

Migration and fate of $^{14}\text{CH}_4$ in subsoil: tracer experiments to inform model development

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ABSTRACT

The degree of transport and retention of $^{14}\text{CH}_4$ in soil is being investigated in a series of laboratory experiments in preparation for field scale trials at the University of Nottingham. The experimental programme focusses on the behaviour and fate of $^{14}\text{CH}_4$ injected into subsoil and its subsequent incorporation into vegetation under field conditions. Due to restrictions on the use of radioactive tracers in the field, $^{13}\text{CH}_4$ is being used as a surrogate gas which can be handled conveniently in the laboratory and field and which can be measured with high precision using gas chromatography with isotope ratio mass spectrometry. The laboratory data indicate significant differences between the diffusion and oxidation rates of $^{13}\text{CH}_4$ in re-packed and undisturbed soil columns, with both rates appearing to be significantly lower in undisturbed soils. Data from both laboratory and field experiments will be used to inform the development of a model of $^{14}\text{CH}_4$ migration and its fate in the biosphere above a geological disposal facility.

KEYWORDS: carbon-14, gas migration, geological disposal, radioactive waste.

Introduction

STUDIES have shown that radioactive gases, including $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$, may be produced in geological disposal facilities (GDF) for intermediate-level wastes (Thorne, 2005). Carbon-14 is expected to be released from a GDF over a timescale of several thousand years (5730 year radioactive half life). Both $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ may be generated within a GDF, but $^{14}\text{CH}_4$ is likely to be the dominant form of ^{14}C transported in the gas phase; this may ultimately reach the biosphere at very low fluxes (Hoch and Swift, 2010).

Despite much recent work on the behaviour of both CH_4 and CO_2 in soils, considerable uncertainty remains with regard to (1) the potential for incorporation of $^{14}\text{CH}_4$ -derived ^{14}C by plants and subsequent ^{14}C exposures to grazing animals and human consumers; and (2) the interaction and storage of ^{14}C within soil micro-organisms and organic matter (Fig. 1). A combined experimental and modelling programme, funded by the Nuclear Decommissioning Authority Radioactive Waste Management Directorate (NDA RWMD), has been specifically designed to obtain and interpret experimental data on the behaviour of $^{14}\text{CH}_4$ and $^{14}\text{CO}_2$ in soil and any subsequent uptake of ^{14}C by plants. The experimental programme focusses on the behaviour and fate of $^{14}\text{CH}_4$ introduced into subsurface soil and its subsequent incorporation

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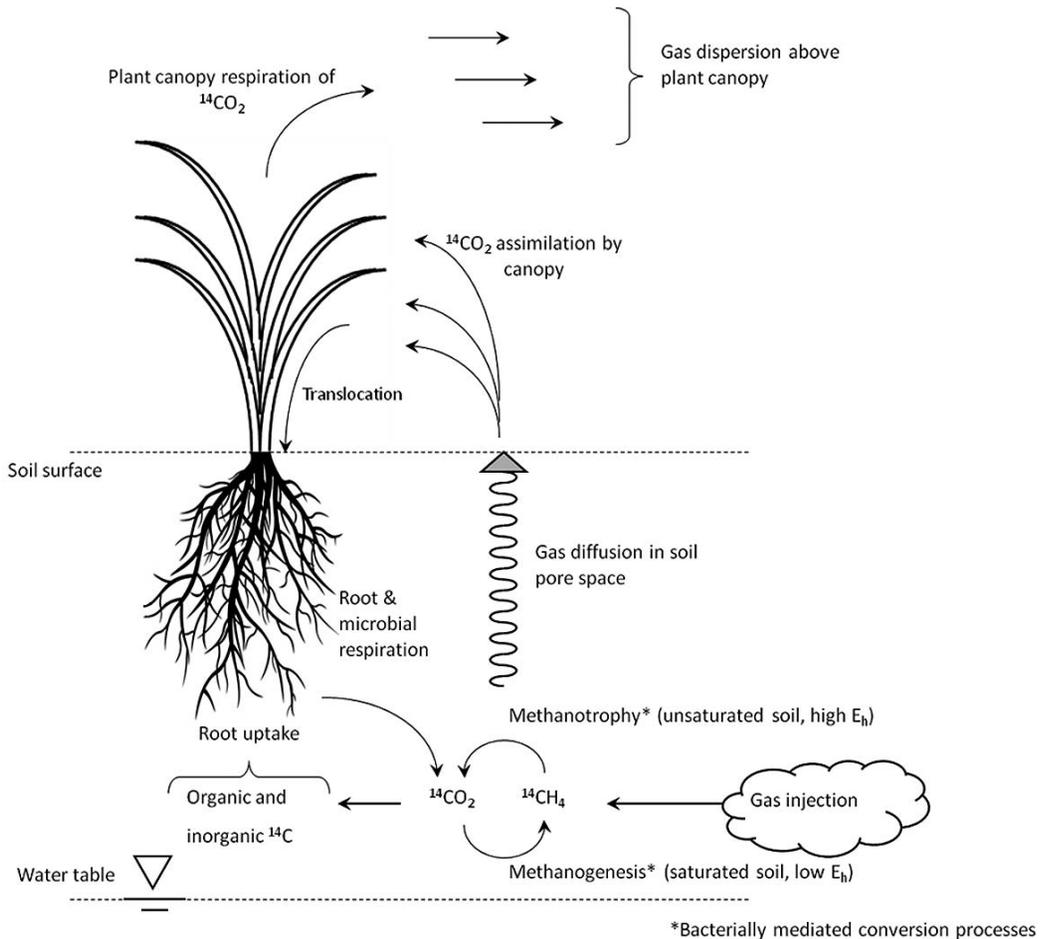


FIG. 1. Conceptual model of $^{14}\text{CH}_4$ and $^{14}\text{CO}_2$ behaviour following injection in the subsoil.

into vegetation under field conditions. In practice, $^{13}\text{CH}_4$ is used as a non-radioactive, but traceable, surrogate for $^{14}\text{CH}_4$.

The key experiments in this study involve injection of $^{13}\text{CH}_4$ into agricultural soils under field conditions. The design of field experiments has been guided by a detailed literature review which provided relevant information to support experimental and modelling studies of ^{14}C behaviour following injection of labelled methane into the subsoil (Shaw and Atkinson, 2012). However, in order to explore suitable methods for injecting and sampling small quantities of $^{13}\text{CH}_4$ in such large-scale experiments, a series of laboratory scale experiments was designed as a pilot study. The first two of these (experiments 1 and 2) involved the

establishment of small (50 cm high \times 15 cm diameter) soil columns in the laboratory into which $^{13}\text{CH}_4$ could be injected and sampled. These experiments have provided useful data on $^{13}\text{CH}_4$ diffusion and oxidation in (1) homogenized and re-packed soil columns and (2) undisturbed soil columns taken directly from the site at which field experiments have subsequently been carried out.

This paper describes these two experiments and provides a description and initial interpretation of the results obtained. Experiments 1 and 2 were designed to quantify the migration of an isotopic mixture of methane (75% $^{12}\text{CH}_4$ and 25% $^{13}\text{CH}_4$) through (1) homogeneously packed (experiment 1) and (2) undisturbed (experiment 2) soil columns over a period of 15 days (360 hours) following an

instantaneous pulse injection of the gas at the base of the columns. The isotopic ratio of the source gas was selected after test analyses by gas chromatography with isotope ratio mass spectrometry (GC-IRMS) indicated that it provided an optimal compromise between isotopic sensitivity and instrumental detectability. The migration of total ('bulk') methane (CH_4) and carbon dioxide (CO_2) concentrations were measured over the period of the experiment, as well as the $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$) of both gases within the soil column gas space and above the soil surface. A closed sampling chamber was placed on top of each soil column to collect 'head space' gas and the measured concentrations were used to calculate the fluxes of bulk and labelled CH_4 and CO_2 into the free atmosphere.

Methods

Soil collection and column preparation was undertaken for experiment 1 by collecting top soil (to a depth of 10 cm) in August 2010 from the University of Nottingham experimental farm at Bunny, Nottinghamshire, UK (52.52°N, 1.07°W). The soil is a loamy sand of the Newport series (FAO class: stagno-gleyic brown earth, consisting of 79% sand, 9% silt and 12% clay). The soil was dried and sieved to <6 mm to remove chaff, stones and large aggregates. Sieved soil was then packed to a consistent bulk density of 1.3 g cm^{-3} into a length of uPVC drainage pipe (16 cm diameter, 50 cm length with a wall thickness of 6 mm), the base of which was sealed using a 6 mm thick uPVC sheet. Small holes (3 mm diameter) were then drilled along the length of the pipe to allow the insertion of Rhizon samplers (Van Walt, Rhizon sampler, 10 cm length) at 10, 20, 30 and 40 cm distances measured from the top of the pipe. A larger diameter hole (10 mm) was drilled at 45 cm depth and a 3 cm long air diffuser cylinder (Elite Air Diffuser) was inserted so that it was positioned centrally in the soil column, with its long axis horizontal. The diffuser cylinder was attached to a 10 cm length of 4 mm internal diameter silicon tubing, which was routed through the column wall. The Rhizon sampler and the air diffuser holes were all sealed using silicone sealant. The columns were prepared in triplicate.

Soil collection and column preparation were performed for experiment 2 in September 2010. Three lengths of uPVC pipe (as for experiment 1) were taken to the University of Nottingham experimental farm (Bunny, Nottinghamshire)

and driven into the soil using a combination of hammering and careful excavation of the soil around each column. In this way, three soil columns with undisturbed structure were collected *in situ*. The upper part of the soil columns was a loamy sand of the Newport series which extended to a depth of approximately 40 cm, below which the soil texture changed to a clay sand containing small to medium pebbles. Each core was wrapped in cling film *in situ*, carefully removed from the ground and taken back to the laboratory where it was stored at 4°C until required, thus minimizing any change in moisture content and biological activity within the columns. Prior to experiment 2, uPVC base plates were fitted to the undisturbed cores and gas injection and sampling equipment was installed, as for experiment 1. Mean moisture content within experiment 1 was measured at ~20% after column saturation and drainage. In experiment 2 the columns were maintained at the original field moisture content of the soil, of the order of 5 to 10% by weight.

Two sources of methane with known isotopic purities were acquired for these experiments, specifically CH_4 with 99.95% ^{12}C (CK Gases, Hook, Hampshire) and CH_4 with 99% ^{13}C (Isotec, Sigma-Aldrich). Small volumes (~20 ml) of each gas were dispensed using a bubble trap apparatus (Fig. 2) then accurately measured aliquots removed using a precision Hamilton gastight syringe via a Luer stopcock. The gas aliquots (9 ml $^{12}\text{CH}_4$ and 3 ml $^{13}\text{CH}_4$, both at atmospheric pressure) were injected via a rubber septum into an evacuated 12 ml ^{13}C breath test 'Exetainer' vial (Labco, UK) to achieve a 75% to 25% mix of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. Aliquots of the mixed isotopic gas from the Exetainer vial were then extracted using a Hamilton 500 μl gastight syringe and injected into the base of the columns (45 cm from the soil surface) through the air diffuser. This was performed in two consecutive injection volumes of 500 μl , giving a total injection volume of 1 ml.

Soil gas sampling was performed using Rhizon samplers previously installed at 10, 20, 30 and 40 cm depths. A negative pressure was applied to each Rhizon sampler using a 20 ml sterile syringe and each sampler was left for five minutes until the pressure in the syringe had equilibrated with atmospheric pressure. The syringes were then removed one at a time and the gas samples injected into sealed Exetainer gas vials for storage. This was performed at predetermined periods of 0.25, 1, 2, 5, 10, 24, 48, 120, 240 and 360 hours (with an additional 8 hour sampling

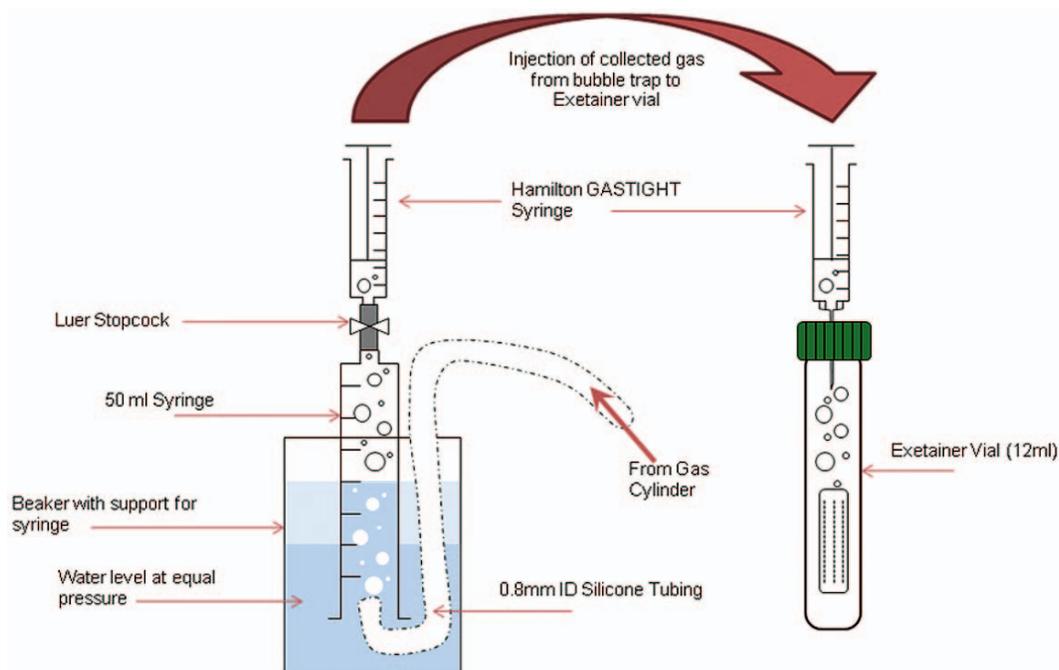


FIG. 2. Illustration of bubble trap design used for gas dispensing and subsequent mixing within 'Exetainer' vials ready for gas injection.

period for experiment 2) after injection. Measurements of gas flux from the soil column surfaces were made using 2.6 litre headspace chambers fitted to the tops of soil columns for a period of two hours. Samples were taken every 30 min (i.e. 0, 30, 60, 90, 120 min) using a 20 ml syringe needle inserted through a rubber septum on top of each chamber. Headspace sampling was performed at pre-determined intervals over the 15 day experiment period, viz. 6–8, 12–14, 24–26, 72–74, 120–122, 168–170, 216–218, 264–266, 312–314 and 360–362 hours for experiment 1 and 3–5, 6–8, 9–11, 12–14, 24–26, 72–74, 120–122, 168–170, 240–242 and 360–362 hours for experiment 2. Prior to gas injection into the columns, antecedent soil gas and headspace samples were taken and the CH_4 and CO_2 concentrations obtained for both were used as a baseline against which soil and headspace gas concentrations were compared after injection.

Gas measurements for total concentrations of CH_4 and CO_2 were determined using a gas chromatograph (GC-2014, Shimadzu Corp, Japan) fitted with thermal conductivity and flame ionization detectors in parallel. Samples were calibrated using a single gas standard

containing 500 ppmv CO_2 and two CH_4 standards of 50 and 5 ppmv. The $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$) isotope ratios for CO_2 and CH_4 were determined using a Delta^{plus}XP ThermoFinnigan gas chromatography-combustion-isotope ratio mass spectrometer (GC-C-IRMS). Injection of samples was performed in split mode (ratio 3:1, injection temperature 60°C) with separation performed on a Varian CP-PoraPLOT Q-HT column (10 m × 0.53 mm; 20 μm film thickness) with helium as the carrier gas (1.5 ml min⁻¹), at a temperature of 30°C held isothermally for 20 min. The ratio of stable carbon isotopes was then expressed in relation to an international standard reference material, the VPDB (Vienna PeeDee Belemnite), in units of ‰, calculated as:

$$\delta^{13}\text{C} = \left[\frac{\left(\frac{^{13}\text{C}/^{12}\text{C}}{\right)_{\text{sample}}}{\left(\frac{^{13}\text{C}/^{12}\text{C}}{\right)_{\text{standard}}} - 1 \right] \times 10^3 \quad (1)$$

Results and discussion

Antecedent measurements of both CH_4 and CO_2 made in experiment 1 showed a dynamic response

of the Bunny Farm soil to a wetting and drying cycle, during which the concentration profiles of both gases were significantly altered (Atkinson *et al.*, 2011). The concentration profile of CH_4 , in particular, underwent a complete reversal during this cycle: methanogenesis during a 'wet' (anoxic) phase led to an increase in methane concentration at the column bases and a net flux of methane upwards through the soil columns and out into the free atmosphere. Conversely, a 'dry' (oxic) phase led to strong methane consumption (methanotrophy) within the soil column and a net movement of CH_4 from the free atmosphere into the soil columns in which the methanotrophic microflora provided a sink for atmospheric methane. For a freely draining agricultural site such as Bunny Farm methanotrophy would be expected to dominate over methanogenesis, thus the soil is likely to act as a net sink for atmospheric methane. Assuming that the two key processes which shaped the antecedent soil profiles of methane concentrations prior to experiments 1 and 2 are (1) diffusion and (2) methane consumption within the soil, the antecedent gas profile data from both experiments have been analysed by fitting a one-dimensional solution of the diffusion equation (Fick's second law), modified by assuming that consumption of CH_4 occurs uniformly throughout the soil columns (Fig. 3). The effective diffusion coefficient for CH_4 in the experimental soil columns has been calculated using the relationship

proposed by Moldrup *et al.* (1997) which combines the Penman (1940) and Millington and Quirk (1961) models and also provides a dimensionless scaling parameter (m) for both intact ($m = 3$) and re-packed ($m = 6$) soils:

$$\frac{D_s}{D_o} = 0.660\theta_a \left(\frac{\theta_a}{\Phi} \right)^{\frac{12-m}{3}} \quad (2)$$

where D_s ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient in the soil gas space, D_o ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient in the free atmosphere, θ_a ($\text{m}^3 \text{m}^{-3}$) is the air-filled porosity of the soil and Φ ($\text{m}^3 \text{m}^{-3}$) is the fractional volume occupied by the soil pore space.

After calculating the effective diffusion coefficient, the two curves in Fig. 3 have been fitted by adjusting only one parameter: a rate coefficient for oxidation of CH_4 . It can be seen from the figure that this fitted rate coefficient was estimated to be twenty times lower for experiment 2 (0.002 h^{-1}) than for experiment 1 (0.04 h^{-1}). It should be noted that the differences between CH_4 concentrations at the soil depths sampled were close to the analytical errors, although a systematic reduction in CH_4 concentration with depth was evident.

Experiment 1 used triplicate soil columns into which only topsoil from Bunny farm had been uniformly packed, whereas experiment 2 used undisturbed soil columns from the same site. It is to be expected that the average population of soil

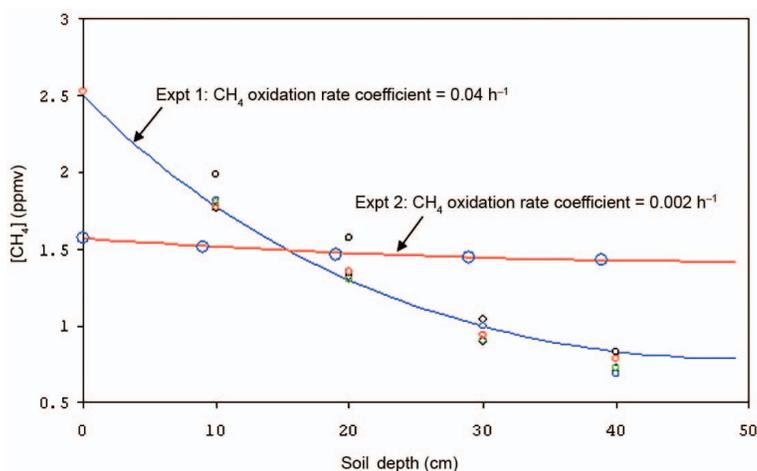


FIG. 3. Antecedent soil profiles of CH_4 in experiments 1 and 2. Curves are fitted solutions of one dimensional diffusion modified by CH_4 oxidation (a constant mean diffusion coefficient and a constant oxidation rate coefficient throughout the columns are assumed).

microorganisms, including methanotrophs and methanogens, would have been substantially higher in experiment 1 than in experiment 2, as the topsoil is richer in organic matter and microorganisms than the subsoil. This is reflected in the shape of the antecedent CH₄ profiles (Fig. 3). The differences in the degree of methane oxidation in both experiments were also reflected in the measured conversion of

CH₄ to CO₂, as determined by the δ¹³CO₂ values for soil and headspace gases in both experiments. After injection at 45 cm below the soil surface, labelled methane diffuses rapidly to the soil surface and into the free atmosphere. This process is complete within 10 hours in re-packed soils (experiment 1) and 48 hours in undisturbed soils (experiment 2) indicating significantly faster diffusion in the former (Figs 4 and 5). In the case

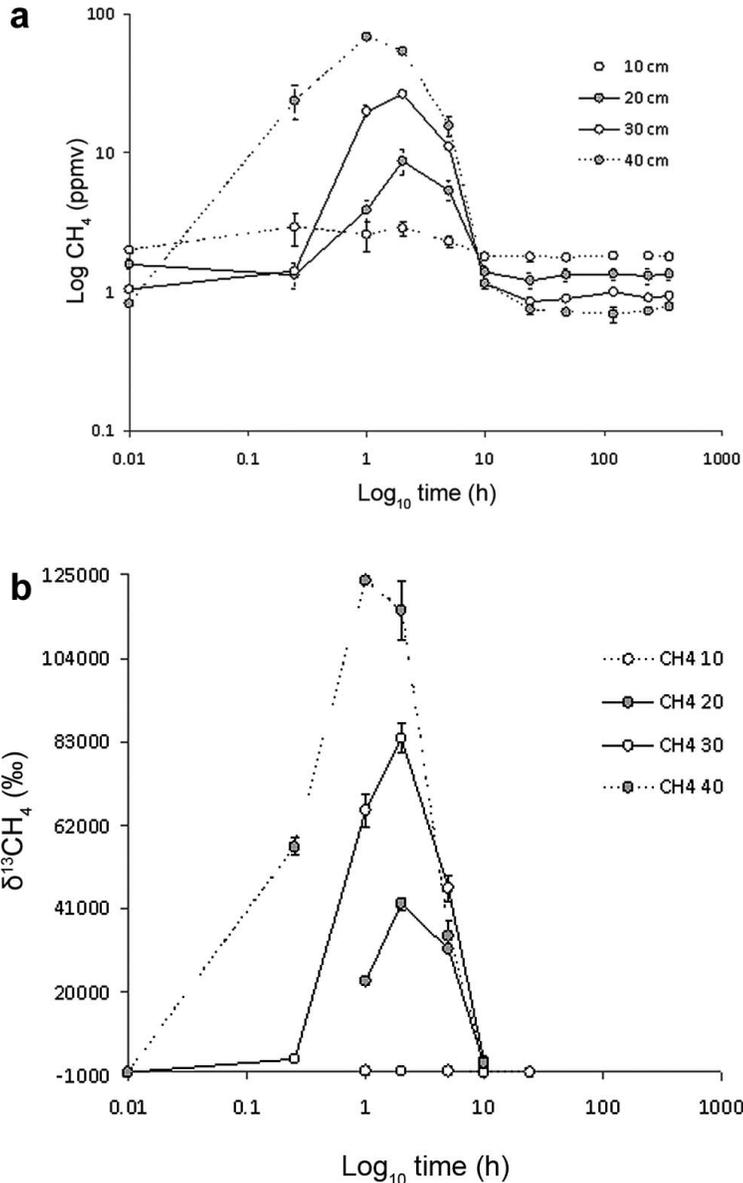


FIG. 4. (a) Bulk methane and (b) δ¹³CH₄ in soil gas samples from re-packed soil columns (experiment 1).

MIGRATION OF $^{14}\text{CH}_4$ IN SUBSOIL

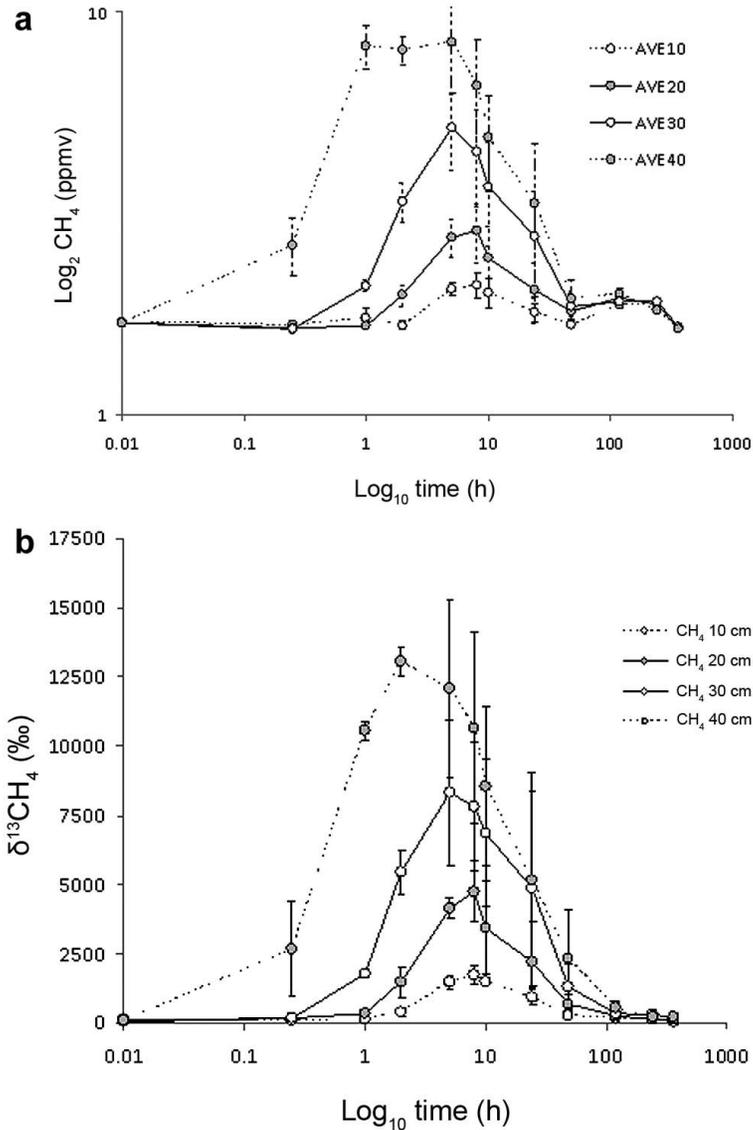


FIG. 5. (a) Bulk methane and (b) $\delta^{13}\text{CH}_4$ in soil gas samples from undisturbed soil columns (experiment 2).

of experiment 1 there was a clear deviation in the $\delta^{13}\text{CO}_2$ values in both soil (Fig. 6a) and head space gases (data shown in Atkinson et al., 2011) in response to the injection (and oxidation) of labelled methane. However, in experiment 2 any conversion of CH_4 to CO_2 was undetectable, even when examining the $\delta^{13}\text{CO}_2$ values in both soil (Fig. 6b) and head space gases (data shown in Atkinson et al., 2011).

The head space CH_4 concentration curves (over the 2 hour sampling period) were used to calculate

fluxes of CH_4 from the free atmosphere to the soil columns in experiments 1 and 2, as shown in Tables 1 and 2, respectively. In experiment 1 it can be seen that, with the exception of the period 6 hours after gas injection, there was a net flux of atmospheric methane into the columns, with an average flux of $1.13 \mu\text{mol CH}_4 \text{ m}^{-2} \text{ h}^{-1}$. In contrast, outgassing of CH_4 from experiment 2 columns was much greater and more sustained, between 3 and 24 hours after gas injection. Before and after this period of net outgassing from

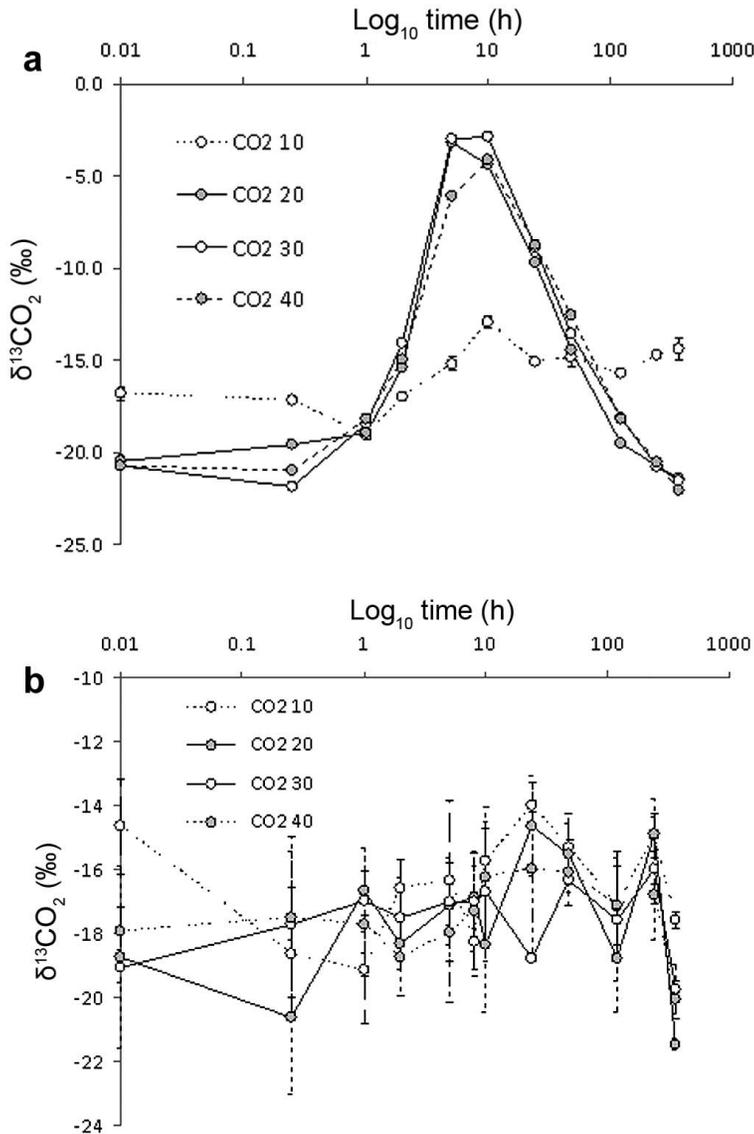


FIG. 6. The $\delta^{13}\text{C}_{\text{CO}_2}$ in soil gas samples in (a) re-packed and (b) undisturbed soil columns.

experiment 2, the average net flux from the atmosphere into the columns was $0.59 \mu\text{mol CH}_4 \text{ m}^{-2} \text{ h}^{-1}$. The higher average net flux into the experiment 1 columns supports the deduction from Fig. 3 that the experiment 1 columns had a higher rate of CH_4 oxidation than the experiment 2 columns. This interpretation, however, is predicated on the assumption that the two sets of columns had identical diffusion coefficients, which is unlikely as experiment 1 columns were

highly disturbed and experiment 2 columns were not.

The 'realism' of the estimates of CH_4 fluxes in the two laboratory column experiments in this study can be judged by comparison with values reported in the literature using similar methods of flux measurement but different soils (Table 3). The average values for atmosphere to soil fluxes (i.e. positive values in Tables 1 and 2) of 1.13 and $0.59 \mu\text{mol CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ for

MIGRATION OF ¹⁴CH₄ IN SUBSOIL

TABLE 1. Fluxes of atmospheric methane into soil columns determined in experiment 1 (re-packed) using column headspace sampling. Negative fluxes (in bold) are due to outgassing of injected labelled methane, as confirmed by δ¹³CH₄ measurements.

Hours after injection	-24	6	12	24	72	120	168	216	264	312
μmol CH ₄ m ⁻² h ⁻¹	1.15	-1.20	0.59	0.98	1.20	1.19	1.13	1.17	1.21	1.54
R ² (linear regression on head space [CH ₄] over 2 hour sampling period)	0.99	0.96	0.70	0.92	0.98	0.94	1.00	0.99	0.98	0.99

TABLE 2. Fluxes of atmospheric methane into soil columns determined in experiment 2 (undisturbed) using column headspace sampling. Negative fluxes (in bold) are due to outgassing of injected labelled methane, as confirmed by δ¹³CH₄ measurements.

Hours after injection	0	3	6	9	12	24	72	120	168	240	360
μmol CH ₄ m ⁻² h ⁻¹	0.49	-40.7	-58.6	-41.0	-28.2	-3.7	0.66	0.57	0.77	0.48	0.55
R ² (linear regression on head space [CH ₄] over 2 hour sampling period)	0.75	0.96	0.99	1.00	0.96	1.00	0.98	0.95	0.95	0.82	0.90

experiments 1 and 2 are not dissimilar from those in Table 3. Particularly noticeable, however, is the high outgassing flux for CH₄ reported by McNamara *et al.* (2006) for forest soil with a high water table, which exceeds the highest outgassing flux measured in this study (experiment 2) by a factor of 2. This strong flux of methane from soil to atmosphere under high

water table conditions is similar to the wetting response observed in antecedent measurements observed in experiment 1 and confirms the highly responsive nature of methanogenesis to soil wetting, even though drier soils are generally seen to be dominated by methanotrophy and a net consumption of atmospheric CH₄.

TABLE 3. Literature values for methane fluxes into soil columns. Negative fluxes (outgassing) are shown in bold.

Authors	Study	μmol m ⁻² h ⁻¹	Original units
Andersen <i>et al.</i> (1998)	Intact forest soil cores in laboratory, ¹⁴ CH ₄ and ¹² CH ₄	6.5 7.1	μmol CH ₄ m ⁻² h ⁻¹ μmol CH ₄ m ⁻² h ⁻¹
McNamara <i>et al.</i> (2006)	CH ₄ flux from UK forest soil in laboratory soil cores	-120.3 (high water-table) 0.21 (low water table)	μg CH ₄ m ⁻² h ⁻¹ μg CH ₄ m ⁻² h ⁻¹
Reeburgh <i>et al.</i> (1997)	Loess, Alaska	<5.2	mg CH ₄ m ⁻² d ⁻¹

From the two soil column experiments reported here it appears that the methane fluxes from atmosphere to soil are approximately twice as high for re-packed soil columns as for undisturbed columns, even when considering soils sampled from the same site. It is likely that the results obtained for the undisturbed soil columns are more reflective of methane diffusion and oxidation under field conditions. Nevertheless, both experiments also provide datasets with which to help develop models of both diffusion and oxidation of methane under both steady state (antecedent gas profiles) and non-steady state (injected CH₄ pulses) conditions. They have also achieved their primary objective of assisting in the development and testing of suitable methods for injection and sampling of small quantities of ¹³CH₄ in larger scale field experiments.

Conclusions

The laboratory data indicate significant differences between the diffusion and oxidation rates of ¹³CH₄ in re-packed vs. undisturbed soil columns, with both rates appearing to be significantly lower in undisturbed soils, as confirmed by δ¹³CO₂ measurements in soil gas samples. Data from both laboratory and field experiments are being used to inform the development of a model of ¹⁴CH₄ migration and fate in the biosphere above a GDF.

Acknowledgements

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