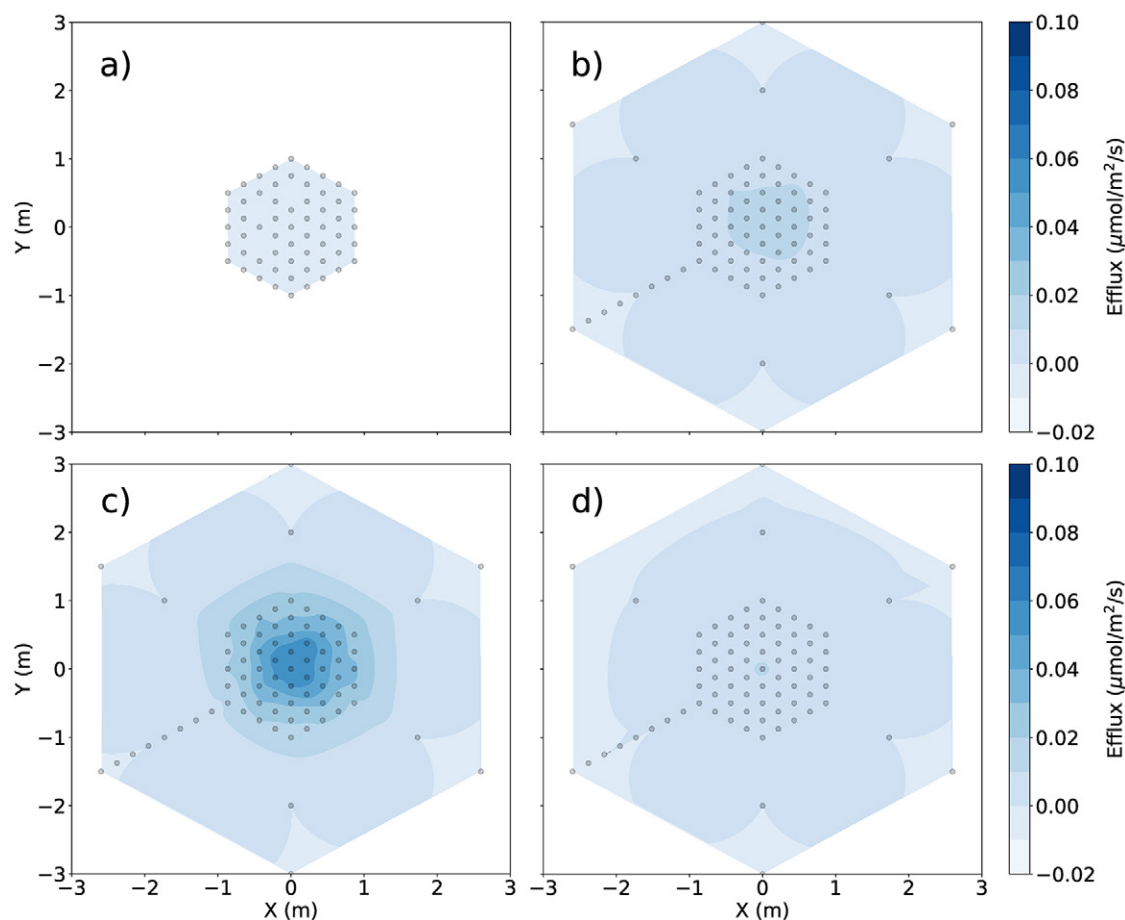
Fig. 6. Contour plots of efflux snapshots taken (a) prior to the start of CH_4 injection (30 Apr. 2014), (b) during 25% CH_4 injection (8 Oct. 2014), (c) during 100% CH_4 injection (11 Sept. 2014), and (d) during 100% CH_4 injection following a period of precipitation and declining efflux (15 Jan. 2015). Negative efflux indicates net consumption of CH_4 by the soil, and positive efflux indicates net emissions of CH_4 to the atmosphere. Sampling points are represented by circles. Contouring estimated using Delauney triangulation.

and negative efflux detected in some areas. The temporal changes in CH_4 efflux during the final 100% CH_4 injection period followed a similar trend at all sampling locations (Fig. 7).

Carbon dioxide efflux did not form a discernible spatial pattern and did not correspond spatially to CH_4 efflux. Carbon dioxide did show significant seasonal variation, with efflux increasing during the latter stages of the experiment when soil moisture was high.

1,1 Difluoroethane and Ethene Injection

In February 2015, 1 wk of injecting 100% 1,1-difluoroethane (1,1-DFE) as a conservative tracer appeared to induce some inhibition of CH_4 oxidation. During the 100% 1,1-DFE injection, CH_4 efflux was higher above the injection point and decreased outward, switching from net CH_4 emission to net CH_4 consumption at the outer edges of the monitoring network (Supplemental Fig. S4). This contrasts with the pre-release efflux, which showed negative rates across the site, with no spatial pattern clearly associated with the CH_4 injection point.

When CH_4 was co-injected with an equal volume of ethene as a CH_4−oxidation inhibitor or 1,1-DFE, efflux was not detectable, but

soil gas concentrations of CH_4 were lower than both ethene and 1,1-DFE concentrations at corresponding sampling locations, indicating that these gases were undergoing different processes. Soil gas CH_4 concentrations were approximately 20 and 61% of soil gas 1,1-DFE and ethene concentrations, respectively (Supplemental Fig. S5).

Discussion

Efflux: Methane

Negative efflux observed prior to CH_4 injection shows that this soil was a net CH_4 sink (Fig. 6a) and suggests an active community of CH_4−oxidizing bacteria with similar oxidation rates to those observed in situ for grasslands in several other studies (0.000043–0.0010 µmol m^{-2} s^{-1}) (Kammann et al., 2001; Rong et al., 2015; van den Pol-van Dasselaar et al., 1998). However, CH_4 consumption rates were lower than those observed in pine (0.0032 µmol m^{-2} s^{-1}) and hardwood (0.0030 µmol m^{-2} s^{-1}) forests (Gulledge et al., 2004). The positive CH_4 efflux observed shortly after the beginning of CH_4 injection shows that the existing methanotroph community was unable to fully oxidize the added CH_4 inputs.
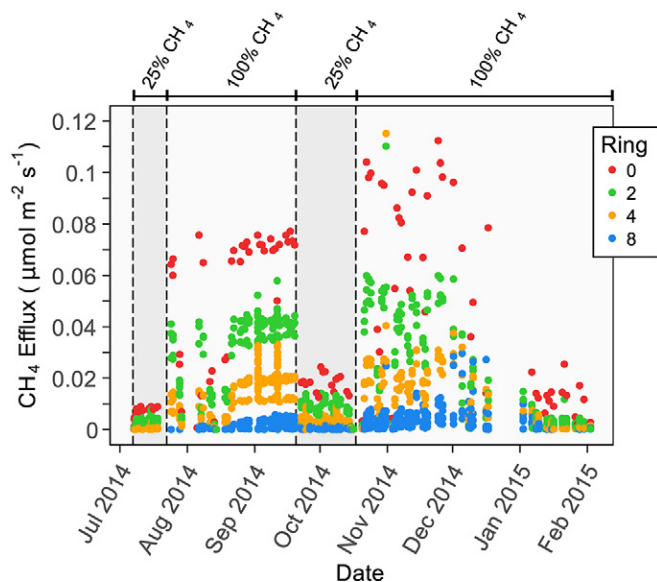
Fig. 7. Efflux throughout the duration of the experiment. Rings 2, 4, and 8 represent the efflux collars placed hexagonally around the injection point (Ring 0) with circumradii of 0.5, 1.0, and 2.0 m, respectively.

Methane efflux observed in this study during the injection period was within the range of CH_4 efflux detected at dryland sites with low to moderate levels of CH_4 seepage (Etiope and Klusman, 2010) but lower than in studies of landfills, rice paddies, or catastrophic fuel releases with subsurface CH_4 generation (Table 3). The relative effluxes are consistent with relative CH_4 inputs, which in this experiment fall between the well-studied low inputs of atmospheric CH_4 and the high inputs of landfills, wetlands, and catastrophic fuel spills.

Despite the relatively low CH_4 inputs, the increase in CH_4 efflux relative to the injection rate suggests that the CH_4−oxidizing capacity of the methanotroph community was already saturated at the lower 25% CH_4 injection rate under the conditions at that time and was unable to significantly increase the oxidation rate even with increased CH_4 inputs. Other researchers have observed the inability of methanotrophs to oxidize additional CH_4 in

proportion to increased inputs. A study of two landfills found that the percentage of generated CH_4 that was oxidized increased as CH_4 emissions decreased, fitting an exponential decay curve (Chanton et al., 2011). A similar exponential function related the fraction of CH_4 oxidized as a function of total CH_4 production in a modeling study of the effects of climate, landfill cover type, and CH_4 emission rates in California (Abichou et al., 2010). Another study, which examined landfill and volcanic pasture and forest soils in New Zealand, suggested that the specific methanotroph community was responsible for an observed decline in CH_4 oxidation efficiency as CH_4 concentrations increased. High-affinity Type II methanotrophs in the forest soil were present, and these soils showed a decline in CH_4 oxidation efficiency as CH_4 concentrations increased to relatively low concentrations of 0.004%, whereas landfill cover soils adapted to high CH_4 concentrations, and pasture soils dominated by Type I methanotrophs showed relatively constant or increasing CH_4 oxidation efficiency to concentrations as high as 0.75%. Kinetics suggest that a methanotroph population consisting of only 10% high-affinity methanotrophs could account for the observed trends (Tate et al., 2012).

Changes in CH_4 efflux under steady injection rates were related to the onset of precipitation and increased soil moisture content. During the dry periods, efflux rapidly reached steady state and remained stable. However, efflux began to decline in December 2014 following periods of precipitation and increased soil moisture content (Fig. 7). Moisture may have decreased efflux through two mechanisms: (i) directly through increasing the water-filled pore space and thus decreasing soil gas diffusivity; and (ii) increasing CH_4 oxidation activity by providing optimal conditions for methanotroph activity. Estimates of soil diffusivity under different moisture contents reveal the potential impact of soil moisture on physical transport processes.

The Millington–Quirk relationship can be used to estimate the effective diffusion coefficient in soil gas (D_s) from the total porosity (f), air-filled porosity (f_a), and the free-air diffusion coefficient (D_0):

$$D_s = \frac{f_a^{10/3}}{f^2} D_0 \qquad [1]$$

Table 3. Comparison of efflux measured during this and other studies.

Efflux	Study setting	Reference
μmol m^{-2} s^{-1}		
0.49–9.3	landfill	Mønster et al. (2015)
0.44	cropland	Raich and Schlesinger (1992)
2	landfill	Czepiel et al. (1996)
0.19	rice paddy	Chen et al. (2013)
1.4	above denatured fuel-grade ethanol release	Sihota et al. (2013)
24	above denatured fuel-grade ethanol release	Sihota et al. (2013)
0.004–0.04	drylands with low-moderate microseepage	Etiope and Klusman (2010)
0.003†	present study (25% CH_4 injection)	present study
0.011†	present study (100% CH_4 injection)	present study

† Efflux above the injection point averaged across all sampling dates at respective injection level.

Using this equation, the estimated effective diffusion coefficient for CH_4 dropped by a factor of 3.4 from the driest to the wettest period. Other field studies have shown this effect of moisture as well. For example, moisture content and air permeability were the most important parameters influencing CH_4 and CO_2 transport through soil from a landfill, based on sensitivity analysis of numerical transport models (Poulsen et al., 2001). However, we observed a drop in efflux as a fraction of injected CH_4 of approximately 25 times, a much larger decrease than predictions based solely on changes in soil gas diffusivity, which strongly suggests that physical transport processes are not the sole control on CH_4 efflux. Additional support for the hypothesis that microbial CH_4 oxidation is involved in reducing CH_4 efflux is the observation that the fraction of injected CH_4 measured as efflux remained consistently low through the end of the experiment, even as the soil began to dry out and diffusivity increased.

While we hypothesize that the increased moisture content following precipitation events relieved moisture stress, allowing higher CH_4 oxidation rates, theoretically, a drop in diffusivity could potentially reduce CH_4 oxidation rates if it sufficiently limited O_2 available to CH_4–oxidizing bacteria. However, optimal CH_4 oxidation rates are achieved when the moisture content is low enough to allow adequate CH_4 and O_2 diffusion but high enough to eliminate physiological moisture stress. The moisture content observed at our site during the period of decreased efflux fell within the optimal moisture content for CH_4 oxidation found by several studies (Bender and Conrad, 1995; Gulledge and Schimel, 1998; Schnell and King, 1996; van den Pol-van Dasselaar et al., 1998; Whalen and Reeburgh, 1996).

Efflux: Carbon Dioxide

Carbon dioxide efflux during this experiment was generally within or below the range of values for natural soil respiration reported in the literature. For example, a review of soil respiration studies found efflux of 1.16 μmol m^{-2} s^{-1} in temperate grasslands and 1.43 μmol m^{-2} s^{-1} in croplands (Raich and Schlesinger, 1992). Near denatured ethanol spills in southwestern Minnesota, natural soil respiration generated CO_2 efflux of 3.7 to 7 μmol m^{-2} s^{-1} (Sihota et al., 2013). A study of a petroleum pipeline rupture site found natural soil respiration contributing CO_2 efflux of 0.4 to 5.1 μmol m^{-2} s^{-1} (Sihota et al., 2016). Due to the relatively small C inputs from CH_4 in this study, changes in CO_2 efflux above natural soil respiration may have been difficult to detect. Assuming complete oxidation of all injected CH_4, 1000 mL d^{-1} (0.47 μmol s^{-1}) of injected CH_4 could generate as much as 0.47 μmol s^{-1} of CO_2. Assuming a uniform distribution of CO_2 efflux across an area of 1 to 12.6 m^2, which is the areal extent of the efflux monitoring network, CO_2 efflux from CH_4 oxidation should be in the range of 0.02 to 0.5 μmol m^{-2} s^{-1}, which is much smaller than the natural spatial variation in CO_2 efflux observed at the site. For example, one initial pre-experiment monitoring found CO_2 efflux between 2.28 and 6.19 μmol m^{-2} s^{-1}.

Therefore, the lack of a clear spatial relationship between CH_4 efflux and CO_2 in this study is not surprising.

Soil Gas: Methane

The subsurface CH_4 concentrations at the depths and distances distal to the injection point also tracked with soil moisture content, but unlike efflux, the soil CH_4 concentrations appeared to increase during the periods of highest precipitation and surface soil moisture, which is consistent with diffusion limitation caused by increasing water-filled pore space limiting gases from migrating away from the injection point. Interestingly, subsurface CH_4 concentrations at the injection point continued to increase and remained high at the end of the experiment, whereas CH_4 concentrations at distal points began to decrease again as the soil began to dry out near the end of the experiment. Because changes in soil gas diffusivity in a particular uniform soil should change only through changes in moisture content and water-filled pore space, we would expect the soil gas concentrations distal to the injection point to be inversely related to soil moisture content, which appears true throughout most of the experiment. However, the data appear inconsistent with this trend during the final month of the experiment, when soil gas concentrations begin to decline despite declining soil moisture content. This suggests that another mechanism, such as microbial CH_4 oxidation may also be involved.

During the co-injection of CH_4 and 1,1-DFE or ethene, 1,1-DFE and ethene concentrations were higher than corresponding CH_4 concentrations (Supplemental Fig. S5). We expected physical transport processes to have a similar effect on CH_4, 1,1-DFE, and ethene, so the lack of concordance in concentrations between CH_4 and these other two gases suggests biological CH_4 oxidation. Both 1,1-DFE and ethene are much more recalcitrant than CH_4. No data on 1,1-DFE biodegradation were available, and ethene degradation rates of 22.3 to 136 pmol g^{-1} soil h^{-1} with 0.002 to 0.005% headspace have been reported (Zechmeister-Boltenstern and Smith, 1998). The relative concentrations of CH_4 are higher in the ethene co-injection than the 1,1-DFE co-injection, which may be the result of some ethene degradation or slight inhibition of CH_4 oxidation. One study demonstrated complete methanotroph inhibition in a landfill cover soil at 0.1% ethene (Chan and Parkin, 2000), and another showed total inhibition of atmospheric CH_4 oxidation in volcanic forest soils at 0.002% (Xu and Inubushi, 2009), while ethene was present at concentrations ranging from below the detection limit to approximately 0.45% in this study. Positive CH_4 efflux during the 100% 1,1-DFE injection period compared with negative efflux during pre-experiment characterization suggests that 1,1-DFE inhibited atmospheric CH_4 oxidation. Although 1,1-DFE has not been reported as a methanotroph inhibitor, difluoromethane is an effective methanotroph inhibitor (Miller et al., 1998).

Conclusions

Methane migration occurred rapidly, with surface efflux and soil gas concentrations achieving a steady state within several

days of the start of or changes in injection rates. Soil moisture conditions appeared to control CH_4 efflux, which was probably a combination of biological CH_4 oxidation and reduced soil gas diffusivity due to increased water-filled pore space. While our study suggests a larger role for biological CH_4 oxidation, numerical model simulations could be used to further elucidate the controls on CH_4 fate and transport in this system.

This experiment was conducted in the context of assessing the risks posed by CH_4 generated in the vadose zone from the degradation of ethanol released during shallow small-rate fuel releases. Our CH_4 injection rate represented an intermediate severity of small-rate fuel release from a UST that would go undetected with standard leak detection systems (3.8×10^{-3}–1.5×10^{-2} L d^{-1}). A survey of California USTs found fuel release rates between 7.6×10^{-4} and 1.5 L d^{-1} (Young and Golding, 2002), and our CH_4 injection rate assumed that ethanol was the only fuel constituent broken down methanogenically, meaning that the rates estimated in this experiment may underestimate CH_4 generation at many small-rate fuel release sites. Higher ethanol blends of fuel, such as E85, are becoming more common and could also potentially increase CH_4 generation. However, further studies adding E10 or E85 fuel blends to the vadose zone are needed to more accurately estimate actual rates of CH_4 generation expected from shallow small-rate fuel releases and further elucidate the risks of small-rate shallow fuel releases.

Acknowledgments

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