Doctoral Thesis

Quantification of methane dynamics in a landfill-cover soil Method development and application

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Publication Date:
2010

Permanent Link:
https://doi.org/10.3929/ethz-a-006397554

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Quantification of Methane Dynamics in a Landfill-cover Soil: Method Development and Application

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of
Doctor of Sciences

presented by
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Zürich 2010
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Summary

Landfills are one of the major sources of emissions of the greenhouse gas methane (CH$_4$) to the atmosphere. Through effective management practices, including installation of a cover soil, the CH$_4$ produced during the anaerobic digestion of waste in the landfill-body can be partially or completely consumed by indigenous methanotrophic bacteria before reaching the landfill surface. Quantification of the capability of methanotrophic bacteria to oxidize CH$_4$ to CO$_2$ is important for the estimation of global CH$_4$ emissions and for global warming predictive models, and could also influence local landfill management strategies.

The objective of this thesis was to quantify rates of CH$_4$ oxidation in the cover soil of the Lindenstock landfill, a closed municipal waste landfill located near Liestal, Switzerland. For this purpose, the Gas Push-Pull Test (GPPT), a previously developed method used to measure in-situ rates of CH$_4$ oxidation above a methanogenic aquifer and in a peat bog, was adapted for use in a landfill-cover soil.

An initial laboratory study was conducted in an abiotic sand-fill tank to gain a better understanding of gas transport during GPPTs. GPPTs were performed at different degrees of water saturations to evaluate which of the noble gas tracers (He, Ne, or Ar) had physical transport properties most similar to those of CH$_4$. It was determined that at all water saturations the physical transport of Ar was most similar to that of CH$_4$, but as water saturation increased molecular diffusive transport became less important relative to advective transport and at the highest water saturation ($S_w=0.61$) any of the tracers could have been used.

An additional study was performed in the abiotic laboratory sand tank to evaluate whether stable carbon-isotope analysis of CH$_4$ could be used to complement the GPPT method. Strong fractionation of CH$_4$ due to faster molecular diffusion of the lighter isotope was shown to occur at all GPPT gas injection/extraction flow rates. Therefore, to quantify rates of microbial CH$_4$ oxidation using stable carbon-isotope analysis, fractionation due to
diffusion must be accounted for by either estimating physical transport properties using a co-injected non-reactive tracer, or by conducting a second GPPT with an added inhibitor of methane oxidation.

After having studied the physical transport of gases during GPPTs in the abiotic laboratory studies, we performed field GPPTs in the Lindenstock landfill-cover soil where gas concentrations were not only influenced by advection and diffusion but also by microbial CH$_4$ oxidation. Methane oxidation at two locations was quantified using either Ar as the non-reactive tracer gas, or CH$_4$ itself from a subsequent inhibited GPPT. First-order rate constants of $24.8 \pm 0.8$ h$^{-1}$ at location 1 and $18.9 \pm 0.6$ h$^{-1}$ at location 2 were calculated. It was noted that during periods of high background CH$_4$ concentrations, influx of the landfill-produced CH$_4$ into the soil volume being probed during the GPPT, offset some of the decrease due to CH$_4$ oxidation, thereby resulting in lower calculated first-order rate constants.

In a second field study we quantified CH$_4$ dynamics within and above the cover soil of the Lindenstock landfill using GPPTs, eddy covariance flux measurements, static chamber flux measurements, surface concentration measurements and soil-gas concentration profiles. Experiments performed during the two week study indicated that the CH$_4$ oxidation rate of landfill-produced CH$_4$ was stable (first order rate constant $13.0 \pm 2.3$ h$^{-1}$). In contrast, estimates of CH$_4$ fluxes across the soil surface were highly variable with chamber flux measurements indicated that the landfill-cover soil was usually a net sink for atmospheric CH$_4$ (maximum rate of 380 µmol m$^{-2}$ d$^{-1}$), whereas eddy covariance flux measurements recorded that the cover soil was a net CH$_4$ source on four of the five measurement days. Each method provided unique information that when combined allowed a better understanding of the fate of CH$_4$ in the cover soil.

In conclusion, in this thesis we successfully quantified CH$_4$ oxidation in a landfill-cover soil using the GPPT method. Results from GPPT experiments were combined with results obtained using state-of-the-art methods to gain a more comprehensive understanding
of the CH₄ dynamics of the cover soil. In addition, the laboratory experiments provided insight into gas transport during GPPTs and aided in the design of GPPT experiments.
Zusammenfassung

Deponien sind eine der Hauptemissionsquellen des Treibhausgases Methan (CH$_4$) in die Atmosphäre. Durch effektive Massnahmen, einschließlich der Installation einer Oberflächenabdeckung, kann das während des anaeroben Abbaus von Abfall im Deponiekörper produzierte CH$_4$ teilweise oder vollständig von indigenen methanotrophen Bakterien umgesetzt werden, bevor es die Deponieoberfläche erreicht. Die Quantifizierung des Potentials von methanotrophen Bakterien, CH$_4$ zu CO$_2$ zu oxidieren, ist von grosser Bedeutung für die Abschätzung globaler CH$_4$-Emissionen und für Prognosemodelle der Klimaerwärmung. Zudem könnte es auch Managementstrategien lokaler Abfalldeponien beeinflussen.

Ziel dieser Arbeit war es, Reaktionsraten der CH$_4$-Oxidation in der Oberflächenabdeckung der stillgelegten kommunalen Abfalldeponie Lindenstock bei Liestal, Schweiz, zu quantifizieren. Zu diesem Zweck wurde der Gas Push-Pull Test (GPPT), eine vorgängig entwickelte Methode für die in-situ Messung von CH$_4$-Oxidationsraten über einem methanogenen Grundwasserleiter und in einem Torfmoor, für die Applikation in der Oberflächenabdeckung einer Deponie adaptiert.

Eine Vorstudie im Labor wurde in einem mit abiotischem Sand gefüllten Tank durchgeführt, um die Eigenschaften des Gastransports während eines GPPTs besser abschätzen zu können. Bei unterschiedlichen Wassersättigungsgraden wurden im Labortank GPPTs mit verschiedenen Edelgastracern (He, Ne oder Ar) durchgeführt, um denjenigen Tracer zu bestimmen, welcher möglichst ähnliche physikalische Transporteigenschaften wie CH$_4$ aufweist. Es wurde festgestellt, dass während aller Wassersättigungsgrade das physikalische Transportverhalten von Argon demjenigen von CH$_4$ am Nächsten kommt. Mit steigender Wassersättigung wurde jedoch der Transport durch molekulare Diffusion relativ zum advektiven Transport
vernachlässigbar klein, so dass bei der höchsten Wassersättigung ($S_w = 0.61$) jeder Tracer hätte verwendet werden können.

Der abiotische Tank wurde für eine weitere Studie verwendet, um zu beurteilen, ob die stabile Isotopenanalyse von Kohlenstoff die GPPT Methode komplementiert. Bei allen GPPTs wurde unabhängig von der Gasflussrate eine starke Fraktionierung von CH$_4$ beobachtet. Das Ausmass dieser Fraktionierung durch Diffusion muss abgeschätzt werden, um mikrobielle Oxidation von CH$_4$ mittels Isotopenanalyse quantifizieren zu können, entweder über die physikalischen Transporteigenschaften eines mitgeführten nicht-reactiven Tracers oder über einen weiteren GPPT unter Zugabe eines Inhibitors der CH$_4$-Oxidation.

Im Anschluss an die abiotischen Laborstudien zur Bestimmung des physikalischen Gastransports während der GPPTs wurden Feldstudien in der Oberflächenabdeckung der Deponie Lindenstock durchgeführt. Hier wurden CH$_4$-Konzentrationen nicht nur durch Advektion und Diffusion, sondern auch durch mikrobielle Oxidation beeinflusst. Die CH$_4$-Oxidation wurde an zwei Standorten quantifiziert, wobei entweder Ar oder in einem nachfolgenden inhibierten GPPT CH$_4$ selbst als inertes Tracergas verwendet wurden. Die berechneten Ratenkonstanten erster Ordnung waren $24.8 \pm 0.8 \ h^{-1}$ am Standort 1 und $18.9 \pm 0.6 \ h^{-1}$ am Standort 2. Während Perioden hoher CH$_4$-Hintergrundkonzentrationen kompensierte der Zustrom von produziertem CH$_4$ in das Beprobungsvolumen des Bodens die Konzentrationsabnahme durch CH$_4$-Oxidation, weshalb unter diesen Bedingungen tiefere Ratenkonstanten erster Ordnung berechnet wurden.

In einer zweiten Feldstudie wurde die CH$_4$-Dynamik innerhalb und über der Oberflächenabdeckung der Deponie Lindenstock mit verschiedenen Methoden quantifiziert: GPPTs, Eddy-Kovarianz-Methode, Emissionsmessungen mit statischen
Hauben, Konzentrationsmessungen an der Bodenoberfläche und Bodengas-
Konzentrationsprofile. Versuche in einer zweiwöchigen Studie zeigten, dass die
Oxidationsrate von produziertem CH₄ stabil blieb (Ratenkonstante erster Ordnung:
13.0 ± 2.3 h⁻¹). Im Gegensatz dazu war der CH₄-Flux durch die Bodenoberfläche stark
schwankend. Gemäß den Haubenmessungen war die Deponie-Oberflächenabdeckung
eine Senke für atmosphärisches CH₄ (maximale Rate von 380 µmol m⁻² d⁻¹),
wohingegen die Flussmessungen über die Eddy-Kovarianz-Methode die
Oberflächenabdeckung an vier von fünf Tagen als Nettoquelle von CH₄ erfassten.
Jede Methode lieferte einzeln jeweils spezifische Informationen, wobei die
Kombination aller Methoden ein besseres Verständnis der Dynamik des CH₄-
Umsatzes ermöglichte.

In dieser Doktorarbeit konnten wir erfolgreich die Oxidation von CH₄ in der
Oberflächenabdeckung einer Deponie unter Verwendung der GPPT Methode
quantifizieren. Ergebnisse der GPPTs wurden mit Ergebnissen modernster Methoden
kombiniert, um ein besseres Gesamtverständnis der CH₄-Dynamik einer
Oberflächenabdeckung zu gewinnen. Darüber hinaus lieferten die Laborversuche
Einblicke in den Gastransport während eines GPPTs und verbesserten damit das
Design von GPPT Experimenten.
1

Introduction

Katherine Gómez
1.1 The methane cycle

1.1.1 Methane and global warming

The average surface temperature of the Earth is approximately 1°C higher than it was a century ago (Solomon et al., 2007). This rise in the average global temperature has been linked to increasing concentrations of greenhouse gases in the atmosphere which absorb outgoing long-wave radiation from the Earth, thereby retaining heat that would otherwise be radiated into space. The dramatic increase in the abundance of greenhouse gases in the atmosphere since the industrial revolution (ca. 1750) is largely due to human activities (Solomon et al., 2007). Methane (CH$_4$), one of the major greenhouse gases of concern for global warming, is currently more than twice as abundant in the atmosphere as it was prior to the industrial revolution; and polar ice-core records of pre-industrial atmospheric composition indicate that the current CH$_4$ concentration of 1800 ppb far exceeds that at any time over the last 650,000 years (Figure 1-1).

![Figure 1-1. The concentration and radiative forcing by CH$_4$ over the last 20,000 years reconstructed from Antarctic and Greenland ice and firn data and direct atmospheric measurements. The grey bar shows the reconstructed range of natural variability for the past 650,000 years. NH = Northern hemisphere, SH = Southern hemisphere (Solomon et al., 2007).]
Chapter 1: General Introduction

The effect that the increase in the atmospheric CH$_4$ concentration has on global warming can be interpreted using the concept of radiative forcing. Radiative forcing quantifies the influence of a concentration of a greenhouse gas on the balance of absorption and emission of radiation in the Earth’s atmosphere, the global radiative balance (Serreze, 2010). A gas with a positive radiative forcing value means that it tends to warm the surface of the Earth, whereas a negative value tends to cool it. Values are expressed in units of Watts per square metre (W m$^{-2}$) and are relative to background concentrations in 1750. The current atmospheric CH$_4$ abundance causes a radiative forcing of +0.48 ± 0.05 W m$^{-2}$; which is second only to that of carbon dioxide (CO$_2$) at +1.66 ± 0.17 W m$^{-2}$ (Solomon et al., 2007). Compared to CO$_2$ (current abundance ca. 385 ppm) the atmospheric abundance of CH$_4$ (1.8 ppm) is considerably lower and CH$_4$ has a shorter atmospheric residence time per molecule. However, due to strong absorbance of infrared radiation and the resulting heating effect, CH$_4$ is considered the third most important greenhouse gas after water vapour and CO$_2$ (Rogers & Whitman, 1991).

To predict future trends in global warming and the associated extreme weather and climate events that are occurring as a result of the build up of greenhouse gases in the atmosphere, we need to identify, comprehend and quantify the sources and sinks of CH$_4$.

1.1.2 Methane sources

Methane is produced by both natural and anthropogenic sources (Table 1-1). Among the natural sources of CH$_4$ are wetlands, CH$_4$ hydrates, oceans and termites. Of these natural CH$_4$ sources, the source strength of wetlands is the most uncertain (from 100 to 231 Tg CH$_4$ yr$^{-1}$) because of the sensitivity of CH$_4$ production and emission in this environment to fluctuations in hydrology and temperature (Moosavi et al., 1996). Fluctuations in emissions and sudden large releases of gas from CH$_4$ hydrates have been hypothesized to be contributing factors to past catastrophic climatic events and extinctions (Heydari et al., 2008).
and it is predicted that global warming will cause the release of large amounts of \( \text{CH}_4 \) from hydrates in permafrost regions (Archer, 2007).

Table 1-1. Estimates of global emissions of \( \text{CH}_4 \) from natural and anthropogenic sources (Denman et al., 2007).

<table>
<thead>
<tr>
<th>Source</th>
<th>Minimum estimate [Tg CH(_4) yr(^{-1})]</th>
<th>Maximum estimate [Tg CH(_4) yr(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands</td>
<td>100</td>
<td>231</td>
</tr>
<tr>
<td>Ruminants</td>
<td>76</td>
<td>92</td>
</tr>
<tr>
<td>Energy</td>
<td>74</td>
<td>77</td>
</tr>
<tr>
<td>Gas, oil, industry</td>
<td>36</td>
<td>68</td>
</tr>
<tr>
<td>Rice agriculture</td>
<td>31</td>
<td>112</td>
</tr>
<tr>
<td>Landfills &amp; waste</td>
<td>35</td>
<td>73</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>14</td>
<td>88</td>
</tr>
<tr>
<td>Termites</td>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>Ocean</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>CH(_4) hydrates</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Other</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>503</strong></td>
<td><strong>610</strong></td>
</tr>
</tbody>
</table>

Methane emissions from anthropogenic or human influenced sources are considered to be mainly responsible for the rise in the global atmospheric \( \text{CH}_4 \) abundance over the past 250 years. The recent transition from a plant-based diet to one more focused on food of animal origin is associated not only with an increase in obesity in humans, but has also contributed to global warming through production of animal feed, animal transport and an increase in the amount of manure. In addition, change in the diet of ruminants from pasture to grain has increased the amount of \( \text{CH}_4 \) produced by the animals during enteric fermentation (Koneswaran & Nierenberg, 2008).
Another change that occurred following the industrial revolution was that material became more available than labour and the earlier concept of reuse and recycling was no longer vital. With the demographic shift to industrial centres, available space for accumulating waste decreased and societies had to develop waste management systems. Landfills were generally preferred over early incinerators which emitted ashes and partially burned debris that fell on surrounding communities. In the 20th century new chemical and plastic wastes were dumped in landfills and only later as environmental awareness increased did the problems of water pollution from hazardous leachates and the contribution of landfills to global warming through release of CH$_4$ become evident (WasteWatch, 2004).

### 1.1.3 Methane production

Methane is produced by methanogenic prokaryotes belonging to the domain Archaea, during the anaerobic digestion of organic matter. Production of CH$_4$, or methanogenesis, is the final step in the decay of organic matter after other electron acceptors including O$_2$, sulphate, nitrate and oxidised iron or manganese have been depleted and hydrogen (H$_2$), CO$_2$ and acetate have accumulated. Compared to aerobic degradation or other anaerobic degradation processes, methanogenesis yields the lowest energy per molecule converted. To survive on this low energy yield, the microorganisms form syntrophic relationships in which two or more different types of microorganisms depend upon each other to perform a metabolic activity (Thauer et al., 2008). At least four different groups of bacteria cooperate syntrophically to digest organic matter into CH$_4$ and CO$_2$ (Schink, 1997). Initially the organic matter polymers are converted by fermenting bacteria to oligomers and monomers which are then converted to alcohols, succinate, lactate and fatty acids. These products are further digested by other fermenters to acetate, CO$_2$, H$_2$ and formate which can then be consumed by the methanogens (Figure 1-2).
Figure 1-2. Pathway of methanogenic degradation of organic matter (polymers) to CH$_4$. Intermediates are shown in boxes. Groups of bacteria involved (in circles) are: 1, primary fermenting bacteria; 2, hydrogen-oxidizing methanogens; 3, acetate-cleaving methanogens; 4, secondary fermenting bacteria; 5, homoacetogenic bacteria (Schink, 1997)

Methanogens use carbon in the form of CO$_2$ (+ H$_2$) or acetic acid (Equation 1-1 and Equation 1-2), or other less well-known simple substrates including formic acid, methanol, methylamines, dimethyl sulphate, or methanethiol (Le Mer & Roger, 2001).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$  \hspace{1cm} \text{Equation 1-1}

$$CH_3COOH \rightarrow CH_4 + CO_2$$  \hspace{1cm} \text{Equation 1-2}

Methanogenesis occurs under anaerobic conditions such as the water-saturated zone in rice paddies or wetland soils, anoxic zones in landfills and in lake sediments. Methanogens in the O$_2$-free digestive system of ruminants assist in the digestion of cellulose into short chain fatty acids that can be absorbed by the animal’s gut and CH$_4$ which is emitted from the animal in volumes of up to 250 L CH$_4$ per day (McAllister et al., 1996). Production of CH$_4$ in each of these environments depends on available degradable organic matter and anoxic conditions.
1.1.4  Methane sinks

The main means for removal of CH₄ from the atmosphere is through oxidation in the troposphere by hydroxyl radicals. This method is estimated to account for the loss of up to 511 Tg CH₄ y⁻¹ (Denman et al., 2007). Additional losses occur through reaction with chlorine atoms in the marine boundary layer, and reaction in the stratosphere with either hydroxyl radicals, chlorine or electronically excited oxygen atoms (O(^1D)) (Ehhalt et al., 2001). In addition to abiotic removal of CH₄ from the atmosphere, biotic oxidation by methanotrophic microorganisms also serves as a CH₄ sink.

1.1.5  Biological methane oxidation

Biotic CH₄ oxidation occurs both aerobically and anaerobically. Anaerobic methanotrophic archaea (ANME), a close relative of methanogens, consume CH₄ using sulphate or nitrite (Ettwig et al., 2008), nitrate (Raghoebarsing et al., 2006), manganese or iron (Beal et al., 2009) as the final electron acceptor. These microorganisms are known to live in sediments at the depth at which sulphate oxidation gives way to methanogenesis, the sulphate to CH₄ transition (Valentine, 2002). This zone of anaerobic methane oxidation on the sea floor effectively prevents CH₄ effluxes from oceans by consuming more than 90 % of the CH₄ produced in ocean sediments before it can migrate to the oxic zone (Knittel & Boetius, 2009).

Instead of sulphate or nitrate, aerobic methanotrophs use O₂ as the final electron acceptor during oxidation of CH₄ (Equation 1-3).

\[
CH_4 + 2O_2 \rightarrow CO_2 + H_2O \quad \text{Equation 1-3}
\]

The thirteen genera of aerobic methanotrophs have generally been classified as either type I (γ Proteobacteria) or type II (α Proteobacteria). The two types differ in numerous ways
including the pathway used to assimilate carbon, the morphology of the internal membranes and in the dominant phospholipid fatty acids (Conrad, 2007).

Aerobic methanotrophs synthesise an enzyme, methane monooxygenase (MMO), in either a particulate (pMMO) or soluble (sMMO) form that mediates the first step in the oxidation of CH$_4$ enabling them to use the one-carbon compound as their sole source of carbon and energy. Unlike sMMO which is only expressed in low-copper environments, all aerobic methanotrophs except *Methylocella* spp. have the enzyme pMMO (Conrad, 2007). The gene encoding the alpha subunit of pMMO has been used extensively in molecular microbiology to select for aerobic methanotrophs. Aerobic methanotrophs can be found both in soils exposed to high CH$_4$ concentrations such as landfill-cover soils and peat bogs, and also in environments where the only CH$_4$ available for consumption is the 1.8 ppm in the atmosphere. The kinetics of CH$_4$ oxidation in environments where methanotrophs are exposed to high CH$_4$ concentrations is quite different from that of methanotrophs exposed to atmospheric CH$_4$ levels (Table 1-2).

Table 1-2. Kinetics of CH$_4$ oxidation measured in soil from different environments

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>$v_{max}$ (nmol·gdw$^{-1}$·h$^{-1}$)</th>
<th>$K_M$ (nM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 fresh soils (meadow, forest)</td>
<td>0.6 - 3.6</td>
<td>0.83 - 1.9</td>
<td>(Bender &amp; Conrad, 1993)</td>
</tr>
<tr>
<td>3 fresh soils</td>
<td>0.7 - 3.6</td>
<td>30 - 51</td>
<td>(Bender &amp; Conrad, 1992)</td>
</tr>
<tr>
<td>Soil from an alder forest</td>
<td>1.1</td>
<td>4.9</td>
<td>(Reay &amp; Nedwell, 2004)</td>
</tr>
<tr>
<td>Soil from an oak forest</td>
<td>240</td>
<td>790</td>
<td>(Reay &amp; Nedwell, 2004)</td>
</tr>
<tr>
<td>Subarctic peat soil</td>
<td>40 - 55</td>
<td>1000</td>
<td>(Dunfield et al., 1993)</td>
</tr>
<tr>
<td>4 CH$_4$ pre-incubated soils</td>
<td>270 - 3690</td>
<td>1740 - 27900</td>
<td>(Bender &amp; Conrad, 1992)</td>
</tr>
<tr>
<td>Landfill cover soil (sandy)</td>
<td>440 - 1600</td>
<td>5200 - 75000</td>
<td>(Park et al., 2005)</td>
</tr>
<tr>
<td>Peat soil</td>
<td>44500</td>
<td>100000</td>
<td>(Bender &amp; Conrad, 1992)</td>
</tr>
<tr>
<td>Landfill cover soil (coarse sand)</td>
<td>998</td>
<td>1000000</td>
<td>(Kightley et al., 1995)</td>
</tr>
</tbody>
</table>
1.2 Field methods to quantify methane dynamics

To predict future trends in atmospheric CH$_4$ abundance and global warming, a good understanding of CH$_4$ sources and sinks is required. Precise measurements of fluxes and estimates of kinetic parameters from specific anthropogenic and natural sources are needed. Efforts to quantify CH$_4$ dynamics in various environments of interest have been explored using a wide range of methods.

1.2.1 Surface methods

1.2.1.1 Aircraft and satellite methods

Airplanes and balloons can be used to measure fluxes of CH$_4$ on a landscape scale above surfaces such as wetlands, large landfills or arctic permafrost regions. Average CH$_4$ fluxes from pastoral agriculture and wetlands have been estimated from vertical concentration profiles from air samples collected by aircraft flying upwind and downwind from the region of interest (Lassey et al., 2000, Gallagher et al., 1994). In addition, CH$_4$ emissions from biomass burning have been quantified from air samples measured in an airplane at different heights (Delmas et al., 1991). Previously CH$_4$ concentrations of the air samples were quantified via gas chromatography, however newer methods such as laser spectrophotometry have more recently been applied to measure the concentration of CH$_4$ in the troposphere (Romanini et al., 2006).

Remote sensing of CH$_4$ using satellite system sensors such as the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) located on the European environmental satellite (ENVISAT) has also been explored as a means to quantify CH$_4$ emissions from ecosystems of interest. Because satellites produce large amounts of data from around the globe in a short period of time they promise to be valuable tools in the assessment of CH$_4$ sources and sinks. Use of aircraft or satellite methods allows direct...
measurement of fluxes and avoids the scaling up of sparsely distributed ground measurements to estimate landscape to regional level fluxes (Frankenberg et al., 2005).

1.2.1.2 Eddy covariance

The eddy covariance technique is an ecosystem to landscape scale (several $\text{m}^2$ to $\approx 1 \text{ km}^2$) micrometeorological method for measuring gas exchange fluxes between an ecosystem and the atmosphere. It is a well-established technique, that has been implemented, for example, to measure CO$_2$ fluxes above tropical (Grace et al., 1995), temperate and boreal forests (Baldocchi & Vogel, 1996); and CH$_4$ fluxes above rice paddies (Miyata et al., 2000), peat bogs (Hargreaves et al., 2001) and landfills (Laurila et al., 2005).

The eddy covariance system consists of a tower with an ultrasonic anemometer and an instrument for gas analysis. The anemometer measures turbulent vertical wind velocity at the Earth’s surface while the gas analyser simultaneously measures the concentration of the gas of interest at high temporal resolution (10-20 Hz). A statistical method is used to calculate the covariance between the high frequency measurements.

The principle of eddy covariance relies upon the fact that in the atmosphere closest to the Earth’s surface, the atmospheric boundary layer, turbulent eddies induce vertical mixing that carries gaseous components along concentration gradients (Figure 1-3). Calculated fluxes are most accurate when wind velocity, air temperature, humidity, and gas component concentration are steady, and when the underlying vegetation is homogenous and the terrain is flat for an extended distance upwind.
Figure 1-3. Eddy movement of parcels of air (c₁ and c₂) either upwards or downwards at velocity V₁ or V₂.

The area from which the flux is being measured, the “footprint”, can be described probabilistically and depends upon the height of the sensors on the tower, the horizontal wind speed, the atmospheric stability and the roughness of the terrain. Therefore, while the equipment may remain stationary and the site location unchanged, the footprint measured may vary from one day to the next due to changes in local micrometeorological conditions.

1.2.1.3 Flux chambers

Flux chambers have the advantage of being relatively inexpensive, simple to install, and highly sensitive at detecting even very small fluxes and therefore have frequently been used to quantify fluxes of greenhouse gases including CH₄, CO₂ and nitrous oxide (N₂O) across the soil-atmosphere interface (e.g. Reth et al., 2005, Weslien et al., 2009, Ellert & Janzen, 2008). Installation generally involves insertion of a circular collar several cm into the ground followed by positioning of the flux chamber on the collar. The chamber is well sealed from the surrounding air and samples of gas from inside the chamber are withdrawn periodically through a gas-tight port. The concentration of the component gases in the samples can then be quantified using e.g. gas chromatography with a flame ionization detector for CH₄. A linear increase in the concentration of a gas component in the chamber over time indicates that there is a positive flux, or emission, from the soil into the atmosphere,
whereas a decrease indicates a negative flux from the atmosphere into the soil, as for example, during oxidation of atmospheric CH$_4$ by methanotrophs inhabiting surface soils. Gas component fluxes can be calculated by regression of the sample concentration against sampling time.

Closed-static chambers are the simplest flux chambers to use, however they have the disadvantage that an increase in a gas component concentration in the chamber can result in a decrease in the diffusion gradient between the headspace of the chamber and the soil, thereby suppressing surface fluxes into the chamber, leading to an underestimation of emissions (Norman et al., 1997). Alterations in the heat and water balance of the soil can also be caused by placement of chambers over the soil, therefore deployment periods for closed-static chambers should be relatively short to minimize disturbance of the measured surface. Modifications to flux chambers including addition of a fan or passing a gas flow through the chamber to minimize pressure differences have been explored as means to better estimate fluxes (Norman et al., 1997).

In some environments, for example landfill cover soils, the inherent spatial heterogeneity in fluxes can be high, resulting in large variations between chamber measurements. Scaling up flux chamber measurements to estimate fluxes for a larger area is therefore challenging and requires many measuring points. In addition, chambers only capture fluxes across the area of soil surface on the spot where they are installed, if there are “hot spots” of large fluxes that are not covered by a chamber, they will not be measured and estimates of fluxes for the area will therefore be underestimated.

Although discrepancies between estimates of fluxes calculated from chamber measurements (indirect approach) compared with (a) the direct methods via eddy covariance or (b) for tracer gas release methods can be high (Borjesson et al., 2000); for an example see Figure 1-4), chambers are ideal for determining the heterogeneity of fluxes across a site and for measuring the differences in fluxes between different treatment plots.
Figure 1-4. Comparison of the CO$_2$ flux in a forest soil measured using the eddy covariance technique (EC) and the dynamic closed chamber system (DC-1) (Janssens et al., 2000).

1.2.2 Subsurface methods

1.2.2.1 Soil-air concentration profiles

In addition to aboveground methods for measuring gas fluxes between the soil and the atmosphere, measurements of underground gas dynamics also provide valuable information regarding microbial processes in the subsurface that influence whether an environment is a CH$_4$ source or a sink. Soil-air sampling is a relatively inexpensive and easily performed technique that causes little disturbance to the soil. Gas-sampling needles or tubes are inserted into the ground with their tips at different depths in the soil. After waiting a short time to allow the soil-air to re-equilibrate, several mL of soil-air sample is withdrawn through the needle or tube and is either analysed using a field portable instrument or injected into a vial that is returned to the lab to be analysed, e.g. by gas chromatography. The concentration of one or several measured gas components can be plotted against the depth in the soil from
which samples were taken. This technique has been used to visualise counter-gradients of \( \text{CH}_4 \) and \( \text{O}_2 \) in environments exposed to elevated \( \text{CH}_4 \) concentrations and to pinpoint the zone of maximum methanotrophic activity where both \( \text{CH}_4 \) and \( \text{O}_2 \) are depleted due to consumption by methanotrophic microorganisms (Damgaard et al., 1998, Urmann et al., 2007b, for example see Figure 1-5).

![Figure 1-5. Gas concentration profiles in a landfill-cover soil (Visvanathan et al., 1999)](image)

Rates of \( \text{CH}_4 \) oxidation can be estimated from profile sample concentration gradients by calculating the diffusive flux into and out of the zone of methanotrophic activity then calculating a conversion rate. The diffusive flux of a gas in a soil can be estimated from soil-air profile sample gradients using Fick’s first law of diffusion:

\[
J = -D_{\text{eff}} \frac{dC}{dZ}
\]

Equation 1-4
Where $J$ is the diffusive flux, $D_{\text{eff}}$ is the effective diffusion coefficient of the gas in the soil, and $\frac{dC}{dZ}$ is the change in the gas component concentration over a certain depth. $D_{\text{eff}}$ can either be measured via a gas tracer method (Johnson et al., 1998), or can be empirically derived from soil porosity and water content data (e.g. Millington & Quirk, 1959).

Fluxes or oxidation rates calculated from soil-gas profiles are often highly variable both temporally and spatially. This may be because the soil gas samples collected are small-volume point samples and gas-component concentrations can therefore be highly variable due to soil heterogeneity along the vertical depth profile or because the location is not in a steady state. In addition, $D_{\text{eff}}$ values have been shown to fluctuate seasonally (Kusa et al., 2008), therefore, further uncertainty is introduced into flux calculations from profile gradients if $D_{\text{eff}}$ is not measured each time profile samples are taken.

1.2.2.2 Gas Push-Pull Tests

The “Gas Push-Pull Test” (GPPT) was developed to quantify in situ rates of microbial processes in the unsaturated subsurface. It evolved from the Push-Pull Test (PPT), a single-well aqueous test used to quantify rates of microbial processes including methanogenesis, sulphate reduction and denitrification in aquifers (Istok et al., 1997). Additional earlier abiotic uses of the PPT include estimation of residual oil saturation in reservoirs (Tomich et al., 1973), measurement of resident water saturation (Deans & Mut, 1997), and enhancement of light-oil recovery (Zhang et al., 2006). Like the PPT, the GPPT is a single-well test in which one or more reactants is injected into the subsurface along with a non-reactive tracer(s), however, instead of a liquid injection into the saturated zone, gases are injected into the unsaturated subsurface. Following injection of the tracer/reactant gas mixture, the direction of the pump is reversed and the injected gases mixed with soil air are extracted from the same location into a series of sample vials. The gas component concentrations of the samples can
be measured using gas chromatography and rates of microbial processes can be quantified from analysis of the breakthrough curves (Figure 1-6).

![Breakthrough curves for CH\textsubscript{4} and noble gases during the extraction phase of a GPPT. The relative concentration (concentration of gas component in extraction phase sample divided by concentration in injected gas mixture) is plotted versus the extracted divided by the injected volume of gas](image)

Figure 1-6. Breakthrough curves for CH\textsubscript{4} and noble gases during the extraction phase of a GPPT. The relative concentration (concentration of gas component in extraction phase sample divided by concentration in injected gas mixture) is plotted versus the extracted divided by the injected volume of gas.

During GPPTs transport of the injected gases in the subsurface occurs mainly due to the physical transport processes of advection and molecular diffusion. Advection transport of the gas mixture due to the pressure gradient generated by the gas pump is independent of the molecular mass of the gas components and is therefore non-segregative. In contrast, diffusive transport is the movement of gas components along their concentration gradients and depends upon the molecular mass of the gas and the tortuosity of the soil. In addition to advective and diffusive transport towards or away from the injection point, the concentration of the reactant gases can also be influenced by microbial processes, such as methane oxidation. If a tracer gas and a reactant have similar physical transport properties during a GPPT, then simplified methods to quantify microbial kinetics from breakthrough curves can be implemented (Snodgrass & Kitanidis, 1998, Schroth & Istok, 2006, Haggerty et al., 1998).
GPPTs have previously been used to quantify rates of CH$_4$ oxidation in a peat bog (Urmann et al., 2007a), above a hydrocarbon-contaminated aquifer (Urmann et al., 2005) and to measure rates of oxidation of atmospheric CH$_4$ by methanotrophs in surface soils (Nauer, 2007).

1.2.3 Supporting methods

1.2.3.1 Stable isotopes

Many elements exist in nature as several different non-radioactive or “stable” isotopes that have the same number of protons, but different numbers of neutrons. The slight disparity in atomic mass between the stable isotopes of an element (resulting from the different number of neutrons) generally does not influence the chemical characteristics of an element, but it can influence both the physical transport properties and reaction kinetics. A heavier isotope of an element diffuses at a slightly slower rate and additionally is consumed by microorganisms at a slightly slower rate compared to a lighter isotope. These processes can therefore result in a change in the ratio of one stable isotope of an element to another.

The lighter isotopes are generally much more abundant in nature than the heavier isotopes, e.g. $^{12}$C makes up ca. 99% of all carbon while $^{13}$C makes up only ca. 1%. The isotopic composition of the carbon atoms in CH$_4$ in a gas sample can be measured using gas chromatography coupled to an isotope-ratio mass spectrophotometer (GC-IRMS) and the ratio between the two stable isotopes of carbon can be calculated in reference to the carbon standard Pee Dee Belemnite and represented in the $\delta$ notation as follows:

$$ \delta^{13}C \ (\permil) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 $$

**Equation 1-5**

where $R$ is the ratio between $^{13}$C and $^{12}$C in a sample and the standard, respectively.
Measurement of the stable carbon isotope ratio of CH$_4$ has been used in combination with flux chambers to determine the fraction of CH$_4$ oxidised as it passes through a landfill-cover soil (Chanton et al., 2008a, Stern et al., 2007, Abichou et al., 2006a). The $\delta^{13}$C of CH$_4$ in a gas sample taken from within the waste (typically $<-55$‰, (Abichou et al., 2006a)) is compared with the isotopic signature of CH$_4$ emitted into flux chambers (may range from -30 to -50‰ (Abichou et al., 2006a)), a laboratory determined fractionation factor for CH$_4$ oxidation ($\alpha_{ox}$) is then used to calculate the percentage of CH$_4$ oxidised during passage through the cover soil. If, in addition, the stable carbon isotope ratio of profile samples are measured then the depth of maximum CH$_4$ oxidation in the cover soil can be confirmed (Abichou et al., 2006a).

A source of error in using stable carbon isotope ratios to quantify the fraction of CH$_4$ oxidised during migration through a landfill-cover soil arises from the selection of $\alpha_{ox}$. These factors are determined from laboratory studies and have been reported to be specific to the soil type and sensitive to a number of parameters including temperature and CH$_4$ oxidation rate (Chanton et al., 2008a). In addition, it is generally assumed that gas transport in the cover soil is dominated by advection and that fractionation of CH$_4$ due to different rates of molecular diffusion of $^{12}$CH$_4$ and $^{13}$CH$_4$ does not need to be considered. This assumption was shown to lead to conservative estimates of CH$_4$ oxidation (De Visscher et al., 2004).

An additional use of stable carbon isotopes is to verify methanotrophic activity during GPPTs. A normal active GPPT is performed first followed by an inactive GPPT that includes a methanotrophic inhibitor in the injection gas mixture. During the inactive GPPT any fractionation of CH$_4$ that occurs is due to physical processes, whereas during the active GPPT fractionation due to physical processes and microbial consumption occur. Therefore, differences between the two GPPTs confirms oxidation of CH$_4$ by microbial activity (Urmann et al., 2005).
1.2.3.2 Radon

Radium 226 (\(^{226}\text{Ra}\)), the most common and most stable isotope of radium, is formed as part of the normal decay of uranium (half-life 4.5 billion years). \(^{226}\text{Ra}\) is a radioactive trace compound found in all soils that slowly decays (half-life 1602 years) to produce radon 222 (\(^{222}\text{Rn}\)). Production of \(^{226}\text{Ra}\) from uranium and subsequent production of \(^{222}\text{Rn}\) are therefore constant and concentrations will remain stable for millions of years.

\(^{222}\text{Rn}\) is a radioactive noble gas (half-life of 3.8 days) that has been used as a tracer gas to study transport fluxes from the soil to the atmosphere. It is ideally suited for this purpose because it is emitted almost exclusively from soils and it is a chemically inert gas. Concentrations of \(^{222}\text{Rn}\) can be measured indirectly via detection of alpha particles emitted directly from the decay of its short-lived daughter, \(^{218}\text{Polonium}\).

Measurements of \(^{222}\text{Rn}\) and \(\text{CH}_4\) concentrations in profile samples and the flux of \(^{222}\text{Rn}\) at the soil surface were used to calculate \(\text{CH}_4\) fluxes across the surface of several field soils. Results indicated that the main parameter controlling the flux of atmospheric \(\text{CH}_4\) into the soil was gas transfer in the soil air by gas molecular diffusion rather than the rate of microbial consumption of atmospheric \(\text{CH}_4\) (Born et al., 1990).

Exhalation of \(^{222}\text{Rn}\) from a soil in Germany was calculated to be nearly constant with time at 4000 dpm m\(^{-2}\) h\(^{-1}\) (Dorr et al., 1983). This constant flux was then used to calibrate \(\text{CO}_2\) flux measurements from the soil to estimate the \(\text{CO}_2\) respiration rate from the soil and from plant leaves. The use of \(^{222}\text{Rn}\) as a transport tracer was also explored for forest canopy to atmosphere \(\text{CO}_2\) exchange and it was reported that \(\text{CO}_2\) exchange rates calculated from \(^{222}\text{Rn}\) measurements were a good substitute for eddy covariance values when low turbulence during periods of calm made eddy covariance estimates less certain (Martens et al., 2004).
## 1.3 Methane dynamics in landfills

### 1.3.1 Methane production in landfills

Landfill gas produced during bacterial decomposition of organic waste is a mixture mainly consisting of CH$_4$ and CO$_2$ (50-70% and 30-50% v/v, respectively), but also includes small amounts of nitrogen, hydrogen sulphide and other non-methane hydrocarbons (Farquhar & Rovers, 1973). Bacterial degradation of landfill waste generally occurs in four phases with different gases produced during each phase (Figure 1-7). During phase I aerobic bacteria initiate decomposition of the waste by breaking apart complex carbohydrates, proteins and lipids. By the end of this phase CO$_2$ has been produced and the available O$_2$ consumed. In Phase II anaerobic bacteria begin to convert the breakdown products of aerobic decomposition into acids and alcohols resulting in acidification of the waste which in turn results in the release of the essential nutrients nitrogen and phosphorous. Hydrogen and CO$_2$ are produced during this phase. The waste becomes more neutral again during phase III when the organic acids from phase II are consumed and acetate is released. At this stage methanogenic bacteria begin to establish and consume CO$_2$ and acetate. During phase IV gas is produced at a steady rate and the composition of the gas is relatively constant. This phase can continue for 20 years or more depending upon the composition and fraction of organic matter in the waste.

### 1.3.2 Methane consumption in landfills

Production of landfill gas from the decomposition of solid waste leads to both a concentration gradient and a pressure build-up within the landfill which cause migration of the gas out of the anaerobic zone. Most well-managed landfills in industrialised countries are installed with a cover soil that serves to both prevent lateral migration of the waste and mitigate emissions of CH$_4$ to the atmosphere.
Table 1-7 Changes in the composition of landfill gas during the four phases of landfill waste decomposition (ATSDR, 2009)

![Diagram showing gas component changes](Image)

Although it has been reported that at some landfills CH\textsubscript{4} oxidation in landfill-cover soils can consume all the produced CH\textsubscript{4} before it can be emitted to the atmosphere (Jones & Nedwell, 1993), landfills are a major contributor to global CH\textsubscript{4} emissions. Reduction of CH\textsubscript{4} emissions from landfills through effective landfill design and management practices could significantly contribute to reducing global CH\textsubscript{4} emissions in a relatively short period of time due to the short atmospheric lifetime of CH\textsubscript{4}.

## 1.4 Landfill design

### 1.4.1 Regulations on landfill design

The major objective considered when designing landfills is the protection of the environment from contaminants that may be present in the solid waste. This includes in
particular protection of surface- and ground-water, soil, air and human health. To meet this objective landfills are not built in environmentally sensitive areas and are monitored for landfill gas and for any signs of groundwater contamination. United States federal regulations for establishment of a landfill include the following conditions: 1) located away from geological faults, wetlands and floodplains 2) to protect groundwater and underlying soil from leachate a flexible geomembrane overlaying 60cm of compact clay soil must be installed on the bottom and sides 3) a leachate collection and removal system must be installed 4) a groundwater monitoring system to test for waste leaks must be established (USEPA, 2010).

While a reduction in the emission of greenhouse gases from landfills is not the primary consideration in landfill design, programs are now in place to encourage recovery of and beneficial use of landfill gas as an energy source (USEPA, 2010). Using a series of wells and a blower/flare or vacuum system, landfill gas can be extracted from landfills and either flared or used as an energy source. This may not be possible in older landfills in which the gas production rate may be low or variable making the utilisation or flaring of the landfill gas not viable. Although recovery and subsequent burning or use of landfill gas is seen as a positive move in global warning politics, complications regarding further environmental pollution through burning of landfill gas and creation of dioxins and furans and release of mercury and tritium have been raised (Energy-Justice-Network, 2007).

1.4.2 Landfill-cover soil design

The USEPA regulations for municipal solid waste landfills include a specification that the waste be frequently covered with several inches of soil to help reduce odour, control litter, insects, and rodents and protect human health (USEPA, 2010). Once landfills have reached their full capacity a more permanent landfill cover can be installed. Landfill cover soils are typically composed of locally derived excavated soil of various textures overlain with topsoil and can vary in depth from 15 to 125 cm (Abichou et al., 2006b, Bogner et al., 1997, Borjesson et al., 2000). Other materials that have been explored for their capacity to oxidise...
CH$_4$ include sewage sludge and wood chips (Borjesson et al., 2007) and compost (Chanton et al., 2008b). Conventional landfill-cover design systems use low-permeability barrier layers constructed of compacted clay, geomembranes or geosynthetic clay liners with low hydraulic conductivities (USEPA, 2003). The material selected for the landfill-cover soil must both retard downward movement of water, while simultaneously allowing water to move laterally through the topsoil formation in order to minimize the potential for slope failure and to allow for development of vegetation (USEPA, 2003).

1.5 Research objectives

The aim of this thesis was to quantify in situ rates of CH$_4$ oxidation in a landfill-cover soil. To meet this aim we adapted the GPPT method for use in a landfill-cover soil. This method has previously been implemented to quantify rates of CH$_4$ oxidation in a peat bog and above a petroleum-contaminated aquifer. In this work gas transport during GPPTs was first investigated in abiotic laboratory studies, followed by field experiments to evaluate the feasibility of performing GPPTs in a landfill-cover soil and to contrast the information gained from GPPTs with other state-of-the-art methods for measuring CH$_4$ dynamics. The specific objectives of the individual studies were:

Chapter 2: to evaluate the relative importance of molecular diffusion, advection and transfer into the water phase of CH$_4$ and noble gases during GPPTs. GPPTs were performed at two different gas flow rates and five different water saturations in a large sand-filled laboratory tank equipped with vents to simulate an open system.

Chapter 3: to investigate if natural abundance stable carbon isotope fractionation of CH$_4$ during GPPTs could be used to quantify the kinetics of CH$_4$ oxidation. GPPTs and
numerical modelling were utilized to evaluate the importance of diffusional and microbial fractionation during GPPTs performed in soils with different microbial activities.

Chapter 4: to perform a field-scale study of the use of GPPTs to quantify the kinetics of CH$_4$ oxidation in the cover-soil of a landfill. Four active GPPTs were performed at two locations in the cover soil of the Lindenstock landfill (Liestal, Switzerland) and reaction kinetics were calculated.

Chapter 5: to quantify CH$_4$ dynamics in and above the cover soil of the Lindenstock landfill. A field campaign was conducted over five days to compare the results of GPPTs, soil-gas profiles, flux chambers, surface emission measurements and eddy covariance.

Chapter 6: a final discussion of the methods used in this thesis and their application in landfill-cover soil. Considerations in regards to landfill-cover design, seasonal fluctuations and the impact of global warming on landfill CH$_4$ dynamics are discussed.

1.6 References

Chapter 1: General Introduction


Chapter 1: General Introduction


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Chapter 1: General Introduction


http://www.epa.gov/epawaste/nonhaz/ [accessed 05.04.2010]


Transport of Methane and Noble Gases during Gas Push-Pull Tests in Variably Saturated Porous Media

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Published in Environmental Science & Technology (2008), 42, 2515-2521
2.1 Abstract

The gas push–pull test (GPPT) is a single-well gas-tracer method to quantify in situ rates of CH$_4$ oxidation in soils. To improve the design and interpretation of GPPT field experiments, gas component transport during GPPTs was examined in abiotic porous media over a range of water saturations (0.0 $\leq S_w \leq$ 0.61). A series of GPPTs using He, Ne, and Ar as tracers for CH$_4$ were performed at two injection/extraction gas flow rates (~200 and ~700 mL min$^{-1}$) in a laboratory tank. Extraction phase breakthrough curves and mass recovery curves of the gaseous components became more similar at higher $S_w$ as water in the pore space restricted diffusive gas-phase transport. Diffusional fractionation of the stable carbon isotopes of CH$_4$ during the extraction period of GPPTs also decreased with increasing $S_w$ (particularly when $S_w > 0.42$). Gas-component transport during GPPTs was numerically simulated using estimated hydraulic parameters for the porous media and no fitting of data for the GPPTs. Numerical simulations accurately predicted the relative decline of the gaseous components in the breakthrough curves, but slightly overestimated recoveries at low $S_w$ ($\leq$0.35) and underestimated recoveries at high $S_w$ ($\geq$0.49). Comparison of numerical simulations considering and not considering air-water partitioning indicated that removal of gaseous components through dissolution in pore water was not significant during GPPTs, even at $S_w = 0.61$. These data indicate that Ar is a good tracer for CH$_4$ physical transport over the full range of $S_w$ studied, whereas, at $S_w > 0.61$, any of the tracers could be used. Greater mass recovery at higher $S_w$ raises the possibility to reduce gas flow rates, thereby extending GPPT times in environments such as tundra soils where low activity due to low temperatures may
require longer test times to establish a quantifiable difference between reactant and tracer breakthrough curves.

2.2 Introduction

The atmospheric abundance of the greenhouse gas, methane (CH$_4$), has more than doubled since the preindustrial period (Ehhalt et al., 2001). Because CH$_4$ contributes to global warming, identification and quantification of terrestrial methane sources and sinks is needed for global balances and local emissions reduction strategies. While some new CH$_4$ sources are being explored (Keppler et al., 2006), the majority of natural and human-influenced CH$_4$ sources including wetlands, rice paddies, ruminants, and landfills have likely been identified (Bogner et al., 1995, Whiting & Chanton, 1993, Seiler et al., 1984, Kirchgessner et al., 1991). From an anaerobic source, produced CH$_4$ may be advectively or diffusively transported into an aerated zone where indigenous methanotrophic bacteria act as a sink by oxidizing some or all of the CH$_4$ before emission to the atmosphere. Soils are estimated to be a sink for between 10 and 44 Tg CH$_4$/year (Ehhalt et al., 2001). Quantification of CH$_4$ oxidation rates in particular subsurface environments and evaluation of influencing factors could facilitate implementation of local measures to enhance the CH$_4$-oxidizing capacity of sinks.

Rates of aerobic methane oxidation in soils have been quantified in laboratory-based incubation studies, and it has been shown that methanotrophic activity is influenced by pH, temperature, moisture, depth in soil, and in situ O$_2$ and CH$_4$ concentrations (Czepiel et al., 1996, Park et al., 2005, Whalen et al., 1990, Borjesson et al., 2004, Dunfield et al., 1993). Laboratory conditions, however, do not necessarily reflect field conditions, and laboratory derived rates of CH$_4$ oxidation may be
substantially different from those in the field. The “gas push-pull test” (GPPT) field method was developed to meet the need to quantify in situ rates of microbial processes, and specifically CH$_4$ oxidation (Urmann et al., 2005). The GPPT was adapted from the push-pull test (PPT), an aqueous tracer test that has been used to measure rates of diverse microbial processes such as methanogenesis, sulfate reduction, and denitrification in aquifers (Istok et al., 1997). Early PPTs or single-well tracer tests (SWTTs) were performed with radioactive tracers to measure aquifer properties (Sternau et al., 1967, Borowczyk et al., 1967), later, SWTTs (frequently referred to as “huff and puff” tests) were used in petroleum research to estimate residual oil saturation in reservoirs (e.g., Tomich et al., 1973, Wellington & Richardson, 1994), resident water saturation (Deans & Mut, 1997), and to enhance light-oil recovery (Zhang et al., 2006). To date, the GPPT method has been used to determine rates of CH$_4$ oxidation above a contaminated aquifer (Urmann et al., 2005) and in a peat bog (Urmann et al., 2007), and the test is currently being investigated as a tool to measure CH$_4$ oxidation rates in the cover soil of a landfill.

The GPPT is a single-well gas-tracer test in which inert gases are used as nonreactive tracers for the reactive gas, CH$_4$. During a GPPT, a mixture of tracer and reactive gases is injected (pushed) into the test site, the flow direction of the pump is reversed (transition phase), and then during the extraction phase the injected gas mixed with soil air is extracted (pulled) from the same location. Quantification of CH$_4$ oxidation rates is based upon analysis of the breakthrough curves of CH$_4$ and tracer concentrations. Throughout the GPPT, tracer concentrations at the injection/extraction point decrease as a result of physical transport processes, whereas the concentration of CH$_4$ decreases as a result of
both physical transport processes and, if methanotrophs are active, microbial CH$_4$ oxidation.

Interpretation of GPPT data depends upon the governing physical transport processes operating on the gaseous components. The major gas-phase physical transport processes experienced during a GPPT are advection, mechanical dispersion, and molecular diffusion. Advection during GPPTs is a function of the pressure gradient generated by the gas pump and is independent of the gaseous components’ molecular mass. Mechanical dispersion also does not segregate gas components, it is dependent on the physical properties of the system (i.e., available pore space) and is generally not significant for gas transport except when gas velocities are greater than 40 cm min$^{-1}$ (Popovicova & Brusseau, 1997). Molecular diffusion is a segregative process that occurs along a concentration gradient and is a function of the components’ molecular mass and soil tortuosity. If CH$_4$ and a tracer exhibit similar physical transport during a GPPT, simplified methods to interpret breakthrough curves from single-well PPTs can be applied and microbial kinetics (zero- or first-order) can be quantified according to (Snodgrass & Kitanidis, 1998, Haggerty et al., 1998, Schroth & Istok, 2006). Alternatively, if CH$_4$ and tracer transport are dissimilar, rate parameters can be calculated using reactive-transport models when additional soil properties are measured.

Another sensitive tool to examine CH$_4$ transport in porous media is stable isotope fractionation. The slight difference in mass of the two predominant stable isotopes of carbon, $^{12}$C and $^{13}$C, results in a greater gaseous diffusion rate of $^{12}$CH$_4$ compared to $^{13}$CH$_4$ (De Visscher et al., 2004). Stable isotope fractionation of CH$_4$ due to molecular diffusion has been shown to occur during GPPTs in the laboratory in dry porous media.
(Gonzalez-Gil et al., 2008), but it is uncertain how CH$_4$ isotope fractionation during GPPTs will be influenced by varying degrees of water saturation ($S_w$), as in field soils.

While CH$_4$ oxidation occurs over a wide range of $S_w$, activity is greatest in the range from approximately 0.2 to 0.4 (Whalen et al., 1990, Czepiel et al., 1996, Park et al., 2005). Below this range methanotrophs suffer from desiccation and temperature fluctuations, while at higher $S_w$ slow diffusion of gases through pore water limits CH$_4$ oxidation. Water saturation also influences advective, dispersive, and diffusive gas transport in the subsurface by reducing the pore volume available for gaseous migration and through air-water partitioning of gases. Although the dimensionless air-water partition (Henry’s) coefficients of noble gases and CH$_4$ are high, values in (mol/L gas)/(mol/L water) at 25°C are 105.8 for He, 90.8 for Ne, 29.4 for Ar and CH$_4$ (calculated from (Wilhelm et al., 1977), in soils with values of $S_w$ close to one, the air relative permeability in porous media is so reduced (Corey, 1957) that partitioning into the water phase could be considerable.

Previously, laboratory GPPTs were performed in a dry, abiotic porous medium in a tank to examine gas component transport under different test conditions without having to consider loss due to air-water partitioning (Gonzalez-Gil et al., 2007). Diffusion was experimentally shown to dominate gas transport even at gas flows as high as 850 mL min$^{-1}$ and numerical simulations of GPPTs showed that unrealistic gas flows greater than 10 L min$^{-1}$ are required for advection to dominate gas transport and for breakthrough curves of all gaseous components to be similar, thus permitting use of simplified data analysis methods. Advection-dominated gas transport during GPPTs could also be
possible if tests are conducted in a system that is partially confined by physical barriers or by pore water.

The main objective of this work was to investigate the physical transport of CH$_4$ and tracer noble gases during GPPTs in porous media for different values of $S_w$. Specifically, we wanted to determine (i) whether gas component transport during GPPTs is dominated by molecular diffusion over a wide range of $S_w$, (ii) if the cumulative mass of gas components recovered during GPPTs is influenced by $S_w$, (iii) if air-water partitioning of the gas components during GPPTs is relevant, and (iv) if diffusive stable carbon isotope fractionation during GPPTs is influenced by $S_w$. To this end, we performed a series of GPPTs in an abiotic laboratory system containing porous media at $0 \leq S_w \leq 0.61$. The GPPTs were also numerically simulated. These data can aid in design and interpretation of GPPTs in the field.

2.3 Materials and Methods

2.3.1 Experimental Design

The laboratory system was a cylindrical polypropylene tank (1-m diameter, 1-m height) with evenly spaced gas vents around the inner wall to mimic an open system (Figure 2-1). For GPPTs 1 to 6, the tank was dry-packed with 0.1 to 0.5-mm diameter quartz sand (fine sand total porosity, $\theta_t = 0.49$), and for GPPTs 7 to 12 it was packed with 0.7 to 1.2-mm diameter quartz sand (coarse sand $\theta_t = 0.43$). Data for GPPTs 7 and 8 were taken from the literature (Gonzalez-Gil et al., 2007) and were included to complete the data set. Sand of different particle sizes enabled us to attain $S_w$ values over the range from 0.0 (dry) to 0.61. Initially, tests were performed in dry sand, and then water was pumped
into the tank from the bottom to saturate the sand packs. Following saturation, the tap at
the bottom of the tank was opened and water drained from the tank into a reservoir.
Simultaneously, the shower system was turned on and after discarding the initial drainage
water to remove any debris, water from the reservoir was recirculated. Steady state water
flow conditions are needed to maintain different values of $S_w$ near the injection/extraction
point for each specific GPPT. This was achieved through regulation of the shower system
consisting of a submersible water pump (Grundfos MP1, Fällanden, Switzerland)
connected by pressure-resistant tubing to interchangeable shower heads (Jato-Düsenbau,
Reussbühl, Switzerland) capable of delivering a homogeneous full cone at water flow
rates between 400 and 5000 mL min$^{-1}$. During GPPTs, the water in the reservoir was
sparged with air to remove any dissolved CH$_4$ or noble gases from the recirculating
water, and microbial activity within the sand pack and the reservoir was minimized
through addition of a biocide to the water (Micropur MT10, Katadyn Products,
Wallisellen, Switzerland). Water saturation in the sand was measured during GPPTs by
eight horizontal time-domain reflectometry probes (TDR) (Campbell Scientific Inc.,
Logan, UT).
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Figure 2-1. Schematic representation of the injection phase of a GPPT in a laboratory tank containing quartz sand. The irrigation system, consisting of a water pump, tubing, water-flow meter, shower head, and support, was regulated to maintain the desired $S_w$. Four of eight TDR probes are shown. For the extraction phase, the direction of the gas flow controller pump was reversed and samples were collected in serum bottles.

2.3.2 Gas Push-Pull Tests

Once steady-state water flow was achieved, a total of 10 GPPTs were conducted at five different water-flow rates and two injection/extraction gas-flow rates (Table 2-1). For each water-flow rate, one GPPT was run at a fast gas-flow rate and one at a slow rate. Each GPPT was composed of an injection, transition, and extraction phase (Table 2-1). During the injection phase, a gas mixture ($5.5 \pm 0.07$ L) was pumped from an aluminum gas bag into the sand pack through a stainless steel injection/extraction rod (o.d., 8 mm; i.d., 5 mm) with a perforated tip set 43 cm below the sand surface. The gas mixture
containing ca. 25% (v/v) each of He, Ne, Ar, and CH₄ was injected using a gas-flow controller with a mass-flow meter (for details see (Urmann et al., 2005). Gas volumes reported are normalized volumes. During the short transition period, the direction of the pump was reversed, after which a blend of the gas mixture and soil air (14.1 ± 0.07 L) was extracted from the same location. Gas samples were taken periodically in 15-mL serum bottles with butyl rubber septa and metal crimp caps, and which contained CaO granules to remove water vapor. Bottles were flushed with at least 200 mL of sample using an inflow and an outflow needle. Tests were performed at 25 ± 1 °C.

Table 2-1. Experimental Conditions and Gas Push-Pull Test Operational Conditions and Parameters

<table>
<thead>
<tr>
<th>GPPT</th>
<th>sand type</th>
<th>Q_{water} (mL min⁻¹)</th>
<th>S_w</th>
<th>injection rate (mL min⁻¹)</th>
<th>transition phase (min)</th>
<th>extraction rate (mL min⁻¹)</th>
<th>total time (min)</th>
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<tbody>
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<td>fine</td>
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<td>0</td>
<td>213</td>
<td>0.65</td>
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<td>210</td>
<td>0.65</td>
<td>176</td>
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<td>0.88</td>
<td>504</td>
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<tr>
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<tr>
<td>6</td>
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<td>0.60</td>
<td>166</td>
<td>113.70</td>
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<tr>
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<td>0.42</td>
<td>720</td>
<td>0.10</td>
<td>520</td>
<td>34.88</td>
</tr>
</tbody>
</table>

a GPPT 7 and 8 were previously reported in (Gonzalez-Gil et al., 2007).
b S_w = water saturation [−] as measured by TDR in the vicinity of the injection/extraction location.
2.3.3 Analytical Methods

Sample CH$_4$ concentration was measured by GC-FID and the stable carbon isotope composition of CH$_4$ was determined by GC−IRMS as described by Urmann et al. (2005). The isotope ratio of the samples was calculated in reference to Vienna Pee Dee Belemnite (VPDB). Isotope values are given as $\delta^{13}C$ (‰) according to,

$$\delta^{13}C = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000$$  \hspace{1cm} (1)

where $R$ is the ratio between $^{13}C$ and $^{12}C$ in samples and standard, respectively. The precision in the measurements was better than ± 0.4‰.

Noble gases were quantified on a trace GC ultra GC−TCD (Thermo Electron Corp., Rodano, Italy) according to Urmann et al. (2007). Quantification was based upon calibration by a series of external standards. Gas samples were injected at room temperature and atmospheric pressure using pressure-lok syringes (Vici Precision Sampling Corp., Baton Rouge, LA).

2.3.4 Numerical Simulations

Transient simulations of water and gas flow as well as gas-component transport during GPPTs were performed using the air-water operational mode of the subsurface transport over multiple phases (STOMP) simulator (White & Oostrom, 2000). STOMP is a fully implicit, volume-integrated finite-difference simulator to solve mass- and energy-balance equations and has been used previously to describe PPTs (Schroth et al., 2000, Davis et al., 2005) and GPPTs (Gonzalez-Gil et al., 2007). For our simulations, we made the following assumptions: (1) diffusive transport and mechanical dispersion are
described by the generalized form of Fick’s law, (2) porous media are homogeneous and isotropic, (3) solid-phase partitioning can be neglected, (4) air-water partitioning is either negligible or at local equilibrium. The total-variation-diminishing scheme was used to minimize numerical dispersion (33). Simulation parameters and additional details have been included in the Supporting Information section. To evaluate the influence of air-water partitioning on the loss of CH$_4$ and noble gases during a GPPT, numerical simulations of GPPT 5 were run with both the actual Henry’s coefficients and with the parameter set at $1.0 \times 10^6$ to make air-water partitioning negligible. GPPT 5 was chosen for these simulations, because it was performed at the highest $S_w$ and with a slow gas-flow rate, and is therefore the GPPT for which air-water partitioning is most likely to play a role. Acetylene was additionally included in the simulations as an example of a gas with a comparatively low dimensionless Henry’s coefficient of 1.0.

2.4 Results

2.4.1 Breakthrough Curves

For each GPPT, breakthrough curves of noble gases and CH$_4$ during the extraction phase were plotted as extracted divided by injected concentration ($C_{\text{ex}}/C_{\text{inj}}$) versus extracted divided by injected volume ($V_{\text{ex}}/V_{\text{inj}}$). Representative breakthrough curves are shown for GPPTs with fast injection/extraction gas flow rates, GPPTs 10, 4, 12, and 6 (Figure 2-2 A, C, E, and G). For all 10 experimental and 2 literature (Gonzalez-Gil et al., 2007) GPPTs, the order of the relative concentrations of the gases was as follows: He decreased the fastest, followed by Ne, CH$_4$, and then Ar (Figure 2-2 A, C, E, and G; correction for background was unnecessary as gas mixture component
concentrations were at least 20 times higher than background). This trend was expected based upon the diffusion coefficients in air of each of the gases (He $6.65 \times 10^{-5}$, Ne $3.07 \times 10^{-5}$, Ar $1.86 \times 10^{-5}$, CH$_4$ $2.11 \times 10^{-5}$, at 25 °C from (Fuller et al., 1966). While the order of the gases was independent of $S_w$, the initial decrease in relative concentration was not as steep, and the difference between the breakthrough curves of the gaseous components decreased with increasing $S_w$. For example, at $S_w = 0.61$ the breakthrough curves of Ne, Ar, and CH$_4$ were similar, and the He relative concentrations were only slightly lower than the others (Figure 2-2G). For all $S_w$, gas component concentrations decreased faster for tests with slow injection/extraction gas flow rates compared to those with fast gas flow rates (not shown).

Numerical simulations of GPPT breakthrough curves showed reasonable agreement between modeled and experimental data in terms of the order of the gases and the shapes of the breakthrough curves. However, the simulations overestimated the observed relative concentrations of gaseous components of tests at low $S_w$ (Figure 2-2A), and underestimated the data for high $S_w$ (Figure 2-2 G).
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Figure 2-2. Breakthrough curves and cumulative mass recovered at injection/extraction point for CH₄ and noble gases during GPPT 10 (A and B), GPPT 4 (C and D), GPPT 12 (E and F), and GPPT 6 (G and H). Data points are experimental values, lines are numerically simulated data (referred to as “sim” in the legend). Simulated data do not take into account potential loss due to air–water partitioning
2.4.2 Mass Recovery

Breakthrough curves were integrated to calculate the cumulative mass of the injected gaseous components recovered during the extraction period. A recovery of 100% would indicate that an injected gas component was entirely recovered. For all GPPTs, the cumulative mass recovered of the gaseous components followed the order He < Ne < CH\textsubscript{4} < Ar, except for GPPT 6 (S\textsubscript{w} = 0.61, fast gas flow), for which Ne was slightly higher than CH\textsubscript{4} (Figure 2-2 B, D, F, and H). For each of the gaseous components, there was only a small increase in the total cumulative mass recovered during GPPTs at S\textsubscript{w} = 0.35 compared to dry conditions, whereas for S\textsubscript{w} > 0.35 the cumulative mass recovered of each of the gases increased sharply with increasing S\textsubscript{w} (Figure 2-3). The cumulative mass recovered was also dependent upon the gas flow rate with slow gas flow resulting in less mass recovered than tests with fast gas flow rates at equivalent water contents (Figure 2-3).

Figure 2-3. Cumulative mass of CH\textsubscript{4} and noble gases recovered at the end of the GPPTs performed at low and high gas-flow rates (Q\textsubscript{gas}) as a function of S\textsubscript{w}. Data from two different sand packs. Low Q\textsubscript{gas} range from 194 to 213 mL min\textsuperscript{-1}. High Q\textsubscript{gas} range from 685 to 789 mL min\textsuperscript{-1}. 
2.4.3 Air-Water Partitioning

There was no difference between the breakthrough curves of CH$_4$ and noble gases from the numerical simulations including or excluding air-water partitioning during GPPT 5 ($S_w = 0.61$, $Q_{gas} = 212$ mL min$^{-1}$, only results for CH$_4$ shown in Figure 2-4). This was not the case for C$_2$H$_2$, which exhibited a faster decrease in relative concentration when air-water partitioning was considered (Figure 2-4). At the end of GPPT 5 the fraction of CH$_4$ remaining in the tank for the simulation considering partitioning was 0.213 compared to 0.193 for the simulation neglecting partitioning. For C$_2$H$_2$ the respective values were 0.460 and 0.176.

![Graph showing relative concentrations of CH$_4$ and C$_2$H$_2$ during GPPT 5](image)

Figure 2-4. Numerical simulations of relative concentrations of CH$_4$ and C$_2$H$_2$ during GPPT 5 ($Q_{gas} = 212$ mL min$^{-1}$, $S_w = 0.61$), considering and not considering air-water partitioning. The line for CH$_4$ with no partitioning is not visible as it is the same as CH$_4$ with partitioning.
2.4.4 Stable Carbon Isotope Fractionation of CH$_4$

The stable carbon isotope ratio of CH$_4$ was measured for the injected gas mixture and for samples taken during the extraction phase of all experimental GPPTs. The $\delta^{13}$C of CH$_4$ in the injection gas mixture ranged from −46.0 to −47.9 ‰. During the GPPTs, CH$_4$ at the injection point became rapidly enriched in $^{13}$CH$_4$, as the lighter $^{12}$CH$_4$ molecules diffused away faster (Figure 2-5). This enrichment was seen in all GPPTs, but the degree to which fractionation occurred decreased with increasing $S_w$, and was smaller in GPPTs performed at fast gas flow rates (Figure 2-5).

![Figure 2-5. Stable carbon isotope composition of extracted CH$_4$ during the extraction phase of GPPTs conducted at high and low $Q_{gas}$.

2.5 Discussion

2.5.1 The Influence of $S_w$ on GPPT Breakthrough Curves

In low $S_w$ soils, soil-water usually occupies the smallest pores and has therefore little effect on gas transport. As $S_w$ increases, larger pores fill with water thereby
restricting gas-phase flow and transport to a smaller volume of air space, increasing the
tortuosity and raising the likelihood for gas component partitioning into the aqueous
phase (Collin & Rasmuson, 1988). Previous experiments in a dry porous medium showed
that during GPPTs the diffusive component of the test overshadowed the advective
component as evidenced by the dissimilar transport of CH$_4$ and the tracer gases
(Gonzalez-Gil et al., 2007). In this work, we saw that with increasing $S_w$, and the
simultaneous decrease in air pore volume, breakthrough curves of the GPPT gaseous
components became increasingly similar (Figure 2-2 A, C, E, and G). This increasing
similarity reflects the declining relative contribution of gas-phase diffusion to gas-
component transport during GPPTs and the increasing relative contribution of advection-
dispersion, a nonsegregative transport process, at higher $S_w$. At the highest saturation
studied, $S_w = 0.61$, the similarity in the breakthrough curves of CH$_4$, Ar, and Ne is
evidence that transport was advection dominated.

2.5.2 The Influence of $S_w$ on GPPT Mass Recovery

In dry porous media, mass recovery was poor (<40% at high gas flow and <20%
at low gas flow) for all gaseous components, due to the strong diffusive component of the
GPPT. Mass recovery was only slightly higher at $S_w = 0.35$ than for dry porous media,
therefore soils that fall within the range of 0 < $S_w$ < 0.35 could be considered as dry in
this respect. Above $S_w = 0.35$, mass recoveries rose sharply as gaseous transport away
from the injection/extraction point became increasingly restricted. Although the data for
Figure 2-3 were from two different sand packs and there was some variability in gas flow
rates from one GPPT to another, $S_w$ is clearly an important factor in regards to mass
recovery during GPPTs. At the highest saturation, $S_w = 0.61$, gas component mass
recoveries (up to 80% for CH$_4$) were close to those for Br$^-$ during aqueous PPTs (Istok et al., 1997). By a $V_{ex}/V_{inj}$ of 2.5 (Figure 2-2 B, D, F, and H), the values of cumulative mass recovered reached a plateau; therefore, further gas extraction beyond this volume would contribute little to the overall mass recovery of a GPPT.

### 2.5.3 Numerical Simulation of Breakthrough Curves and Mass Recovery

Simulated breakthrough curves and mass recovery curves accurately described the relative order of the gaseous-component experimental data at all water saturations. However, because of experimental uncertainty and inherent assumptions for the simulations, simulated curves overestimated relative concentrations at low $S_w$ and underestimated relative concentrations at high $S_w$. The van Genuchten (van Genuchten, 1980) water-retention parameters in the model were initially adjusted to estimate the TDR readings of the distribution of water in the laboratory tank during GPPTs. While TDR gives a good estimate of water saturation, the placing of only eight probes in the 1 m diameter by 1 m high laboratory tank means that the TDR data give only a rough estimate of the water distribution throughout the porous media. Additionally, we assumed homogeneity of the porous media, but as we filled the tank incrementally with sand, layering could have occurred that may have affected gas transport pathways in the porous media.

Another possible source of error in the simulations lies in the choice of boundary conditions. The right boundary of the tank was set as a gas hydraulic gradient boundary thereby allowing gas flow out of every cell in the outer circumference of the tank based upon the gas hydraulic pressure. In reality, gas flow from the vertical sides of the tank only occurred through the 12 gas vents placed around the inner circumference of the tank.
wall. Actual gas flow and solute transport through the gas vents was probably less than the gas flow and solute transport across the right boundary predicted by the simulator.

2.5.4 Air-Water Partitioning during GPPTs

Over the range of $S_w$ that we might expect at a potential GPPT field site, $S_w \leq 0.61$, loss of CH$_4$ and tracers due to air-water partitioning during GPPTs is inconsequential. The fraction of CH$_4$ remaining in the tank after simulated GPPT 5 was 10% greater when partitioning was considered, but the difference in the mass fraction left in the tank (0.213 compared to 0.193) was not detectable in the breakthrough curves (Figure 2-4). Although the Henry’s coefficients of CH$_4$ and the tracer gases are high, with further increases in water saturation (e.g., above $S_w \approx 0.85$) air-filled pores would become mostly discontinuous (Corey, 1957) and partitioning of the gaseous components into the aqueous-phase would rise. At very high $S_w$, GPPTs would not be possible because of pressure build-up during injection of the gas mixture. In contrast, for C$_2$H$_2$, the fraction of mass remaining in the tank following the simulated GPPT was 50% greater for the test considering partitioning, establishing that partitioning into the aqueous-phase is significant for C$_2$H$_2$ at $S_w = 0.61$. As a commonly used inhibitor of CH$_4$ oxidation, partitioning of C$_2$H$_2$ into the aqueous phase needs to be considered when planning inhibited GPPT as described in (Urmann et al., 2005). Partitioning into the aqueous phase would reduce the concentration of C$_2$H$_2$ in the gas phase, raising the possibility that C$_2$H$_2$ insufficiently covers the area probed by the injected CH$_4$, thus incompletely inhibiting methanotrophic activity.
2.5.5 Influence of $S_w$ on Stable Carbon Isotope Fractionation of CH$_4$ during GPPTs

In GPPTs, microbial CH$_4$ oxidation rates may be estimated from stable carbon isotope fractionation data only if the fractionation factor due to diffusion is known (De Visscher et al., 2004). Here we have seen that diffusive fractionation of CH$_4$ during GPPTs is reduced at (i) faster $Q_{gas}$ and/or (ii) increased $S_w$. The former modifies the importance of diffusion by increasing the advective-dispersive transport, while the latter modifies diffusion by restricting gas transport. We can see (Figure 2-5) that at $S_w < 0.42$ diffusional fractionation of CH$_4$ is only slightly affected by water contained in smaller pores. However, at $S_w > 0.42$, water in the larger pores hindered overall gaseous diffusion, thereby considerably reducing the diffusive stable carbon isotope fractionation of CH$_4$. Because diffusive stable carbon isotope fractionation varies with the physical properties of the soil, and somewhat with the GPPT $Q_{gas}$, separating fractionation owing to diffusion from fractionation due to microbial activity remains challenging.

2.5.6 Implications for field GPPTs

Undoubtedly, field GPPTs are more complicated both to perform and analyze than those in a laboratory tank where the particle size, porosity, bulk density, and approximate $S_w$ are known. Measuring these properties in the field is problematic because of soil heterogeneity and estimates of these values for the volume probed by the GPPT will be rough. To aid in design and interpretation of field GPPTs, we can make some generalizations from this laboratory research that can be applied to the field.

In soils covering the typical moisture range for high methanotrophic activity, from $0.2 \leq S_w \leq 0.4$ the breakthrough curves for each of the gaseous components are different
from one another and transport is diffusion dominated. Under these conditions, Ar transport is most similar to CH$_4$ and would be the most appropriate tracer when injected at high concentrations, for example, $\geq 25\%$ v/v, to minimize interference from background atmospheric concentrations. Above $S_w \approx 0.42$ the breakthrough curves for all gaseous components became more similar, indicating increasingly advection-dispersion-dominated transport under which the choice of an appropriate tracer gas becomes less critical and at $S_w \geq 0.6$, Ar or Ne could be used to trace CH$_4$.

Greater cumulative mass recovered at higher saturations raises the possibility to extend test times in moist soils and still recover sufficient mass to be able to quantify microbial processes. This could be important at field sites such as tundra or peat bogs where in situ CH$_4$ oxidation rates might be low and water saturations high. For field sites that are close to saturation, the soil air volume is small and gas injection and extraction might cause pressure or vacuum buildup, therefore a traditional PPT with reactant and tracer gases dissolved in the aqueous solution could be performed.

Variable diffusion during GPPTs makes calculation of CH$_4$ oxidation rates from stable carbon isotope fractionation measurements alone unfeasible. However, isotopic data could complement tracer and reactant gas concentration measurements to confirm that microbial methane oxidation is occurring.

2.6 Acknowledgments

We thank M. Oostrom and M.D. White (PNNL) for continuing support with the STOMP simulator. We also thank H. Läser (ETHZ) for assistance in designing and constructing the equipment and R. Siegwolf and M. Saurer (PSI, Villigen) for assistance
with stable carbon isotope measurements. This research was funded by a grant no. 200021–103619 from the Swiss National Science Foundation.

2.7 Supporting information

2.7.1 Numerical simulations

The actual dimensions of the tank were simulated using a computational domain with a cylindrical coordinate system, which, assuming axial symmetry, was reduced to two active dimensions. The computational domain was divided into 1075 evenly spaced nodes with \( \Delta r \) and \( \Delta z \) of 2 cm (Figure S1). Initially, the \( S_w \) profile in the tank was simulated for a given water-flow rate using the listed aqueous boundary conditions (Table S1). Water retention parameters (\( \alpha, n \), (van Genuchten, 1980)) were varied to fit the simulated data to the TDR measurements of the tank \( S_w \) profile during the specific experiments. Thereafter, GPPTs were simulated using the listed boundary conditions and parameters. The two nodes at the injection/extraction point on the left surface were assigned positive Neumann gas-flow and solute-flux boundary conditions during injection, zero during transition, and negative during extraction. Numerical solution parameters including the convergence criterion (defined as the maximum relative difference in the governing equation residuals between consecutive iteration steps for primary and secondary variables) are included in Table S1.
Figure S1. Grid showing the computational domain used for STOMP simulations of GPPTs. $r_{\text{max}} = 50$ cm, $z_{\text{max}} = 86$ cm. Due to axial symmetry, only two active dimensions are required for simulation purposes.
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**Table S1. Input parameters for GPPT simulations**

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<thead>
<tr>
<th>Simulation boundary conditions</th>
<th>Aqueous phase</th>
<th>Gas phase</th>
<th>Solute</th>
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<td>Neumann</td>
<td>Dirichlet</td>
<td>Zero concentration</td>
</tr>
<tr>
<td>Bottom</td>
<td>Dirichlet</td>
<td>Zero flux</td>
<td>Outflow</td>
</tr>
<tr>
<td>Right</td>
<td>Zero flux</td>
<td>Hydraulic gradient</td>
<td>Zero concentration</td>
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<td>Left (excluding inj/ext nodes)</td>
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<td>Zero flux</td>
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<tr>
<td>Injection/extraction nodes</td>
<td>Zero flux</td>
<td>Neumann</td>
<td>Solute flux (inj) Outflow (ext)</td>
</tr>
</tbody>
</table>

**Fixed simulation parameters for all GPPTs**

- Maximum Newton-Raphson iterations per time step: 8
- Maximum time step (s): 2
- Convergence criterion: $1.0 \times 10^{-6}$

**Variable simulation parameters for the GPPTs**

<table>
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<th>GPPT Number</th>
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<td>.0504</td>
<td>-</td>
<td>.0811</td>
<td>.0811</td>
<td>.0811</td>
</tr>
<tr>
<td>Hydraulic conductivity, $h_c$ (cm min$^{-1}$)</td>
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<td>5.96</td>
<td>5.96</td>
<td>1.0</td>
<td>56.72</td>
<td>56.72</td>
<td>56.72</td>
</tr>
<tr>
<td>Bulk density (kg m$^{-3}$)</td>
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<td>2610</td>
<td>2610</td>
<td>2600</td>
<td>2600</td>
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<td>2600</td>
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<tr>
<td>Longitudinal dispersivity (cm)</td>
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<td>0.015</td>
<td>0.015</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Transverse dispersivity (cm)</td>
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<td>.00075</td>
<td>.00075</td>
<td>.002</td>
<td>.002</td>
<td>.002</td>
<td>.075</td>
</tr>
</tbody>
</table>
2.8 References


Chapter 2: Transport of Methane and Noble Gases during Gas Push-Pull Tests in Variably Saturated Porous Media


Diffusional and Microbial Isotope Fractionation of Methane during Gas Push-Pull Tests

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Published in Geochimica et Cosmochimica Acta (2008), 72, 2115-2124
3.1 Abstract

A field method called gas push–pull test (GPPT) was previously developed for in-situ quantification of methane (CH$_4$) oxidation by soil microorganisms. We examined whether natural-abundance stable carbon-isotope analysis of CH$_4$, a common approach used to measure in-situ bioconversions, could be used as a quantitative tool to complement the GPPT method. During GPPTs strong isotope fractionation of CH$_4$ due to molecular diffusion can occur. This effect was observed in laboratory experiments regardless of the GPPTs’ advective component (i.e., for different injection/extraction rates). Numerical simulations showed that if a GPPT is applied in soils with low microbial CH$_4$ oxidation activities, isotope fractionation may be dominated by molecular diffusion rather than by consumption. Because diffusional and microbial isotope fractionation of CH$_4$ occur simultaneously during a GPPT, CH$_4$ isotope data alone from a single GPPT cannot be used to assess the bioconversion process. However, microbial fractionation may be estimated if the extent of diffusional fractionation is known. This can be achieved either by conducting two sequential GPPTs, with microbial activity being inhibited in the second test, or by estimating physical transport processes via co-injected tracers’ gas analysis. We present a case study, in which we re-analyzed GPPTs previously performed in the unsaturated zone above a petroleum-contaminated aquifer. At this field site the combination of sequential GPPTs, stable carbon-isotope analysis of CH$_4$, and a modeling approach, which considers diffusion and microbial CH$_4$ oxidation, was a powerful tool to estimate in situ both apparent Michaelis–Menten kinetic constants and the microbial kinetic isotope effect.

3.2 Introduction

Methane (CH$_4$) is a greenhouse gas whose atmospheric concentration has increased from 0.75 to 1.8 ppmv over the last 200 years (Blunier et al., 1993), and it is considered that
this increase has played a significant role in global warming (Cicerone & Oremland, 1988, Stauffer et al., 1988; Pearce, 1989). On a per mol basis, CH$_4$ is 20–25 times more effective than CO$_2$ as a greenhouse gas (Blake & Rowland, 1988; Rodhe, 1990). Methane is produced in diverse ecosystems including rice paddies, wetlands, landfills (Hanson & Hanson, 1996), and contaminated aquifers (Conrad et al., 1999). Aerobic methane-oxidizing microorganisms are ubiquitous in subsurface environments (Hanson & Hanson, 1996) and it has been estimated that globally more than half of the produced CH$_4$ is oxidized by soil microorganisms before it reaches the atmosphere (Le Mer & Roger, 2001). To date, however, research to assess rates of production and consumption of greenhouse gases by indigenous soil microorganisms has largely been performed in microcosms and under laboratory conditions. Although data obtained in this manner can give important information, it is often difficult to extrapolate the latter directly to the field (Madsen, 1998).

Over the past decade, the use of stable isotope analyses to study the CH$_4$ cycle has increased rapidly, because stable isotope data can give information about source and sink processes (Whiticar, 1999). For example, field methods like chambers and the analysis of chemical profiles have been coupled with stable carbon-isotope analyses to study microbial CH$_4$ oxidation (Liptay et al., 1998, Chanton & Liptay, 2000; Krüger et al., 2002). The rationale is that methane-oxidizing microorganisms (i.e., methanotrophs) oxidize CH$_4$ containing $^{12}$C ($^{12}$C–CH$_4$) faster than CH$_4$ containing $^{13}$C ($^{13}$C–CH$_4$). Consequently, residual CH$_4$ becomes enriched in $^{13}$C (Barker & Fritz, 1981; Coleman et al., 1981). Enrichment of residual CH$_4$ in $^{13}$C is commonly used as a qualitative indicator of microbial CH$_4$ oxidation. Quantification of rates of microbial CH$_4$ oxidation using stable isotope data, on the other hand, requires knowledge of the microbial fractionation factor (Schmidt et al., 2004) or kinetic isotope effect, which resembles the ratio of $^{12}$C–CH$_4$ and $^{13}$C–CH$_4$ reaction rates (Chanton & Liptay, 2000). This factor is often determined in the laboratory. However, the magnitude of microbial fractionation factors in the field may be affected by diverse
parameters (e.g., temperature and methanotrophic community composition), but the related mechanisms are not yet completely understood (Reeburgh et al., 1997; Krüger et al., 2002). Consequently, methods to study and assess in-situ microbial fractionation factors are needed.

In addition to the microbial CH$_4$ oxidation process, CH$_4$ transport by diffusion can alter CH$_4$ isotopic signatures in the environment, because of its lower molecular mass $^{12}$C–CH$_4$ diffuses faster than $^{13}$C–CH$_4$. To quantify CH$_4$ oxidation in landfills using stable isotope data, it is usually assumed that the only fractionating process is microbial CH$_4$ oxidation, and that CH$_4$ transport is dominated by advection, a mechanism that does not fractionate (Liptay et al., 1998, Chanton & Liptay, 2000; Borjesson et al., 2001). In such systems diffusional fractionation is often neglected. However, neglecting diffusional isotope fractionation may result in inappropriate estimates of CH$_4$ oxidation (De Visscher et al., 2004). Thus, determining the relative importance of microbial and diffusional CH$_4$ fractionation is critical for elucidating the fate of CH$_4$ and computing CH$_4$ budgets in diverse environments (Chanton, 2005 and references therein).

Previously, we developed a field method called gas push–pull test (GPPT) for the in-situ quantification of microbial CH$_4$ oxidation (Urmann et al., 2005). The GPPT method consists of the injection of a gas mixture of CH$_4$, O$_2$ and tracer gases (e.g., Ne and Ar) into the soil at a location of interest. During injection, the gas mixture penetrates air-filled soil pores and travels away from the injection point. After injection, gas flow is reversed and a blend of soil air and the injected gas mixture is extracted from the same location. The period between the end of injection and start of extraction is called the transition phase. Injected CH$_4$ can be oxidized by soil microorganisms during all phases of the test (injection, transition, and extraction), i.e., as long as CH$_4$ travels through the soil and is in contact with microorganisms. First-order rate constants ($k$) of microbial CH$_4$ oxidation may be quantified by comparing the concentrations of extracted CH$_4$ vs. extracted tracer gases when physical transport of the gases is reasonably similar. The GPPT method was successfully applied to quantify microbial
CH$_4$ oxidation $k$-values in the unsaturated zone above a petroleum-contaminated aquifer (Urmann et al., 2005). In that study, selected stable carbon-isotope data were used to qualitatively verify that observed CH$_4$ consumption was microbiologically mediated. However, tests were conducted in a partially confined system, which may have limited CH$_4$ transport and affected isotope fractionation. Thus, the question remains whether isotope fractionation due to diffusion was relevant in these experiments, and to what extent isotope data from GPPTs can be used quantitatively. Results from recent field experiments conducted in an alpine peat bog (Urmann et al., 2007) raised similar questions regarding the quantitative use of natural-abundance isotope fractionation, specifically when microbial isotope fractionation is masked by diffusional fractionation.

The overall objective of this work was to investigate if natural-abundance stable carbon-isotope fractionation of CH$_4$ could be used as a quantitative tool to complement the GPPT method. Specific objectives were: (i) to determine under controlled laboratory conditions whether CH$_4$ isotope fractionation due to molecular diffusion is a relevant process during GPPTs, (ii) to evaluate, using numerical simulations, the relative magnitude of microbial and diffusional isotope fractionation of CH$_4$ to be expected during GPPTs, and (iii) to investigate the GPPT’s potential to estimate in-situ both Michaelis–Menten-type constants and the kinetic isotope effect. To assess the latter issue, we present a case study in which we re-analyzed CH$_4$ concentration and carbon-isotope data from two previous field GPPTs (Urmann et al., 2005). We discuss the distinctive quantitative information on the microbial process, which can potentially be obtained when GPPTs and stable isotope analyses are combined.
3.3 Theory

3.3.1 Mathematical description of GPPT

To describe a GPPT we used the following assumptions: (i) the test is applied in a homogeneous and isotropic porous medium; (ii) mechanical dispersion and diffusive transport is described by the generalized form of Fick’s law, and the diffusion coefficient is constant; (iii) component partitioning onto solid and/or liquid phase is negligible; (iv) since injection and extraction of gas mixtures during GPPTs were performed through a short screened section at the rod tip (Figure 3-1), it is reasonable to assume a spherical gas-flow field during both injection and extraction phases of the test. On the basis of these assumptions, the transport equation for advection, mechanical dispersion–diffusion, and reaction of a gaseous component is then given by (adapted from Crank, 1975):

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - \frac{\partial C}{\partial r} \cdot \nu + R_M
\]  

(1)

where \( C \) (g m\(^{-3}\) soil air) is the gaseous component concentration, \( r \) (m) is the radial distance from the injection/extraction point, \( R_M \) (g m\(^{-3}\) soil air min\(^{-1}\)) is the metabolic reaction rate, \( D \) is the diffusion–dispersion coefficient given by:

\[
D = (D_e / \theta_a) + D_m
\]  

(2)

where \( D_e \) is the effective diffusion coefficient (m\(^2\) min\(^{-1}\)) that is given by:

\[
D_e = \tau \theta_a D_a
\]  

(3)

where \( \tau \) is the tortuosity factor, \( \theta_a \) is the air-filled porosity, and \( D_a \) (m\(^2\) min\(^{-1}\)) is the compound’s molecular diffusion coefficient in air. The \( \tau \) may be described by the following empirical relation of Millington and Quirk (1961):

\[
\tau = \theta_a^{7/3} / \theta_t^2
\]  

(4)

where \( \theta_a \) (m\(^3\) soil air m\(^{-3}\) soil) is the air-filled porosity and \( \theta_t \) is the total porosity. In case of dry sand, \( \theta_a = \theta_t \). For spherical flow, the gas pore velocity, \( \nu \) (m min\(^{-1}\)) is given by:
where $Q$ (m$^3$ min$^{-1}$) is the gas pumping rate, which is positive during injection, null during the transition phase, and negative during extraction. Under most GPPT conditions, mechanical dispersion ($D_m$) may be neglected in Eq. (2), which is a reasonable assumption away from the injection point where the velocity decreases rapidly as a result of the spherical flow field (Eq. (5)).

### 3.3.2 Methane stable carbon-isotope fractionation

To compute stable carbon-isotope fractionation of CH$_4$ during a GPPT, Eq. (1) is solved for the two stable isotopes (using different values of $D_a$ for $^{12}$C–CH$_4$ ($1.2657 \times 10^{-3}$ m$^2$ min$^{-1}$) and $^{13}$C–CH$_4$ ($1.2414 \times 10^{-3}$ m$^2$ min$^{-1}$) (Fuller et al., 1966). Methanotrophs oxidize $^{12}$C–CH$_4$ faster than $^{13}$C–CH$_4$, and the ratio of $^{12}$C–CH$_4$ and $^{13}$C–CH$_4$ reaction rate constants is defined as the kinetic isotope effect (KIE). For small molecules like CH$_4$, KIE can also be referred to as the isotope fractionation factor ($\alpha$) (Schmidt et al., 2004).

For first-order kinetics, metabolic reaction rates for $^{12}$C–CH$_4$ and $^{13}$C–CH$_4$ are given by:

$$^{12}R_M = -^{12}k \cdot C_{^{12}CH_4}$$

(6)

$$^{13}R_M = -^{13}k \cdot C_{^{13}CH_4}$$

(7)

where $k$ (min$^{-1}$) is the first-order rate coefficient, from which KIE can be computed using (Schmidt et al., 2004):

$$\text{KIE} = \frac{^{12}k}{^{13}k}$$

(8)

For enzymatic reactions following Michaelis–Menten (MM) kinetics, reaction rates for the two isotopes can be described using a competitive form of the MM equation (Simon & Palm, 1966):
\[
\frac{^{12}R_M}{^{13}R_M} = \frac{^{12}V_{\text{max}} C_{{^{12}CH}_4}}{^{13}V_{\text{max}} C_{{^{13}CH}_4}} \frac{+^{12}K_m (1 + \frac{C_{{^{12}CH}_4}}{^{12}K_m})}{+^{13}K_m (1 + \frac{C_{{^{13}CH}_4}}{^{13}K_m})} (9)
\]

where \(V_{\text{max}}\) is the maximum reaction velocity (g m\(^{-3}\) soil air min\(^{-1}\)) and \(K_m\) is the (MM) half-velocity coefficient (g m\(^{-3}\) soil air). In Eqs. (9) and (10), oxygen is considered non-limiting.

The kinetic isotope effect can be derived from the ratio of the two reaction rates, i.e., Eqs. (9) and (10) (Simon & Palm, 1966; Hunkeler & Aravena, 2000):

\[
KIE = \frac{^{12}V_{\text{max}} /^{12}K_m}{^{13}V_{\text{max}} /^{13}K_m} (11)
\]

### 3.4 Materials and methods

#### 3.4.1 Experimental system

All laboratory experiments were conducted at 24–25°C in a cylindrical polypropylene tank (1 m diameter, 1 m depth) (Figure 3-1). Twelve perforated PVC tubes (holes i.d. 3 mm), covered with a stainless steel mesh (holes i.d. 0.1 mm) were evenly spaced along the inner periphery of the tank to serve as a homogeneous gas-venting system in an attempt to mimic an open system (Figure 3-1a). A stainless steel perforated plate (holes i.d. 2 mm) covered with a stainless steel mesh (i.d. 0.1 mm) was placed 8 cm above the bottom of the tank yielding a chamber below that was open to the air. The tank was packed with dry quartz sand (0.7–1.2 mm particle diameter), resulting in a total porosity of 0.43. A stainless steel rod (o.d. 8 mm and i.d. 5 mm) was inserted in the center of the tank. The 4-cm-long tip of the rod contained 120 holes (i.d. 0.5 mm) (Figure 3-1 b and c). The tip of the rod was 43 cm below the sand surface. Stainless steel needles (45 cm long, gauge 23) with luer connections were placed
inside the venting tubes. An additional needle was placed alongside the stainless steel rod. These needles served as sampling ports (Figure 3-1 b and c).

Figure 3-1(a) Schematic top view of tank with evenly distributed venting tubes along the periphery. At the center, a needle (gray dot) is beside the injection/extraction rod (black dot). SL indicates sampling locations. Schematic representation of the (b) injection and (c) extraction phases of a GPPT as conducted in the tank. GFC refers to gas flow controller (see text for description). Stainless steel needles were placed inside venting tubes. Note idealized clouds of the gas mixture inside the tank.
3.4.2 Laboratory experiments

Two types of tests were conducted, namely one Gas Push Test (GPT), and three Gas Push–Pull Tests (GPPTs). Tests were conducted in dry sand, i.e., in the absence of microbial activity. The GPT consisted of the injection of 6 L of a gas mixture containing CH$_4$ at 24.5% (v/v) (Table 3-1) into the sand via the rod. For the injection, the gas mixture was pumped from an aluminum bag into the sand using a gas flow controller (GFC). The GFC consists of a diaphragm pump and a mass flow meter, which converts the mass of gases in the gas stream to cumulative volume normalized to 0°C and 1013 mbar (Urmann et al., 2005). Hence, gas volumes in this paper refer to normalized volumes. After injection, the injected gas mixture was left to diffuse, and gas samples (3 mL) were slowly collected from sampling ports at (i) the injection point, and (ii) at two locations 46 cm away from the injection point (Figure 3-1. a).

<table>
<thead>
<tr>
<th>Test</th>
<th>Injection gas mixture$^a$ CH$_4$ (% v/v)</th>
<th>$\delta^{13}$C in injected CH$_4$ (%)</th>
<th>Injection Rate (mL/min)</th>
<th>Vol (L)</th>
<th>Transition time (min)</th>
<th>Extraction Rate (mL/min)</th>
<th>Vol (L)</th>
<th>Total test time (min)</th>
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<tr>
<td>GPT</td>
<td>24.5</td>
<td>-47.6</td>
<td>677</td>
<td>5.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>220</td>
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<tr>
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<td>6.0</td>
<td>1.00</td>
<td>209</td>
<td>14.0</td>
<td>92</td>
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<tr>
<td>GPPT 2</td>
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<td>-50.6</td>
<td>235</td>
<td>5.7</td>
<td>0.95</td>
<td>200</td>
<td>14.0</td>
<td>95</td>
</tr>
<tr>
<td>GPPT 3</td>
<td>96.1</td>
<td>-54.5</td>
<td>200</td>
<td>6.0</td>
<td>0.70</td>
<td>196</td>
<td>20.0</td>
<td>132</td>
</tr>
</tbody>
</table>

The transition time indicates the time between end of injection and start of extraction.
- not applicable
$^a$ Prepared in N$_2$ and noble gases (He, Ne, Ar)

The three GPPTs each consisted of the injection, via the rod into the sand, of ~6 L of a gas mixture containing different CH$_4$ concentrations (Table 3-1). We used the same procedure as for the GPT. Immediately after injection, however, the flow in the GFC was reversed and 14 or 20 L of a blend of injected gas mixture and background air was extracted from the same location. During extraction, the gas blend was sampled periodically. Samples were collected...
with overpressure (+0.5 bar) at the outlet end of the GFC by flushing serum bottles (15 mL) closed with 17-mm-thick butyl rubber septa (Rubber B.V., Hilversum, The Netherlands) and aluminum crimp caps. Bottles were flushed with at least 12 times their volume with the aid of two needles with luer connections.

### 3.4.3 Analytical methods

Methane was measured as described previously (Urmann et al., 2005). Quantification was based on a series of external standards. Samples and standards were injected into the gas chromatograph at atmospheric pressure and room temperature. The carbon-isotope composition of CH$_4$ was measured as described in (Urmann et al., 2005). The isotope ratio of methane ($^{13}$C–CH$_4$/$^{12}$C–CH$_4$) from samples, or from numerical simulations at any time and radial location ($R_{t,r}$) during a GPPT were expressed using the delta notation as follows:

$$
\delta^{13}C (\%o) \text{ in CH}_4 = \left( \frac{R_{t,r} - R_{\text{reference}}}{R_{\text{reference}}} \right) \cdot 1000
$$

(12)

where $R_{\text{reference}}$ is the $^{13}$C–CH$_4$/$^{12}$C–CH$_4$ ratio of the international standard VPDB [Vienna PeeDee Belemnite] (Hoefs, 1997). Gastight syringes (Pressure-Lok, Vici Precision Sampling, Baton Rouge, LA) were used for sampling and in all analyses.

### 3.4.4 Numerical and statistical methods

Finite difference forms of Eq. (1) were solved numerically. We used nonlinear least-squares to fit the transport ($\theta_a$, $\theta_t$) and the kinetic parameters ($V_{\text{max}}$, $K_m$, KIE) for the case study’s GPPT. We performed a grid search to (i) find an optimum set of parameters and to (ii) compute a joint confidence region around the optimum. First, we defined reasonable bounds for each parameter. Then we discretized the hypercube, defined by these bound in the parameter space, by a coarse grid and computed for each grid node the least squares criterion. Around the grid node with the smallest value of the criterion we laid a finer grid, evaluated the criterion again for each node, and, finally, retained the parameter set that minimized the
criterion among the set of all considered nodes. From this set we constructed an approximate joint 95%-confidence region based on a likelihood-ratio test. For more details about this and the employed fitting procedure in general, we refer the reader to Electronic annex.

3.5 Results and discussion

3.5.1 Diffusional isotope fractionation of CH$_4$

Following injection of the gas mixture, the concentration of CH$_4$ at the injection point rapidly decreased during the GPT (Figure 3-2a). Simultaneously, the carbon-isotope composition of CH$_4$ ($\delta^{13}$C in CH$_4$) at the injection point became strongly enriched in $^{13}$C (Figure 3-2b). The maximum isotopic shift was from $-47.6‰$ ($\delta^{13}$C in injected CH$_4$) to $-21.7‰$ at 40 min. The enrichment in $^{13}$C indicates that $^{12}$C–CH$_4$ diffused away from the injection point faster than $^{13}$C–CH$_4$, which is in agreement with theory. This was confirmed during the first 15 min after injection when CH$_4$ at two different radial locations at 46 cm away from the injection point became enriched in $^{12}$C. Enrichment in $^{12}$C was reflected by the very negative $\delta^{13}$C value of ca. $-65‰$ measured at these locations (Figure 3-2c). As test time progressed, CH$_4$ at both locations (i.e., injection point, and at 46 cm away from injection point) became similarly enriched in $^{13}$C with $\delta^{13}$C values around $-30‰$ (Figure 3-2b and c).

In contrast to a GPT, a GPPT includes a transition and an extraction phase in addition to the injection phase. We examined whether the advective component of the extraction phase of GPPTs counteracts the strong isotope fractionation of CH$_4$ observed during the GPT. Samples collected at the injection/extraction point during the extraction phase of GPPTs showed an initial rapid decrease in CH$_4$ concentration followed by a slower decrease (Figure 3-3a–c). With respect to CH$_4$ isotope composition, we observed that in all GPPTs the extracted CH$_4$ became strongly enriched in $^{13}$C (Figure 3-3d–f), i.e., the $\delta^{13}$C in CH$_4$ became less negative. This shows that during GPPTs there is strong isotope fractionation of CH$_4$ due to the two isotopes’ differential diffusion. A comparison of the CH$_4$ isotopic shift within 10
min after the end of injection during GPPTs (26.8 ± 6.4‰, ± 2σ) and during the GPT (23.4‰) indicates that the advective component of the GPPTs’ extraction phase was ineffective in diminishing the strong diffusional isotope fractionation of CH₄.

Figure 3-2. Results of Gas Push Test (GPT). The concentration of injected CH₄ is indicated as CH₄inj (a) Relative concentration of CH₄ at the injection point and stable carbon isotope composition of CH₄ at (b) the injection point, and (c) at 46 cm away from the injection point as a function of time. Open and closed symbols in (c) represent data from two different locations along the tank periphery. Solid lines represent the output of the mathematical model.
Methane fractionation during GPPTs and the GPT were numerically simulated using a finite difference approximation of Eq. (1) considering a quasi-infinite porous medium. The model described the measured CH$_4$ isotope fractionation reasonably well for all tests (solid lines, Figure 3-2 and Figure 3-3). No fitting of experimental data was employed, and the required input parameters were either measured (i.e., Table 3-1), determined independently (i.e., porosity), or taken from the literature (i.e., diffusion coefficients in air). Nevertheless, some deviation between measured and modeled isotope data was observed at late times (e.g., Figure 3-2b). This was likely the result of wall effects during the experiments. Additional simulations using a different domain and different boundary conditions corroborated this hypothesis (Figure 3-4). As the GPPTs’ total test duration was shorter than that of the GPT, wall effects appeared to be somewhat less pronounced during GPPTs (Figure 3-3d–f).

Figure 3-3. Relative extracted CH$_4$ concentration at the injection/extraction point (top panels) as a function of time, and corresponding stable carbon isotope composition of extracted CH$_4$ at the same location (bottom panels) during three different GPPTs. The injected CH$_4$ concentration for each test is indicated as CH$_4^{inj}$. Solid lines represent the output of the mathematical model. Data point in panel (d) at 20 min is likely an outlier.
The effective diffusion coefficients of CH₄ isotopes used for simulations give a value for the theoretical kinetic isotope effect for diffusion ($\frac{12D_e}{13D_e}$) of 1.0195. This same value was used to account for isotope fractionation of CH₄ due to diffusion in studies of microbial methane oxidation in forest soils (Reeburgh et al., 1997). In contrast, De Visscher et al. (2004) used a value of 1.0178 to best fit CH₄ isotope fractionation data for vertical diffusion in a laboratory column.

Figure 3-4. Results of Gas Push Test (GPT). Stable carbon isotopic composition of CH₄ at the injection point. Symbols are measured data. Lines represent the output of the mathematical model using different computation domain size boundary conditions as follows: (a) mimics an open tank with constant atmospheric CH₄ concentration and corresponding atmospheric $\delta^{13}C$ at the tank perimeter (Eq. (EA-4)). (b) mimics a quasi-infinite porous media (Eq. (EA-3)). (c) mimics a closed tank (Eq. (EA-5)).
Figure 3-5 shows that physical properties of the porous medium (or soil) will determine the extent of diffusional fractionation during GPPTs, and thus the shape of the carbon isotope-composition curve of extracted CH₄. For example, in a highly tortuous porous medium (and/or in a system with reduced θₐ), Dₑ of CH₄ may be strongly reduced. As a result of low Dₑ values, the initial enrichment of ¹³C in the extracted CH₄ may be followed by a decrease in enrichment (Figure 3-5a). This shift occurs because some of the light CH₄ that initially diffuses away can be extracted at low Dₑ values. For low Dₑ values, CH₄ mass recoveries are expected to be relatively high (~75%, Figure 3-5b). Conversely, for high Dₑ values the enrichment in ¹³C remains constant throughout the latter part of the extraction phase (Figure 3-5a). For high Dₑ values, the above mentioned shift is not observed due to...
resulting low CH$_4$ mass recoveries (~12%, Figure 3-5b). This trend agreed with experimental GPPTs, in which mass recoveries were low (~12%, Figure EA-1). At high $D_e$ but at much later times during GPPTs, one may observe a decrease in $^{13}$C enrichment. However, this shift would be due to CH$_4$ concentrations approaching atmospheric values with corresponding $\delta^{13}$C values.

3.5.2 Relative magnitude of microbial and diffusional fractionation of CH$_4$

To evaluate the extent of isotope fractionation due to microbial CH$_4$ oxidation, and to compare it to that due to diffusion, we conducted numerical simulations of GPPTs considering a quasi-infinite porous medium. Microbial CH$_4$ oxidation was described by a first-order rate constant, using reported $k$ values as $^{12}k$ (Eq. (6)), while $^{13}k$ (Eq. (7)) was calculated using Eq. (8) with a KIE factor of 1.025 (Coleman et al., 1981). High and low microbial activities were represented using $k$ values of 1.18 h$^{-1}$ and 0.02 h$^{-1}$, respectively. The former is within the high-range $k$ values reported from diverse studies (references in Urmann et al., 2005) and close to average values for microbial methane oxidation in landfill cover soils (Whalen & Reeburgh, 1990), while the latter is within the low-range $k$ values reported for forest soils (Wang et al., 1999).

Simulations of hypothetical GPPTs, in which isotope fractionation of CH$_4$ occurs exclusively due to microbial oxidation show that the isotopic signature of extracted CH$_4$ becomes steadily enriched in $^{13}$C throughout the GPPT, i.e., the isotopic signature steadily shifts towards less negative $\delta$ values (Figure 3-6a). The same trend occurs at low microbial activity, but is too small in magnitude to be noted in Figure 3-6b. To simulate the absence of isotope fractionation due to diffusion, the diffusion coefficients in air of $^{12}$C–CH$_4$ and $^{13}$C–CH$_4$ were set to the same value ($1.2657 \times 10^{-3}$ m$^2$ min$^{-1}$). All other simulation parameters were identical to those of the experimental GPPT 2 (Table 3-1).
When only diffusional fractionation occurs during GPPTs, the isotopic signature of extracted CH$_4$ becomes initially strongly enriched in $^{13}$C (as already discussed in the previous section). The isotopic signature remains constant afterward (Figure 3-6). Simulations of GPPTs in which simultaneous microbial and diffusional fractionation phenomena occur show that microbial isotope fractionation of methane can be in excess of that observed merely due to diffusion only when microbial CH$_4$ oxidation activity is high (Figure 3-6a). Conversely, if microbial activity is low, isotope fractionation may be strongly dominated by diffusional fractionation (Figure 3-6b).

![Image](image_url)

**Figure 3-6.** Simulations of stable carbon isotope composition of extracted CH$_4$ during GPPTs. Three situations were considered: (i) where only diffusion occurs and there is no microbial oxidation (i.e. diffusional fractionation), (ii) where exclusively microbial oxidation occurs (i.e. microbial fractionation), and (iii) where both diffusional and microbial oxidation occur (i.e. diffusional and microbial fractionation). High (a) and low (b) microbial activities were simulated, and a single KIE factor (1.025) was used.
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Not only the level of microbial activity is important, the KIE value will also determine to what extent the observed isotope fractionation of CH$_4$ may be dominated by fractionation due to diffusion. This can be seen from a series of GPPTs, which were simulated with constant, high microbial activity, but with different KIE values (Figure 3-7).

![Figure 3-7. Simulations of stable carbon isotopic composition of extracted CH$_4$ during GPPTs. $D_e =^{12}D_e$. A high microbial activity ($^{13}k=1.18$ h$^{-1}$) was used with different KIE values. All other simulation parameters were those of the experimental GPPT 2.](image)

3.5.3 Diffusional and microbial isotope fractionation of CH$_4$ above a petroleum-contaminated aquifer—case study

To further illustrate the issue of concurrent diffusional and microbial isotope fractionation of CH$_4$, we re-analyzed CH$_4$ isotope data generated during two GPPTs conducted in the unsaturated zone above a petroleum-contaminated aquifer within a 70-cm-diameter concrete well casing (Urmann et al., 2005). These GPPTs were specifically conducted to study microbial CH$_4$ oxidation. In these tests, 30 L of a gas mixture containing CH$_4$, O$_2$, Ne and Ar (3%, 16%, 3% and 20% (v/v), respectively) were injected into the vadose zone (at 2.7 m depth) at a rate of 0.6 L min$^{-1}$. Thereafter, 90 L of a blend of soil air and injected gas mixture was extracted from the same location at a rate of 0.5 L min$^{-1}$. The two
GPPTs were conducted sequentially at the same location. In the second test, 2% (v/v) of acetylene (C$_2$H$_2$) was co-injected to inhibit microbial CH$_4$ oxidation. Hence, the first and second tests are hereafter called “active GPPT” and “inhibited GPPT”, respectively.

### 3.5.4 Inhibited GPPT

Data from the “inhibited GPPT” reflect the physical transport of all injected gases in the absence of microbial activity. Hence, the relative concentration of extracted CH$_4$ for this test allowed, via the GPPT mathematical model and a fitting procedure, the estimation of the total ($\theta_t$) and the air-filled porosity ($\theta_a$). With these parameters, the tortuosity factor ($\tau$) and the effective diffusion coefficient ($D_e$) were calculated. The ability of the resulting parameters to describe the physical transport of gases at this field location (and at the time of the experiments) was verified, as in addition to describing the CH$_4$ data (Figure 3-8a), they also described tracer gases Ne and Ar data quite well (Figure EA-2). At this location, and despite their different diffusion coefficients, transport of CH$_4$ and tracer gases was similar (Figure EA-2). This differs from GPPTs conducted in open systems where CH$_4$ and tracer gases transport was dissimilar (Gonzalez-Gil et al., 2007) and suggests that gas transport was restricted at this field site.

Having fixed $\tau$ and $\theta_a$, and knowing the $\delta^{13}$C of injected CH$_4$ in this test (−46.2‰), the transport of $^{12}$C–CH$_4$ and $^{13}$C–CH$_4$ was simulated (for further details see Section 2 and Eq. (12)). The mathematical model described the measured isotope composition of extracted CH$_4$ from the “inhibited GPPT” reasonably well (Figure 3-8b). Compared to the laboratory GPPTs, the isotope fractionation due to diffusion in this “inhibited GPPT” was far less pronounced (compare Figure 3-8b with Figure 3-3d–f) due to restricted gas transport at the field site (i.e., lower $D_e$ values), as mentioned previously (Figure 3-5).
Figure 3-8. Relative concentration of extracted methane ($\text{CH}_4^{\text{ext}}/\text{CH}_4^{\text{inj}}$), and the corresponding carbon isotope composition during the “inhibited GPPT” (left), and “active GPPT” (right) from the field case study. Symbols represent measured data. Solid lines represent the output of the mathematical model.

3.5.5 Active GPPT

Data from the “active GPPT” reflects the combination of physical transport and microbial CH$_4$ oxidation activity. The parameters that describe the former were taken from the “inhibited GPPT”. Hence, “active GPPT” data was used to estimate the microbial CH$_4$ oxidation kinetic parameters (Eq. (1)). Since $[\text{CH}_4] \approx [^{12}\text{C–CH}_4]$, we set $V_{\text{max}}$ and $K_m$ equal to $^{12}V_{\text{max}}$ and $^{12}K_m$ (Eqs. (9) and (10)). Furthermore, since microbial KIE is a function of the ratio of the kinetic constants (Eq. (11)), we fixed $^{12}V_{\text{max}} = ^{13}V_{\text{max}} = V_{\text{max}}$. Thus, we were left with three free parameters ($V_{\text{max}}$, $K_m$, and KIE) that had to be fitted using the relative concentration and isotope data sets. Using the grid search strategy sketched in Section 3.4.4, we found that $V_{\text{max}} = 2.88 \text{ g CH}_4 \text{ m}^{-3} \text{ soil air h}^{-1}$, $K_m = 1.4 \text{ g CH}_4 \text{ m}^{-3} \text{ soil air}$, and KIE = 1.020 best described the breakthrough curves of the “active GPPT” (Figure 3-8c and d). Using $V_{\text{max}}/K_m$
to estimate a first-order rate constant, the resulting value of 2.06 h\(^{-1}\) agrees favorably with the value of 2.19 h\(^{-1}\) determined by Urmann et al. (2005) at the same location. The obtained KIE value is close to values obtained for forest soils (1.0165–1.0177) using the chamber technique, and a modeling approach that assumed first-order kinetics for microbial CH\(_4\) oxidation and considered diffusional isotope fractionation (Snover & Quay, 2000). It is also within the mid range of KIE values reported for landfill cover soils of 1.008–1.038 (mostly determined from laboratory incubations of soils) (Bergamaschi et al., 1998, Liptay et al., 1998, Chanton & Liptay, 2000 and Borjesson et al., 2001), and 1.013 to 1.025 for methanotrophic enrichment cultures (Coleman et al., 1981).

It is interesting to note that other combinations of \(V_{\text{max}}\) and \(K_m\) adequately described the relative concentration data of extracted CH\(_4\) (Figure EA-3a). However, independent of the choice of KIE value, it was not possible to describe the isotope composition data properly with these parameter sets (Figure EA-3b and c). Hence, the isotope data has the potential of being a fine-tuning instrument for the assessment of in-situ kinetic parameters.

The joint 95%-confidence region around the best-fit kinetic parameters (Figure 3-9) indicates that the estimate of \(K_m\) was the least precise. Projected onto the \(K_m\)-axis the bounds of the 95%-confidence region ranged from 1.2 to 2.4 g CH\(_4\) m\(^{-3}\) soil air. Values of \(V_{\text{max}}\) and KIE were more precisely estimated, the projected 95%-ranges were 2.6–4.1 g CH\(_4\) m\(^{-3}\) soil air h\(^{-1}\) and 1.017–1.022, respectively. The estimates of \(V_{\text{max}}\) and \(K_m\) were strongly correlated (Figure 3-9), other pairs of estimates less so. One might rate the plausible range of variation of \(K_m\) (by a factor of two) as too large. But in view of the many uncertainties associated with the analysis of field experiments, we consider the achieved precision reasonably. Note that we expect the results presented in Figure 3-9 to vary with GPPT experimental conditions. Thus, different experimental conditions (e.g., much smaller CH\(_4\) injection concentration in the range of \(K_m\)) may yield different uncertainties of the fitted parameters. This will be a subject of future investigations.
Figure 3-9. Two-dimensional plots of the joint 95% confidence region surrounding the best fit parameter values (best fit value shown in black squares). Data points for estimation of confidence region (shown as dots) were obtained using the procedure outlined in Electronic annex.

3.6 Practical implications

During GPPTs strong isotope fractionation of CH$_4$ due to diffusion will usually occur and cannot be neglected. If soil microbial activity is low, then isotope fractionation may be dominated by diffusion rather than by microbial consumption. Hence, description of isotope data during GPPTs should include the coupling of diffusional and microbial fractionation, because microbial oxidation can drive diffusion and vice versa.
By conducting two sequential GPPTs, with microbial activity inhibited in the second test, and with the aid of a mathematical model, it may be possible to estimate isotope fractionation (KIE) due to microbial activity. Moreover, including isotope data in the estimation of Michaelis–Menten kinetic parameters is valuable, because estimated $V_{\text{max}}$ and $K_m$ values were unique in describing the isotope data. Other combinations of these parameters could adequately describe the relative concentration data of extracted CH$_4$, but failed to describe the isotope data properly. Hence, the combination of GPPT with CH$_4$ isotope data may be a robust approach for measurements of rate parameters and KIE factors of in-situ microbial methane oxidation in the field. KIE factors are required to estimate CH$_4$ oxidation in e.g., landfills by using source and surface CH$_4$ isotope data. In-situ assessment of KIE values is important, since small variations of KIE result in large uncertainties on estimated oxidized CH$_4$.

Finally, it is noteworthy that instead of using data from two sequential GPPTs (one active and one inhibited test), estimation of $V_{\text{max}}$, $K_m$, and KIE parameters would be possible employing a single, active GPPT. In that case, co-injected tracers (e.g., Ne and Ar) may be used to account for physical transport processes during the GPPT. On the other hand, either method may not be applicable in situations when our modeling approach fails due to excessive heterogeneity in the subsurface, e.g., in layered soils with greatly varying soil–water contents, or when other assumptions made in the model’s derivation are violated.

### 3.7 Acknowledgments

We thank M. Saurer and R. Siegwolf (PSI, Villingen, Switzerland) for help with stable carbon-isotope measurements, and H. Läser (ETH, Zurich) for help in constructing the experimental system. This work was funded by the Swiss National Science Foundation (SNF) and ETH Zurich. Valuable comments from J. Chanton, an anonymous reviewer and the associate editor were greatly appreciated.
3.8 Electronic Annex

3.8.1 Numerical solution

Finite difference forms of eq 1 were solved using the following initial (eq. EA-1) and boundary conditions (eq. EA-2, EA-3):

\[
C_{(r,t)}\big|_{t=0} = 0 
\]

\[
-D \frac{\partial C}{\partial r} \bigg|_{r=r_{\text{rod}}} + v \cdot C_{(r,t)}\big|_{r=r_{\text{rod}}} = \begin{cases} 
    v \cdot C_{\text{injection-gas}} & t = t_{\text{injection}} \\
    0 & t = t_{\text{transition}} \\
    -v \cdot C_{(r,t)}\big|_{r=r_{\text{rod}}} & t = t_{\text{extraction}} 
\end{cases} 
\]

\[
C_{(r,t)}\big|_{r=r_{\text{max}}} = 0 , \quad r_{\text{max}} = 400 \text{ cm} 
\]

where, \( r_{\text{Rod}} \) is the radius of the tip of the rod, and \( r_{\text{max}} \) is the maximum radius of the computational domain which was set to 400 cm, divided into 400 evenly spaced nodes (i.e. shells). This \( r_{\text{max}} \) simulated a quasi-infinite porous media.

To obtain simulation results shown in Figure 3-4, two other boundary and computation domain conditions were used as follows: To mimic an open tank with constant atmospheric CH\(_4\) concentration and corresponding atmospheric \( \delta^{13}\text{C} \) at the tank perimeter, eq. EA-3 becomes:

\[
C_{(r=r_{\text{max}},t)} = C_{\text{atmospheric}} , \quad r_{\text{max}} = r_{\text{tank}} = 50\text{cm} 
\]

To mimic a closed tank, eq. EA-3 becomes:

\[
-D \frac{\partial C}{\partial r} \bigg|_{r=r_{\text{max}}} + v \cdot C_{(r,t)}\big|_{r=r_{\text{atm}}} = 0 , \quad r_{\text{max}} = r_{\text{tank}} = 50\text{cm} 
\]

where \( r_{\text{tank}} \) is the tank radius.
For all simulations a time step of 0.05 s was used. Input parameters to simulate GPT and GPPTs were obtained from measured data (Table 3-1), other parameters were determined as follows: the $\theta_i$ was obtained as $1-(\rho_b/\rho_p)$, where the particle density $\rho_p$ [g m$^{-3}$] was measured using a gravimetric-volumetric technique (Flint & Flint, 2002). The bulk density $\rho_b$ [g m$^{-3}$] was the measured ratio of mass and volume of sand in the tank.

3.8.2 Least squares fitting of kinetic parameters and construction of a joint 95% confidence region.

We used the $n_1$ log$_{10}$-transformed measurements of methane, say $y_{1,i}, i = 1,2,...,n_1$, and the $n_2$ isotopic composition measurements of methane ($\delta^{13}$C in CH$_4$ ext, say $y_{2,i}, i = 1,2,...,n_2$) to fit the parameters $K_m$, $V_{max}$ and KIE for the “active GPPT”. Let $y_1(\phi;t_i)$ denote the modeled log-transformed methane concentration and $y_2(\phi;t_i)$ the isotopic concentration, where $t_i$ is the time when the $i$th measurement was taken, and $\phi$ is the $p$-vector with the kinetic parameters. Formally, we may then write $y_{j,i} = y_j(\phi;t_i) + \epsilon_{j,i}$, where $\epsilon_{j,i}$ is an error with zero mean and constant variance $\sigma^2$.

To find the best-fit parameters, $\hat{\phi}$, we minimized

$$S(\phi) = \sum_{i=1}^{n_1} \left( \frac{y_{1,i} - y_1(\phi;t_i)}{\sigma_1} \right)^2 + \sum_{i=1}^{n_2} \left( \frac{y_{2,i} - y_2(\phi;t_i)}{\sigma_2} \right)^2$$

by a grid search. The residuals, $z_{j,i} = y_{j,i} - y_j(\phi;t_i)$ were thus weighted a priori by the inverse standard deviations, $\sigma_1$ and $\sigma_2$, of the measurement errors. This is common practice in fitting parameters to multi-response data in transport modeling (e.g. Reichert, 1994). For the isotopic composition measurements we knew that $\sigma_2 = 0.3\% e$, and for CH$_4$ we were given the coefficient of variation (CV) of the untransformed measurements (3%). Assuming that the measured values were log-normally distributed, we then computed the measurement error standard deviation of $y_{1,i}$ as $\sigma_1 = \log_{10}(e)\sqrt{\log_e(1+CV^2)} = 0.013$ by inverting the well-known expression for the CV of a log-normally distributed random variable.
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The least squares criterion $S(\phi)$ is closely related to the likelihood-based determinant criterion of Bates and Watts (1988, sec. 4.1.1). For normally distributed, mutually independent errors, the (profile) log-likelihood $L(\phi)$ is related to $S(\phi)$ by

$$L(\phi) = \text{const.} - \left( \frac{n_1 + n_2}{2} \right) \log \left( \sigma(\phi) \right) = \text{const.} - \left( \frac{n_1 + n_2}{2} \right) \log \left( \frac{S(\phi)}{(n_1 + n_2 - p)} \right)$$

(EA-7)

Thus, for Gaussian errors, the least-squares estimate $\hat{\phi}$ is the maximum likelihood estimate of $\phi$. Two remarks are reasonable at this point. First, note that we estimated the variance of the residuals unbiased by $\hat{\sigma}(\phi) = \frac{S(\phi)}{(n_1 + n_2 - p)}$, which is the restricted maximum likelihood estimate of $\sigma^2$ for Gaussian errors. Second, we transformed the methane readings to logarithms to better approximate the Gaussian assumption.

Using eq. (EA-7) we constructed a joint confidence region for the fitted parameters based on a likelihood ratio test (e.g. Bates & Watts, 1988, sect. 4.1.2 and Vugrin et al., 2007 for an application in groundwater hydrology). Under the null hypothesis that the true parameters are equal to $\hat{\phi}$, the log-likelihood difference

$$2(L(\phi) - L(\phi)) = (n_1 + n_2)(\log_e(S(\phi)) - \log_e(S(\phi)))$$

follows a $\chi^2$-distribution with $p$ degrees of freedom. Thus, a 95%-joint confidence region can be constructed by searching for those $\phi$ for which $(n_1 + n_2)(\log_e(S(\phi)) - \log_e(S(\phi)))$ is less than the 95%-quantile of a $\chi^2$-distribution with $p$ degrees of freedom. In our case with $p = 3$ the critical quantile is 7.81. To find the boundary of the confidence region, we added further nodes (for which we computed $S(\phi)$) to the grid in the parameter space.
Figure EA-1. Cumulative mass (CH$_4$) recovered (i.e., extracted) during GPPT 3. Symbols are measured data. Solid lines are the output of the mathematical model. Mass recovered for GPPT 1 and 2 was in the same order of magnitude as GPPT 3.

Figure EA-2. Mathematical description (solid lines) of the transport of tracer gases Ne and Ar during GPPTs from the field case study. Symbols represent measured data. Open symbols correspond to the “inhibited GPPT”, and closed symbols correspond to the “active GPPT”. $C_{\text{ext}} / C_{\text{inj}}$ refers to relative, i.e. extracted / injected gas concentration.
Figure EA-3. (a) Relative concentration of extracted CH₄ of the “active GPPT” described with the kinetic parameters shown in the panel. Corresponding isotopic data described with (b) a low KIE value, and (c) with a high KIE value. The use of a high KIE value improves the agreement between model prediction and experimental data, but the measured trend does not seem to be well described. Symbols are measured data. Solid lines are the output of the mathematical model.

3.8.3 Supporting references.


3.9 References


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Chapter 3: Diffusional and Microbial Isotope Fractionation of Methane during Gas Push-Pull Tests
Quantifying Methane Oxidation in a Landfill-Cover Soil by Gas Push-Pull Tests

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Published in Waste Management (2009), 29, 2518-2526
Chapter 4: Quantifying Methane Oxidation in a Landfill-Cover Soil by Gas Push-Pull Tests

4.1 Abstract

Methane (CH\textsubscript{4}) oxidation by aerobic methanotrophs in landfill-cover soils decreases emissions of landfill-produced CH\textsubscript{4} to the atmosphere. To quantify in-situ rates of CH\textsubscript{4} oxidation we performed five gas push-pull tests (GPPTs) at each of two locations in the cover soil of the Lindenstock landfill (Liestal, Switzerland) over a four week period. GPPTs consist of the injection of a gas mixture containing CH\textsubscript{4}, O\textsubscript{2} and noble-gas tracers followed by extraction from the same location. Quantification of first-order rate constants was based upon comparison of breakthrough curves of CH\textsubscript{4} with either Ar or CH\textsubscript{4} itself from a subsequent inactive GPPT containing acetylene as an inhibitor of CH\textsubscript{4} oxidation. The maximum calculated first-order rate constant was 24.8 ± 0.8 h\textsuperscript{-1} at location 1 and 18.9 ± 0.6 h\textsuperscript{-1} at location 2. In general, location 2 had higher background CH\textsubscript{4} concentrations in vertical profile samples than location 1. High background CH\textsubscript{4} concentrations in the cover soil during some experiments adversely affected GPPT breakthrough curves and data interpretation. Real-time PCR verified the presence of a large population of methanotrophs at the two GPPT locations and comparison of stable carbon isotope fractionation of CH\textsubscript{4} in an active GPPT and a subsequent inactive GPPT confirmed that microbial activity was responsible for the CH\textsubscript{4} oxidation. The GPPT was shown to be a useful tool to reproducibly estimate in situ rates of CH\textsubscript{4} oxidation in a landfill-cover soil when background CH\textsubscript{4} concentrations were low.

4.2 Introduction

Anaerobic microbial decomposition of organic material in landfills produces a gas mixture consisting of 50-70 % (v/v) CH\textsubscript{4}, 30-50 % (v/v) CO\textsubscript{2} and trace amounts of
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nitrogen, hydrogen sulfide and other non-methane hydrocarbons (Farquhar & Rovers, 1973). Pressure and concentration gradients in the landfill can cause migration of the gas away from the source, bringing it into contact with soil surrounding and covering the landfill where methanotrophic bacteria can consume CH$_4$ in the presence of oxygen (O$_2$). Methanotrophs in landfill-cover soils serve as a biofilter for CH$_4$ and have been reported to decrease emissions of CH$_4$ to the atmosphere by oxidizing from 10 to 100% of the produced CH$_4$ (Boeckx et al., 1996, Czepiel et al., 1996, Abichou et al., 2006, Borjesson et al., 2007, Chanton et al., 2008). In addition to oxidizing CH$_4$ that migrates upwards from the waste, the large population of methanotrophs supported by the elevated CH$_4$ concentrations in landfill-cover soils has also been identified as a sink for atmospheric CH$_4$ (Bogner et al., 1997b, Borjesson & Svensson, 1997).

Methanotrophic activity in landfill-cover soils has been shown to vary within and between sites depending upon numerous factors including soil moisture and temperature (Czepiel et al., 1996, Whalen et al., 1990, Boeckx et al., 1996, Christophersen et al., 2000, Stein & Hettiaratchi, 2001), ammonium concentration (Boeckx et al., 1996), soil-gas CH$_4$ concentration (Czepiel et al., 1996, Bogner et al., 1997b) and organic matter content (Christophersen et al., 2000). Estimates of CH$_4$ oxidation rates in landfill-cover soils from laboratory incubation studies range over six orders of magnitude (Bogner et al., 1997a), however, because soil sampling disturbs the soil structure and laboratory manipulations may influence soil microbial communities, rates obtained by these methods are difficult to directly extrapolate back to the field.

Methane oxidation rates in landfill-cover soils have also been estimated from field measurements. Jones and Nedwell (1993) quantified CH$_4$ oxidation rates from vertical
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CH$_4$ concentration gradients using the turnover rate of CH$_4$ in the soil determined from laboratory experiments. Methane concentration gradient data can also be combined with measured fluxes from the anaerobic zone and emission rates from the cover soil to calculate CH$_4$ oxidation rates (Nozhevnikova et al., 2003). Additionally, stable carbon isotope analysis of CH$_4$ from profile and emitted gas samples has been explored as a sensitive tool to quantify CH$_4$ oxidation rates in landfill-cover soils (Chanton et al., 2008).

While these methods are valuable tools to confirm that CH$_4$ oxidation is occurring, rate quantification from profile gradient methods relies upon the assumption of a steady-state system and laboratory-determined CH$_4$ turnover constants or isotopic fractionation factors, which may differ from field values.

An alternative method that has been used recently to estimate the kinetics of CH$_4$ oxidation is the gas push-pull test (GPPT). A GPPT consists of the injection of a mixture containing the reactive gas CH$_4$ and O$_2$ and nonreactive tracer gases into the vadose zone, followed by extraction of the injected gas mixed with soil air from the same location. Rate constants for CH$_4$ oxidation can be calculated from GPPTs by analysis of the breakthrough curves of CH$_4$ and that of a suitable inert tracer gas. This single-well gas-tracer test has previously been implemented in soil above a contaminated methanogenic aquifer (Urmann et al., 2005, Urmann et al., 2008), and in an alpine peat bog (Urmann et al., 2007). More recently, efforts to implement the GPPT in landfill-cover soils are being explored by a European project (Streese-Kleeberg, 2008). In addition to field studies, abiotic laboratory GPPTs have been performed to study the dominant physical transport processes operating during a GPPT in dry or moist porous media (Gonzalez-Gil et al., 2007, Gomez et al., 2008). As a tool for estimating the kinetics of CH$_4$ oxidation, the
GPPT has several advantages over other methods. Firstly, GPPTs can be conducted in situ, therefore resulting estimates are not influenced by changes in soil or microbial community structure during soil sampling or due to laboratory manipulations. Secondly, compared to profile sampling, GPPTs may probe a larger volume of soil and rates can be calculated for a longer testing time, thereby reducing variability due to soil heterogeneity. Thirdly, GPPTs are non-destructive to the cover soil and cause little disturbance to the soil structure. If the physical transport of CH$_4$ and the nonreactive tracer are similar during the GPPT, then simplified methods that do not require knowledge of the soil physical properties can be used (Haggerty et al., 1998, Snodgrass & Kitanidis, 1998, Schroth & Istok, 2006). In a highly diffusive environment such as in a peat bog where the porosity can be as high as 98%, diffusive transport of the noble gas tracers may be so different from CH$_4$ that the only suitable tracer may be CH$_4$ itself from a second GPPT performed in the presence of an inhibitor of CH$_4$ oxidation (Urmann et al., 2007).

In the summer of 2007 we carried out a field investigation to quantify in-situ methanotrophic activity in the cover soil of a closed municipal waste landfill using GPPTs. We aimed to determine the feasibility and reproducibility of GPPTs to estimate the kinetics of CH$_4$ oxidation in this high CH$_4$ turnover environment. To this end, two locations in the cover soil were selected to perform four active GPPTs and one “inactive” GPPT containing the inhibitor acetylene (C$_2$H$_2$) at each location. Soil-gas samples were taken at both locations to assess CH$_4$, CO$_2$ and O$_2$ gradients to a depth of 1 m, and soil samples were collected in the vicinity to quantify the methanotrophic population. Stable carbon isotope analysis of CH$_4$ in GPPT samples was explored as an additional tool to estimate the kinetics of CH$_4$ oxidation in this environment.
Chapter 4: Quantifying Methane Oxidation in a Landfill-Cover Soil by Gas Push-Pull Tests

4.3 Materials and methods

4.3.1 Site description

The Lindenstock Landfill is located near Liestal, in the northwest of Switzerland. The 12.3 ha landfill was opened in 1949 and received ca. 3,000,000 m$^3$ of household, office and construction waste over a 45 year period. In the 1990’s waste deposition ceased and a cover soil was added to a depth of 2.0 to 2.5 m. The cover soil (estimated total porosity 0.49) is a heterogeneous mixture composed primarily of sandy-loam with pebbles, rocks, boulders and construction material with intermittent clay lenses. A gas extraction system was installed, but gas produced from the landfill waste is not currently being actively pumped. The site is 570 m above sea level at the highest point, has an average annual temperature of 8.8 °C and receives on average 0.981 m of precipitation per year. Vegetation is abundant but intermittent, consisting of grass, shrubs, and small trees. Prior to each GPPT the soil temperature at 10 cm below the surface was measured. The volumetric water content of the soil was calculated from gravimetric water content and an estimated bulk density of 1.3 g cm$^{-3}$ for soil samples taken from 30 cm below the surface in the vicinity of the GPPT locations (Table 4-1). Ten minute interval barometric pressure measurements were taken at the Rünenberg automatic monitoring weather station (610 m above sea level) located 12 km north-west of the Lindenstock landfill. During the study period the atmospheric pressure ranged from 1003 to 1023 hPa with an average of 1017 hPa (adjusted to mean sea level).
### Chapter 4: Quantifying Methane Oxidation in a Landfill-Cover Soil by Gas Push-Pull Tests

Table 4-1: Soil physical properties and Gas Push-Pull Test operational parameters at location 1 (1A - 1E) and location 2 (2A - 2E).

<table>
<thead>
<tr>
<th>GPPT</th>
<th>date 2007</th>
<th>soil properties</th>
<th>C$_2$H$_2$ injection rate (mL min$^{-1}$)</th>
<th>transition phase (min)</th>
<th>extraction rate (mL min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>June 29</td>
<td>16.4</td>
<td>0.21</td>
<td>–</td>
<td>686.7</td>
</tr>
<tr>
<td>1B</td>
<td>July 5</td>
<td>15</td>
<td>0.25</td>
<td>–</td>
<td>617.5</td>
</tr>
<tr>
<td>1C</td>
<td>July 16</td>
<td>20.6</td>
<td>0.21</td>
<td>–</td>
<td>640.5</td>
</tr>
<tr>
<td>1D</td>
<td>July 17</td>
<td>20.5</td>
<td>0.26</td>
<td>–</td>
<td>716.8</td>
</tr>
<tr>
<td>1E</td>
<td>July 17</td>
<td>20.5</td>
<td>0.26</td>
<td>+</td>
<td>760.0</td>
</tr>
<tr>
<td>2A</td>
<td>July 17</td>
<td>21.6</td>
<td>0.32</td>
<td>–</td>
<td>721.9</td>
</tr>
<tr>
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<td>July 25</td>
<td>18.3</td>
<td>0.18</td>
<td>–</td>
<td>685.9</td>
</tr>
<tr>
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<td>0.29</td>
<td>–</td>
<td>645.1</td>
</tr>
<tr>
<td>2D</td>
<td>July 27</td>
<td>19.4</td>
<td>0.32</td>
<td>–</td>
<td>682.5</td>
</tr>
<tr>
<td>2E</td>
<td>July 27</td>
<td>20.7</td>
<td>0.32</td>
<td>+</td>
<td>607.7</td>
</tr>
</tbody>
</table>

*Temperature was measured 10 cm below the soil surface

#### 4.3.2 Soil-gas profiles

An initial site survey was undertaken to measure CH$_4$ concentrations in holes drilled incrementally to 30, 60 and 100 cm depth at 18 evenly distributed points across the landfill soil cover. Two of the 18 points were selected as monitoring locations where clusters of 1.5 mm i.d. stainless steel needles (Unimed, Lausanne, Switzerland) were installed for vertical soil-gas profile measurements. The two locations (ca. 100 m apart) were selected because both exhibited steep CH$_4$ gradients with high concentrations at 100 cm below the surface decreasing to near atmospheric concentrations at 30 cm, and a decrease in the CH$_4$ to CO$_2$ ratio closer to the surface, presumably indicative of CH$_4$ oxidation occurring in the cover soil. At each of the two sampling locations, needles were installed at 15 and 60 cm depth in one hole, and at 40 and 100 cm in another hole.
Sampling needles could not be directly inserted into the stony cover soil, therefore, 2.5 cm diameter holes were drilled, a small amount of sand was poured into the holes to keep the needle tips from clogging, and the longest needle was positioned in each hole. A desiccated clay powder (Fango, ZZ Wancor, Regensdorf, Switzerland) was poured into the holes to a depth of 10 cm and water was sprinkled onto the powder to seal around the needles and prevent preferential gas flow paths along the needles to the surface. The holes were re-filled with soil to the depth required for the second needle which was installed in the same way as the first needle in each hole. Subsequently, the holes were filled to the surface with soil. During the study soil-gas samples were collected from the installed needles using a syringe fitted with a luer-lock valve. Syringes were flushed twice with sample prior to injecting 5 mL of sample into 13-mL N₂-flushed vials. The pressure of the vials before and after sample addition was measured using a manometer (Keller AG, Winterthur, Switzerland) and the difference was used to calculate the dilution of the soil-gas sample. Profile samples taken immediately prior to each GPPT experiment were quantified for CH₄, O₂ and CO₂ concentrations and ratios of CH₄ to CO₂ were calculated for each sample. To characterize the gas produced by the waste before migration through the cover soil, a gas sample taken from a gas-collection pipe extending into the waste body was analyzed for concentration and stable carbon isotope composition of CH₄.

4.3.3 Gas Push-Pull Tests

Additional stainless steel rods (o.d., 8 mm; i.d., 5 mm) with a perforated tip were installed at the two sampling locations for GPPTs using the same installation procedure as for needle installation. The tips of the rods were positioned 30 cm below the cover soil
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surface. This injection / extraction depth was selected based upon the initial site survey, which indicated high CH\textsubscript{4} concentrations below this depth and sufficient O\textsubscript{2} for CH\textsubscript{4} oxidation to occur at this depth. Five GPPTs were performed at each location. Each GPPT was composed of an injection, transition, and extraction phase (Table 4-1). During injection a gas mixture (24.1 ± 0.6 L) consisting of ca. 8 % CH\textsubscript{4}, 17 % O\textsubscript{2}, and 25 % each helium (He), neon (Ne), and argon (Ar), was pumped through the rod and into the soil using a gas-flow controller with a mass-flow meter (Urmann et al., 2005). A short transition phase during which the direction of the pump was reversed was followed by extraction and sampling of a blend of the gas mixture and soil air in 20-mL vials containing the drying agent CaO and sealed with butyl rubber septa and metal crimp caps. Sample bottles were flushed with at least 500 mL of sample using an inflow and an outflow needle. The total volume extracted during the GPPT extraction phase was 49.9 ± 0.5 L. For the inactive GPPTs approximately 27 mL L\textsuperscript{-1} of C\textsubscript{2}H\textsubscript{2} was included in the injection gas mixture.

4.3.4 Estimation of kinetic parameters

Because microbial CH\textsubscript{4} oxidation is an enzymatic process, the rate at which CH\textsubscript{4} is consumed depends upon the enzyme concentration for CH\textsubscript{4} oxidation (i.e. the size and activity of the methanotrophic population) and the concentration of CH\textsubscript{4} available to be consumed. Assuming that the number of methanotrophs does not change during the short time of a GPPT, and that O\textsubscript{2} is not limiting, this type of kinetics, known as Michaelis-Menten kinetics, can be described using the equation (Michaelis & Menten, 1913, Segel, 1976):
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\[ \nu = \frac{[CH_4] \cdot \nu_{\text{max}}}{K_M + [CH_4]} \]  

(1)

where \([CH_4]\) is the CH\(_4\) gas concentration, \(\nu\) is the CH\(_4\) oxidation rate, \(\nu_{\text{max}}\) is the maximum CH\(_4\) oxidation rate, and \(K_M\) is the half saturation constant or the \([CH_4]\) at \(\frac{1}{2} \nu_{\text{max}}\). When \([CH_4]\) \(\gg\) \(K_M\) the enzymes used in CH\(_4\) oxidation are saturated with \(CH_4\), the equation reduces to \(\nu = \nu_{\text{max}}\) and CH\(_4\) oxidation is in the zero-order kinetics range.

When \([CH_4]\) \(<<\) \(K_M\), the equation reduces to \(\nu = \frac{\nu_{\text{max}}}{K_M} \cdot [CH_4]\), which may be expressed as \(\nu = k \cdot [CH_4]\), where \(k\) is the apparent first-order rate constant, and \(\nu\) is linearly dependent upon \([CH_4]\).

Apparent first-order rate constants \((k)\) for CH\(_4\) oxidation in the landfill-cover soil were calculated from GPPTs using a simplified method that accounts for reaction during the injection phase (Schroth & Istok, 2006). For each active GPPT the natural logarithm of the relative concentration of CH\(_4\) divided by the relative concentration of Ar (corrected for background Ar concentration) was plotted against residence time (Urmann et al., 2008) and the negative slope of the line was taken as \(k\). Argon was selected as the tracer for the rate calculations because of the three noble gases used, its diffusion coefficient in air is closest to that of CH\(_4\) (Ar = 1.81 \(\times\) 10\(^{-5}\), CH\(_4\) = 2.05 \(\times\) 10\(^{-5}\) m\(^2\) s\(^{-1}\) at 20 °C, from Fuller et al. (1966) and Ar was previous shown in abiotic studies to be the most similar tracer to CH\(_4\) during GPPTs (Gonzalez-Gil et al., 2007, Gomez et al., 2008). He and Ne are included in the injection gas mixture to serve as qualitative indicators of the relative importance of molecular diffusion during the GPPTs. Additionally, \(k\) was estimated for
GPPTs 1D and 2D using CH$_4$ from the consecutive inactive GPPT as the tracer gas instead of Ar (Urmann et al., 2007).

Methane oxidation rates ($\nu$) in the landfill-cover soil prior to GPPTs 1C, 1D, 2A and 2D were determined by multiplying the $k$ values calculated from the individual GPPTs by the mean CH$_4$ concentration of the 15 to 60 cm depth-profile samples prior to each GPPT. To confirm that GPPTs were performed in the CH$_4$ concentration range for first-order kinetics, Michaelis-Menten parameters $\nu_{max}$ and $K_M$ were calculated separately for the two locations. For each active GPPT that was not strongly influenced by the background CH$_4$ concentration (GPPTs 1C, 1D, 2A and 2D) the slope of the natural logarithm plot was calculated for every data point using the one previous and one subsequent data points. These $k$ values were multiplied by the average CH$_4$ concentration of the three data points to calculate a CH$_4$ oxidation rate. Michaelis-Menten parameters, $\nu_{max}$ and $K_M$, were estimated from the y-intercept and slope of Eadie-Hofstee plots of CH$_4$ oxidation rates and average concentrations (Bender & Conrad, 1993, Urmann et al., 2008).

Michaelis-Menten parameters for location 1 were also estimated using an inverse modeling technique as described by Gonzalez-Gil et al. (2008). Briefly, an effective diffusion coefficient ($D_e$) for CH$_4$ was obtained by fitting a numerical model to the CH$_4$ breakthrough curve of inactive GPPT 1E. To quantify the microbial CH$_4$ oxidation rate during the active GPPT 1D, $D_e$ of GPPT 1E was used and the Michaelis-Menten parameters were varied to best fit the numerical model to the GPPT 1D CH$_4$ data set.
4.3.5 Analytical methods

Gas-sample concentrations of CH$_4$ and C$_2$H$_2$ were measured by GC-FID (Urmann et al., 2005) and noble gas concentrations were quantified by GC-TCD (Gonzalez-Gil et al., 2007). Oxygen and CO$_2$ in profile samples were also quantified by GC-TCD (as described for CO$_2$ in Urmann et al. (2005)). Samples and external standards were injected at ambient temperature and pressure using a CTC PAL autosampler (Zwingen, Switzerland). The stable carbon isotope composition of CH$_4$ in injection gas and extraction samples from GPPT 1D and 1E and in profile samples taken immediately prior to GPPT 1D were determined by GC-IRMS as previously described. The isotope ratio of the samples was calculated in reference to Vienna Pee Dee Belemnite (VPDB). Isotope values are given as $\delta^{13}C$ (‰) according to,

$$\delta^{13}C = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000$$

where R is the ratio between $^{13}$C and $^{12}$C in samples and standard, respectively. The precision in the measurements was better than $\pm 0.4$ ‰.

4.3.6 DNA extraction and Real-time PCR

Immediately following each GPPT a hole was dug ca. 1 m away from the GPPT injection rod and a cover soil sample was collected from 30 cm depth. Samples were stored at -20 °C until further analysis. DNA was extracted with the PowerSoil DNA isolation kit (MO BIO, Carlsbad, CA) starting from triplicate 0.25 g samples. Real-time PCR was performed on an Applied Biosystems 7300 (Foster City, CA) with primers specific for the $pmoA$ gene (A189f / mb661) a functional gene that encodes a subunit of the particulate methane monooxygenase, a key enzyme in the methane oxidation pathway.
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(Kolb et al., 2003). These primers target most aerobic methanotrophs except sequences of *Methylomonas, Methylocaldum* and sequences isolated from a forest clone library (Kolb et al., 2003). In parallel, plasmid standards containing the target gene were generated from clones. Plasmids were isolated using GeneJET Plasmid Miniprep Kit (Fermentas, St. Leon-Rot, Germany), with DNA concentrations determined using Nanodrop 1000 (Thermo Scientific, Wilmington, DE, USA). Serial dilutions of the plasmid ranging from $50^1$ to $50^9$ in triplicate were used to determine the calibration curve which was plotted as Ct values as a function of log transformed copy numbers (slope = -3.8, $r^2 = 0.9998$, efficiency = 83%). For each real-time PCR, 5 µL of DNA sample or standard was added to 35 µL of master mix (20 µL of Absolute SYBR Green Rox Mix (Abgene, Epsom, UK), 14.65 µL DEPC treated water (Invitrogen, Basel, Switzerland) and 700 nM of each primer). The 4-step thermoprofile described by Kolb et al. (2003) for the specified primer pair was used with an additional initial enzyme-activation step of 15 min at 95 °C. Forty cycles were run and data was acquired for 45 s at 72 °C.

4.4 Results

4.4.1 Soil-gas profiles

Vertical profiles of CH$_4$ concentrations in the landfill-cover soil at the two locations were plotted for gas samples taken at 15, 40, 60 and 100 cm depth immediately prior to each GPPT (Figure 4-1a, b). Missing data points were excluded because gas sample extraction was not always possible due to temporary clogging of needles. Over the study period the range in CH$_4$ concentrations at the two individual locations was extremely broad (Figure 4-1a, b). At location 1 the CH$_4$ concentrations at 100 cm ranged
from 1.5 to 23 % (v/v), and at location 2 from 0.34 to 44 % (v/v). All concentration
profiles exhibited a decrease in CH₄ concentrations from 100 cm to 15 cm below the
surface, although the extent of the decrease varied. Profile samples taken prior to GPPTs
1C, 1D, 2A and 2D (Figure 4-1a,b) showed at least a 97 % decrease in CH₄
concentrations from 100 cm depth to 60 cm below the soil surface. Whereas, CH₄
concentration profiles for 1B, 2B, and 2C were almost unchanged from 100 cm up to 15
cm below the surface. The scenario for profile 1A was in between the other two
scenarios, from 100 cm to 60 cm depth the CH₄ concentration only decreased by one half,
but the CH₄ concentration at 15 cm was 99.6 % less than that at 100 cm. The sample
taken from the gas collection pipe contained approximately 56 % (v/v) CH₄ (not shown).

Oxygen concentrations of the profile samples decreased with increasing depth
below the surface but were consistently above 8 % (v/v), in contrast to CO₂
concentrations which increased with increasing depth (data not shown). Profiles of the
ratio of CH₄ to CO₂ were very similar to the CH₄ concentration profiles (Figure 4-1c, d).
Profiles 1C, 1D, 2A and 2D had a sharp decrease in CH₄:CO₂ from 100 to 60 cm, profiles
1B, 2B, and 2C were essentially unchanged over the entire profile, and profile 1A
decreased slightly from 100 to 60 cm but had a much greater decrease from 60 to 15 cm
below the surface.
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4.4.2 GPPTs

Relative concentrations ($C^*$) of CH$_4$ and noble gases in extraction phase samples were calculated by dividing the extracted by the injected concentration ($C_{ext}/C_{inj}$) and were plotted against extracted divided by injected volume ($V_{ext}/V_{inj}$) for each GPPT (Figure 4-2). The $C^*$ of CH$_4$ and the noble gases decreased rapidly during the GPPTs due to...

Figure 4-1. Soil gas CH$_4$ concentrations (a,b) and CH$_4$ to CO$_2$ ratios (c,d) in profile samples taken from locations 1 and 2 immediately prior to each GPPT. Symbols indicate which GPPT the CH$_4$ profile preceded. Note that profiles were obtained on different dates at the two locations (see GPPT dates, Table 4-1).
to mixing with cover soil air, however, the $C^\ast$ of CH$_4$ decreased more rapidly in active GPPTs due to both mixing and, presumably, microbial oxidation. For all active GPPTs (except GPPT 1B) the $C^\ast$ of CH$_4$ at the start of the extraction phase was lower than the $C^\ast$ of Ne and Ar and the same as or lower than that of He. When high background CH$_4$ concentrations (e.g. $\geq 0.1$ % v/v at 15 cm depth) were present during a GPPT, rapid influx of the background CH$_4$ into the soil volume being probed caused an increase in the $C^\ast$ of CH$_4$ compared to the noble gases during the extraction phase of the GPPT (Figure 4-2, GPPTs 1A and 1B, 2B, 2C and 2D). In the case of GPPT 1B, the $C^\ast$ of CH$_4$ was higher than Ar even at the start of the extraction phase. The higher the background concentration of CH$_4$ at 15 cm depth (Figure 4-1), the earlier in the extraction phase an increase in the $C^\ast$ of CH$_4$ was detected. Only GPPTs 1C, 1D and 2A, which were performed on a day when background CH$_4$ concentrations were the lowest ($\leq 0.001$ % v/v at 15 cm depth) did not exhibit an increase in the $C^\ast$ of CH$_4$ during the extraction phase.

In general the breakthrough curves of location 2 differed from those of location 1 in that the $C^\ast$ of the noble gases were higher at the start of the extraction phase and did not decrease as rapidly.

In contrast to the active GPPTs 1A to 1D, the breakthrough curves of CH$_4$ and Ar for inactive GPPT 1E were similar. Also, the individual noble gas breakthrough curves for GPPTs 1D and 1E were comparable. The results for the inactive GPPT at location 2 were quite different from location 1 (Figure 4-2, GPPT 2E). The breakthrough curves of CH$_4$ and Ar were dissimilar with the $C^\ast$ of CH$_4$ being much higher than that of Ar. In addition, the noble gas breakthrough curves had higher relative concentrations for GPPT 2D than for GPPT 2E.
Figure 4-2. Breakthrough curves for CH$_4$ and noble gases for extraction phase samples for GPPTs A to E at locations 1 and 2. GPPTs 1E and 2E were inactive GPPTs.
4.4.3 Estimation of kinetic parameters

To estimate apparent first-order rate constants \((k)\) for CH\(_4\) oxidation in the landfill-cover soil, a regression line was fit to the natural logarithm plot of \(C^+\) of CH\(_4\) / \(C^+\) of Ar for each active GPPT using only the early data points before curvature of the graph (Figure 4-3). With increasing residence time the trend of the natural logarithm plots was to level off, become less negative, or even become positive as background CH\(_4\) intruded into the area being probed. The number of data points used to estimate \(k\) ranged from 4 to 8, with more points in the linear range and higher \(r^2\) values when background CH\(_4\) concentrations at 15 cm depth were low (Table 4-2). For GPPTs performed when background CH\(_4\) concentrations were low (GPPTs 1C, 1D, 2A and 2D) the average \(k\) calculated using Ar as the tracer gas was 22.2 h\(^{-1}\) for location 1 and 17.3 h\(^{-1}\) for location 2.

![Figure 4-3. Plots for determination of first-order rate constants \((k)\) for CH\(_4\) oxidation during active GPPTs 1D and 2D. The \(k\) values for GPPTs 1D and 2D were calculated based on Ar as nonreactive tracer \((C^+ CH_4(a)/C^+ Ar(a))\) as well as on CH\(_4\) from the subsequent inactive GPPTs 1E and 2E \((C^+ CH_4(a)/C^+ CH_4(i))\). The \(k\) values were calculated as the negative slope of the linear regression (solid line) of the data points that showed a linear relationship prior to curvature. In addition, the plot for \(C^+ of CH_4(i)/C^+ of Ar(i)\) is included to confirm that in the absence of CH\(_4\) oxidation, the physical transport of Ar was comparable to CH\(_4\).](image-url)
When CH\textsubscript{4} from an inactive (i) GPPT was used as the tracer (instead of Ar) for the preceding active GPPT it resulted in similar natural logarithm plots (Figure 4-3, $C^\ast$ of CH\textsubscript{4} (a)/ $C^\ast$ of CH\textsubscript{4} (i)) and comparable estimates of $k$ (Table 4-2). The natural logarithms of $C^\ast$ of CH\textsubscript{4} (i) / $C^\ast$ of Ar (i) for the inactive GPPTs were also plotted to confirm that in the absence of CH\textsubscript{4} oxidation, the physical transport of Ar was comparable to CH\textsubscript{4}. GPPT 1E had a slightly negative slope giving a $k$ value of 0.83 ± 0.06, whereas for GPPT 2E the slope was slightly positive.

In situ CH\textsubscript{4} oxidation rates estimated from $k$ values and in situ CH\textsubscript{4} concentrations ranged from $1.01 \cdot 10^{-3}$ to 2.56 mmol CH\textsubscript{4} (L soil air)$^{-1}$ day$^{-1}$. Over the range of CH\textsubscript{4} concentrations attained during the GPPTs, calculated CH\textsubscript{4} oxidation rates appeared to be in the first-order range with only slight curvature at the highest concentrations (Figure 4-4). Michaelis-Menten parameters calculated from Eadie-Hofstee plots were similar for the two locations. The $v_{max}$ at locations 1 and 2 were 21.9 ± 3.6 and 29.0 ± 7.5 mmol CH\textsubscript{4} (L soil air)$^{-1}$ h$^{-1}$, respectively. The $K_M$ were 0.75 ± 0.16 and 0.90 ± 0.37 mmol CH\textsubscript{4} (L soil air)$^{-1}$.

Estimates of Michaelis-Menten parameters for location 1 using the modeling approach (Gonzalez-Gil et al., 2008) yielded a $v_{max}$ of 11.3 mmol CH\textsubscript{4} (L soil air)$^{-1}$ h$^{-1}$ and a $K_M$ of 0.83 mmol CH\textsubscript{4} (L soil air)$^{-1}$. The $v_{max}$ is approximately half of that calculated using the Eadie-Hofstee plot whereas the estimated $K_M$ values are similar.
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Figure 4-4. Methane oxidation rates estimated from GPPTs performed during low background CH$_4$ concentrations (symbols), and Michaelis-Menten curves from the estimated K$_m$ and v$_{max}$ values for locations 1 and 2.

Table 4-2. Apparent first-order rate constants ($k$) for CH$_4$ oxidation calculated for each active GPPT using Ar as the non-reactive tracer. Additionally, $k$ values for GPPTs 1D and 2D were calculated using CH$_4$ from the subsequent inactive GPPT (1E and 2E) as the tracer.

<table>
<thead>
<tr>
<th>GPPT</th>
<th>number of data points to calculate</th>
<th>$k$ (h$^{-1}$) ± $\sigma$</th>
<th>$r^2$-value</th>
<th>high background [CH$_4$] during GPPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>5</td>
<td>7.1 ± 0.5</td>
<td>0.986</td>
<td>+</td>
</tr>
<tr>
<td>1B</td>
<td>5</td>
<td>0.9 ± 0.6</td>
<td>0.422</td>
<td>+</td>
</tr>
<tr>
<td>1C</td>
<td>8</td>
<td>20.1 ± 0.7</td>
<td>0.994</td>
<td>–</td>
</tr>
<tr>
<td>1D</td>
<td>8</td>
<td>24.4 ± 0.7</td>
<td>0.995</td>
<td>–</td>
</tr>
<tr>
<td>1D using CH$_4$ from inactive 1E</td>
<td>8</td>
<td>24.8 ± 0.8</td>
<td>0.994</td>
<td>–</td>
</tr>
<tr>
<td>2A</td>
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<td>18.9 ± 0.6</td>
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</tr>
<tr>
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<tr>
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<td>+</td>
</tr>
<tr>
<td>2D</td>
<td>5</td>
<td>15.7 ± 0.1</td>
<td>0.999</td>
<td>–</td>
</tr>
<tr>
<td>2D using CH$_4$ from inactive 2E</td>
<td>6</td>
<td>16.4 ± 0.4</td>
<td>0.997</td>
<td>–</td>
</tr>
</tbody>
</table>

*One standard deviation.
4.4.4 Stable carbon isotope fractionation of CH$_4$

The $\delta^{13}$C of CH$_4$ in the injection gas mixture was -43.8 ‰ for GPPT 1D and -45.1 ‰ for GPPT 1E. Both GPPTs became enriched in $^{13}$CH$_4$ during the extraction phase; however, the enrichment in the active GPPT was much more rapid and greater than in the inactive GPPT (Figure 4-5). After reaching a maximum of -3.2 ‰, the $\delta^{13}$C of active GPPT CH$_4$ decreased to close to that of the inactive GPPT.

The $\delta^{13}$C of CH$_4$ of the gas sample from the gas collection pipe was -65.4 ‰. The CH$_4$ that moved up from the waste through the cover soil became gradually more enriched in $^{13}$C. At 100 cm below the surface the $\delta^{13}$C of CH$_4$ was -53.8 ‰, at 60 and 40 cm it increased to -48.1 and -49.2 ‰, and at 15 cm below the surface the $\delta^{13}$C of CH$_4$ was -36.4 ‰.

4.4.5 Real-time PCR

The results from the real-time PCR yielded an average of $1.1 \times 10^6 \pm 7.3 \times 10^5$ target methanotrophs per g dry soil for four soil samples taken from the vicinity of location 1 immediately following completion of the extraction phase of each GPPT. Location 2 had significantly more targeted methanotrophs ($p > 0.05$), with twenty times as many copies, $2.2 \times 10^7 \pm 1.6 \times 10^7$ targets per g dry soil detected from 3 soil samples with the fourth removed as an outlier. Because soil samples were taken at 30 cm depth from different holes that were freshly dug at the time of each GPPT, the high variability between samples, as indicated by large standard deviations, is likely due to the heterogeneity of the landfill-cover soil.
Figure 4-5. Stable carbon isotope fractionation of CH$_4$ during the extraction phase of active GPPT 1D and inactive GPPT 1E.

4.5 Discussion

4.5.1 Soil-gas profiles

During the four week field study the profiles of CH$_4$ concentration in the Lindenstock landfill-cover soil fluctuated widely over the sampling period and between the two sampling locations. The large temporal variations were probably due to changing meteorological conditions, such as atmospheric pressure changes or precipitation events. Atmospheric pressure fluctuations have been reported to influence both the total flux of landfill gas and the concentration of CH$_4$ in the gas (Young, 1992), whereas, precipitation affects gas transport by reducing available pore space and soil moisture content influences CH$_4$ oxidation rates (Czepiel et al., 1996). The differences between location 1 and 2 could be due to hotspots in the waste distribution, or differences in the composition of the highly heterogeneous cover soil. Because the profiles in this environment likely
reflect non steady-state diffusion, consumption, and advective gas transport of CH₄, we did not use the profile samples to quantitatively calculate CH₄ oxidation rates from the cover soil. The gas profiles were, however, used as a qualitative indication of whether CH₄ oxidation was occurring in the soil, and to define the depth where the highest methanotrophic activity was expected.

On sampling days when the CH₄ concentration at 100 cm depth was low, i.e. 0.3 to 3 %, much of the CH₄ in the gas produced by the landfill waste was probably consumed even below 100 cm depth in the cover-soil. The steep gradients from 100 cm to 60 cm depth indicate that this zone was also very active in CH₄ oxidation. Similar gradients from 100 cm to 50 cm depth were seen in a landfill-cover soil by Bogner et al. (1995). The abundance of O₂ in the profile samples confirms the potential for CH₄ oxidation to occur over the entire profile.

A zone of high methanotrophic activity could not be defined for the profiles that show high CH₄ concentrations even to 15 cm below the surface (Figure 4-1a, b). Apparently, CH₄ oxidation was not sufficient at those times to result in a noticeable decrease in the CH₄ concentration of the profiles.

During migration of landfill-produced gas up through the landfill-cover soil, one would expect to see a gradual decrease in the CO₂ and CH₄ concentrations close to the landfill surface due to dilution with atmospheric air which contains only ca. 385 ppmv CO₂ and 1.8 ppmv CH₄. The decrease in CO₂ concentration close to the landfill surface might be somewhat offset by soil and plant respiration of CO₂. Nevertheless, a decrease in the ratio of CH₄ to CO₂ would be indicative of methanotrophic consumption of CH₄.
The gradients of the ratio of CH\textsubscript{4} to CO\textsubscript{2} support the interpretation of the CH\textsubscript{4} profiles. That is, profiles collected prior to GPPTs 1B, 2B, and 2C showed little evidence for the occurrence of CH\textsubscript{4} oxidation, those collected prior to GPPTs 1C, 1D, 2A and 2D showed high activity between 100 and 60 cm depth, whereas prior to GPPT 1A the greatest activity was between 60 cm and 15 cm depth. The CH\textsubscript{4}:CO\textsubscript{2} for GPPTs 1A, 1C, 1D, 2A, and 2D, therefore, indicate that the decrease in the CH\textsubscript{4} concentration of the profile samples closer to the surface of the landfill was not due to dilution with air, but rather CH\textsubscript{4} oxidation.

4.5.2 Quantification of CH\textsubscript{4} oxidation rates by GPPTs

The highest $k$ values for CH\textsubscript{4} oxidation in the Lindenstock landfill-cover soil correspond to a half-life for CH\textsubscript{4} as short as 2 minutes; these values are many times higher than those derived from GPPTs in other environments. Our highest estimated $k$ values were more than ten times higher than values from GPPTs above a methanogenic aquifer (Urmann et al., 2005) and almost thirty times higher than in a peat bog (Urmann et al., 2007). These differences in $k$ for CH\textsubscript{4} oxidation can be attributed to the dissimilar physical characteristics of the three environments and to the widely different in situ CH\textsubscript{4} concentrations which may influence the population size and structure of the methanotrophic communities. Our highest $k$ values were also much higher than those reported for laboratory incubation studies to quantify CH\textsubscript{4} oxidation in landfill-cover soils. Whalen et al. (1990) reported a maximum $k$ of 2.37 h\textsuperscript{-1} for soil cores taken from an old landfill and incubated in up to 7.7 % CH\textsubscript{4}. They were also higher than those of Kightley et al. (1995) who reported ca. 10 h\textsuperscript{-1} for incubations exposed to a maximum of 5 % CH\textsubscript{4}, and those of Bogner et al (1997b) at ca. 5 h\textsuperscript{-1} for incubations in up to 8.4 % CH\textsubscript{4}.
The highest estimated in situ CH$_4$ oxidation rate that we calculated falls at the lower end of the range of in situ rates in landfill-cover soils reported by Streese-Kleeberg (2008). This author applied a correction procedure (Yang et al., 2007) to account for CH$_4$ background concentrations during experiments, however, actual background CH$_4$ concentrations were not reported. In our experiments we experienced fluctuating background CH$_4$ concentrations which prevented application of this correction procedure. This could be an effect of the specific environment or a result of the larger extraction volume in our experiments. For GPPTs 1C, 1D and 2A, the CH$_4$ concentrations towards the end of the extraction phase ($V_{ex} / V_{inj}$ value of 2) were so low relative to the injection gas mixture that subtraction from the extraction phase samples was irrelevant. Whereas, for GPPTs performed when background CH$_4$ concentrations were high, the CH$_4$ concentration values towards the end of the extraction phase fluctuated and did not come to a constant value that could be subtracted for example using the approach of Yang et al. (2007) (Figure 4-2, 1A, 2B, 2C and 2D). During some GPPTs the CH$_4$ concentrations of the final extraction phase samples were even higher than that of the injected gas mixture.

When background CH$_4$ concentrations were low, $k$ values could be calculated from rate plots using 5 to 8 early extraction phase data points that were minimally influenced by influx of background CH$_4$. When background CH$_4$ concentrations were high, some of the decrease in CH$_4$ concentrations due to CH$_4$ oxidation was offset by an increase in the CH$_4$ concentration due to intrusion of background CH$_4$ into the probed soil volume. This reduced the slope of the regression line, thereby giving lower calculated $k$ values for GPPTs performed when background CH$_4$ concentrations were high.
The wide range in the calculated in situ CH$_4$ oxidation rates was a consequence of the vastly different CH$_4$ concentration profiles over the period of the field campaign. Average concentrations for the 15 to 60 cm depth interval at location 2 prior to GPPT 2D were more than 10$^4$ times higher than they were prior to GPPT 2A. The maximum calculated in situ CH$_4$ oxidation rates were less than one tenth of the estimated $v_{\max}$ for both locations implying that the methanotrophic population could respond rapidly to fluctuating CH$_4$ concentrations in the landfill-cover soil.

The $v_{\max}$ estimated using the modeling approach was reasonably close to the value estimated from the Eadie-Hofstee plots, whereas the $K_m$ values agreed. Better agreement between the estimates of $v_{\max}$ could be expected if additional GPPTs were performed with higher CH$_4$ concentrations in the injection gas mixture. Attempts to use the stable carbon isotope data to further constrain the Michaelis-Menten parameters (as described in (Gonzalez-Gil et al., 2008)) were unsuccessful because the influence of the isotopic signature of the background CH$_4$ could not be incorporated in the modeling approach. Therefore, the stable carbon isotope data in this study only provided qualitative confirmation of methanotrophic activity during GPPTs.

4.5.3 Methanotrophic population size

Multiple lines of evidence are usually required to confirm microbial processes at the field scale (Borden et al., 2003). Apart from geochemical data (here GPPT and vertical gas profile data), the presence of a microbial community capable of catalyzing the process in question (here CH$_4$ oxidation) should be verified. This was accomplished in our study using real-time PCR, which clearly indicated the presence of a large methanotrophic community in the landfill-cover soil. However, there is a lack of
published studies in which real-time PCR was used to quantify methanotrophic population size in a landfill-cover soil; therefore calculated values can only be compared to other environments for which the same primers were used. Kolb et al. (2003) used the same targets in soils from a flooded rice field and found $9 \times 10^5 \pm 3 \times 10^3$ targets per g soil which is very close to the $1.1 \times 10^6 \pm 7.3 \times 10^5$ targets per g soil that we calculated for location 1.

### 4.6 Conclusion

We have presented the first results for GPPTs as a useful tool to reproducibly estimate in situ CH$_4$ oxidation kinetics in a landfill-cover soil when background CH$_4$ concentrations are low. This tool could be used on other landfills with different cover soil properties or waste composition, different background CH$_4$ concentrations, or located in a different climatic zone. Estimating rate constants for this environment presents a challenge because landfill-cover soils can be highly heterogeneous environments under non-steady state conditions. The GPPT therefore presents a promising alternative method, because it doesn’t require definition of laboratory determined values such as CH$_4$ turnover rates or isotopic fractionation factors. Future work in this field will include methods to reduce the influence of high background CH$_4$ concentrations on rate calculations, possibly through use of a temporary enclosure and initial flushing of the soil volume to be probed with an inert gas (Schroth et al., 2007).

### 4.7 Acknowledgements

We thank R. Siegwolf and M. Saurer (PSI, Villigen) for assistance with stable carbon isotope measurements, Juliana Wischnewski for help in the field, R. Sauter
(Forestry Department, Liestal) and Peter Oester (Oester Messtechnik, Thun). The financial support for this research was provided by grant no. 200021-103619 from the Swiss National Science Foundation. Helpful suggestions by anonymous reviewers were highly appreciated.

4.8 References


Chapter 4: Quantifying Methane Oxidation in a Landfill-Cover Soil by Gas Push-Pull Tests


Comparison of Methods to Assess the Fate of Methane in a Landfill-Cover Soil

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Submitted to Environmental Science & Technology February 26, 2010
Chapter 5: Comparison of Methods to Assess the Fate of Methane in a Landfill-Cover Soil

5.1 Abstract

Landfills are major anthropogenic sources of the greenhouse gas methane (CH$_4$). However, much of the CH$_4$ produced during the anaerobic degradation of landfill organic waste is consumed by methanotrophic microorganisms during passage through the cover soil. Experiments were performed to compare several state-of-the-art methods to quantify CH$_4$ dynamics within and above the cover soil of a closed landfill near Liestal (BL), Switzerland, on five days over a two week period in July 2008. Fluxes of CH$_4$ into- or out of- the landfill-cover soil were quantified by eddy-covariance flux and static flux-chamber measurements. In addition, CH$_4$ concentrations at the soil surface were monitored using a field-portable FID detector. Fluxes of CH$_4$ within the cover soil were estimated from soil-gas concentration profiles in conjunction with radon measurements, and gas push-pull tests (GPPTs) were performed to quantify rates of microbial CH$_4$ oxidation. While GPPTs indicated that the rate of CH$_4$ oxidation within the cover soil was stable throughout the study period (first order rate constant $k = 13.0 \pm 2.3$ h$^{-1}$), estimates of CH$_4$ fluxes into- or out of- the cover soil showed high variability. Flux chamber measurements indicated that the cover soil probed was usually a net sink for atmospheric CH$_4$ with a maximum rate of 380 µmol m$^{-2}$ d$^{-1}$, whereas eddy covariance flux measurements showed that the footprint area was a net CH$_4$ source on four of the five sampling dates. Each technique provided unique information about above- or below-the-surface CH$_4$ dynamics that when combined give a better understanding of the fate of CH$_4$ in a heterogeneous landfill-cover soil.

5.2 Introduction

At a global average near 1.8 µL L$^{-1}$, the atmospheric concentration of the greenhouse gas methane (CH$_4$) is more than double pre-industrial values. The current CH$_4$ levels are higher than historical values due to emissions from anthropogenic activities including fossil fuel use, modern agricultural practices and livestock farming, as well as disposal of solid waste in
landfills (Denman et al., 2007). In contrast to earlier open dumps, modern well-managed landfills are installed with a cover soil that prevents waste dispersal, reduces water infiltration to minimize the volume of landfill leachate, and promotes anaerobic decomposition of the organic matter. The gas produced during the methanogenic stage of waste decomposition mainly consists, in v/v, of 50-70 % CH\textsubscript{4}, 30-50 % carbon dioxide (CO\textsubscript{2}) and trace amounts of nitrogen, hydrogen sulfide and non-methane hydrocarbons (Farquhar & Rovers, 1973). The production of gas creates pressure and concentration gradients between the anaerobic zone and the atmosphere leading to advective and diffusive transport of the gas from the waste and emission to the atmosphere. However, not all of the CH\textsubscript{4} produced in the waste is emitted to the atmosphere. Indigenous aerobic methanotrophic microorganisms have been reported to oxidize from negligible to 100 % of the CH\textsubscript{4} produced in landfills to CO\textsubscript{2} as it passes through the cover soil (Borjesson et al., 2007, Boeckx et al., 1996).

The IPCC estimate (Denman et al., 2007) of the contribution of landfills to anthropogenic atmospheric CH\textsubscript{4} emissions is based upon approximation of the amount and composition of the deposited waste and the premise that landfill waste degradation follows a typical first-order decay life cycle (IPCC, 2006). The guidelines for reporting CH\textsubscript{4} emissions recommend that well-managed landfills assume a 10 % reduction in emissions due to CH\textsubscript{4} oxidation in the cover soil. Calculated in such a way, the amount of CH\textsubscript{4} emitted from landfills is estimated to account for 5 to 10 % of global CH\textsubscript{4} emissions (Denman et al., 2007). Microbially-mediated CH\textsubscript{4} production and oxidation are sensitive to many factors, including temperature, soil moisture content, nutrient availability and pH. Therefore, CH\textsubscript{4} oxidation rates and actual CH\textsubscript{4} fluxes from individual landfills may be quite different from the values estimated using the IPCC guidelines, depending on soil texture and local climatic conditions (Chanton et al., 2009).

The composition and distribution of both landfill waste and cover soil is typically heterogeneous, resulting in high spatial variability of CH\textsubscript{4} fluxes across the cover soil surface.
At some locations CH\(_4\) produced from the waste may by-pass the bulk of the landfill-cover soil and be directly emitted to the atmosphere through cracks, holes or vents. In addition to high spatial variability of CH\(_4\) fluxes, landfills may also exhibit high temporal variability in CH\(_4\) fluxes (Laurila et al., 2005) possibly due to variations in gas-transport behaviour in the cover soil resulting from changes in atmospheric pressure or degree of water saturation following precipitation. Changes in the rate of CH\(_4\) oxidation by soil methanotrophs in response to water saturation or soil temperature may also influence CH\(_4\) fluxes.

A number of field methods have been developed to quantify CH\(_4\) fluxes from landfill-cover soils to the atmosphere, the most commonly used of which are enclosure or chamber methods. Chambers can be used to quantify fluxes of CH\(_4\) from cover soils to the atmosphere when emissions occur, or to quantify CH\(_4\) oxidation rates when the cover soil is a sink for atmospheric CH\(_4\). Static flux chambers have the advantage of being relatively inexpensive, simple to set up and operate, and highly sensitive at detecting even very small fluxes. Chambers can only be deployed for short periods to minimize disturbances of the measured surface; therefore, no flux measurements are available for periods between chamber deployments. In addition, the inherent heterogeneity of landfill waste and cover soils, and the resulting spatial variability of CH\(_4\) fluxes, makes variation between chamber measurements large, requiring many measuring points to permit scaling up of chamber measurements to a larger area. As chambers capture fluxes across the area of soil surface on the spot where they are installed, emissions may be either under- or over-estimated depending on the specific chamber location. Methane from the waste may by-pass the landfill-cover soil through cracks or preferential gas flow paths and be emitted directly to the atmosphere (Borjesson et al., 2000). Such cracks or locations of preferential gas flow on the landfill-cover soil (hot spots) can be identified using a field-portable flame-ionization detector to quantify CH\(_4\) in the uppermost soil layer at the landfill surface. When geographic coordinate readings (e.g. using the Global Positioning System
- GPS) are additionally collected, the spatial distribution of hot spots and areas of low CH$_4$ emissions can be visualized.

To quantify emissions of CH$_4$ flux from both hot spots and areas of low emissions, a spatially integrating technique such as a tracer method (Borjesson et al., 2007, Czepiel et al., 1996) or a micrometeorological approach can be employed. The eddy covariance method, the preferred micrometeorological technique, measures the turbulent vertical flux at a point above the soil surface several times per second (e.g. Baldocchi, 2003). This flux is representative for the “flux footprint”, that is the surface area upwind from the eddy covariance flux sensors used to measure this flux (for a review on methods to estimate flux footprint areas see Schmid, 2002). This footprint is typically modeled as a function of the smoothness of the terrain and stability of the atmosphere (for example, expressed by turbulent friction velocity $u^*$ and the turbulent variation of vertical wind speed $\sigma_w$ in the model by Kljun et al. (2004)), the height of the sensors above ground surface and the depth of the atmospheric boundary layer.

To gain a more thorough understanding of landfill CH$_4$ dynamics, CH$_4$ fluxes and methanotrophic activity within the cover soil should also be examined. By measuring the CH$_4$, CO$_2$ and oxygen (O$_2$) concentrations of gas samples collected along a vertical profile in the cover soil, the depth of the zone where CH$_4$ oxidation is occurring (where both CH$_4$ and O$_2$ are present) can be estimated. The vertical gradients of CH$_4$ are also helpful in defining whether a cover soil is a sink for both landfill-produced and atmospheric CH$_4$. Methane fluxes in the cover soil can be estimated from CH$_4$ vertical profiles when combined with estimated effective gas transport properties of CH$_4$ in the soil.

Additional information concerning the kinetics of CH$_4$ oxidation in landfill-cover soils can be gained from Gas Push-Pull Tests (GPPT) (Urmann et al., 2005). During a GPPT, a gas mixture containing CH$_4$ and O$_2$ and inert tracer gases is injected into the cover soil, followed by extraction from the same location of the injection gas diluted with soil air. Extraction-phase breakthrough curves of CH$_4$ and a suitable inert tracer gas can be analysed to calculate rate
constants for \( \text{CH}_4 \) oxidation. While GPPTs have been shown to be valuable tools for determining rate constant of \( \text{CH}_4 \) oxidation in a landfill-cover soil and other environments, high background \( \text{CH}_4 \) concentrations in landfill-cover soils may adversely influence rate constant estimates (Gómez et al., 2009).

In the summer of 2008 we implemented a field campaign to assess the fate of \( \text{CH}_4 \) in the cover soil of a closed municipal-waste landfill in Switzerland. As it is generally recommended that more than one measurement technique be used to ensure robust results, we aimed to evaluate whether unique and complimentary results could be determined from eddy covariance measurements, flux chamber measurements, surface \( \text{CH}_4 \) concentration monitoring, vertical soil profiles and GPPTs. On five days within a two-week period in July, measurements were taken and experiments performed to evaluate the general agreement between these methods and assess some of their limitations when used in a heterogeneous environment.

5.3 Materials and Methods

5.3.1 Experimental Site

The Lindenstock Landfill located near Liestal in the northwest of Switzerland is a 12 ha municipal-waste landfill that received \( \sim 3.2 \times 10^6 \) m\(^3\) of household, construction and commercial waste from 1949 until 1994. Following closure, the waste was capped with a 2 to 2.5 m thick cover soil, consisting primarily of silty loam with intermittent clay lenses, gravel and boulders (estimated total porosity 0.49). During waste deposition and cover soil construction, gas pipes were installed that extend vertically from the waste body up through the cover soil and are covered with a concrete dome on the landfill surface (hereafter referred to as “gas domes”). Additional porous gas seepage pipes were laid horizontally between the waste and the cover soil with closed outlets at the surface (hereafter referred to as “gas collection pipes”). The gas extraction system has been inactive for several years and all pipes were closed throughout the duration of the study.
Barometric pressure and precipitation for the experimental period were taken from the nearest weather stations in the network of MeteoSwiss (www.meteoswiss.ch) (Figure 5-1). Ten minute interval barometric pressure measurements adjusted to mean sea level were taken at the Rünenberg automatic monitoring weather station (610 m above sea level) located 12 km south-east of the Lindenstock landfill. Daily precipitation data were available from the precipitation monitoring network station in the town of Arisdorf located 2 km away from the landfill (430 m above sea level). On days when experiments were performed the volumetric water content of the cover soil was measured in triplicate from 30-cm and 60-cm long time-domain reflectometry (TDR) probes installed vertically in the vicinity of the GPPT location. The volumetric water content for the soil from 30 to 60 cm depth was calculated from the 0 to 30 and 0 to 60 cm measurements (Table 5-1).
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Table 5-1. Methane fluxes at the soil surface (shaded cells indicate emissions) calculated from CH$_4$ concentrations of soil-gas profile samples and effective diffusion coefficients estimated using radon measurements.

<table>
<thead>
<tr>
<th>Date</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 4</td>
<td>16</td>
<td>-6.1</td>
<td>1.9</td>
<td>0.54</td>
<td>-9.5</td>
<td>-9.9</td>
<td>-0.16</td>
</tr>
<tr>
<td>July 8</td>
<td>-</td>
<td>-17</td>
<td>-6.2</td>
<td>-0.81</td>
<td>-6.0</td>
<td>-22</td>
<td>0.92</td>
</tr>
<tr>
<td>July 10</td>
<td>-</td>
<td>-2.7</td>
<td>21</td>
<td>11</td>
<td>-3.7</td>
<td>-3.1</td>
<td>-1.3</td>
</tr>
<tr>
<td>July 15</td>
<td>-</td>
<td>-39</td>
<td>-7.9</td>
<td>2.5·10$^6$</td>
<td>-</td>
<td>-7.8</td>
<td>1.4·10$^4$</td>
</tr>
<tr>
<td>July 17</td>
<td>-18</td>
<td>-4.6</td>
<td>-4.0</td>
<td>2.1·10$^6$</td>
<td>-22</td>
<td>-9.2</td>
<td>-0.60</td>
</tr>
</tbody>
</table>

$^a$ Fluxes calculated from samples taken at 15 and 60 cm depth except for sampling location D on July 15 and 17. These two profiles were clearly not at steady state, therefore to best approximate CH$_4$ fluxes across the cover soil surface fluxes were calculated using the 15 cm depth sample concentration and assuming an atmospheric CH$_4$ concentration of 1.8 µL L$^{-1}$.

- no samples were taken due to blockage of sampling needles or water in the needles.

Measurements were taken and experiments performed on five days over a two week period in July 2008. Experiments were performed on the relatively flat area at ~570 m above sea level on the summit of the landfill (Figure 5-2). This area was vegetated with grass and shrubs with the exception of a few patches where mulch prevented plant growth.

5.3.2 Surface Methane Concentrations

On each of the five sampling dates the CH$_4$ concentration at the soil-gas / atmosphere interface of the landfill was surveyed using a field-portable flame ionization detector with a bell probe (Sewerin, Gütersloh, Germany). The gas sampler pump rate was 1L min$^{-1}$ and the detection limit of the instrument was 1µL CH$_4$ L$^{-1}$. The geographic locations where CH$_4$ measurements were made were determined by a differential two-receiver global positioning system using the United States (NAVSTAR GPS) and Russian (GLONASS GPS) satellite navigation systems. Geographic co-ordinates of the eddy covariance tower, flux chambers,
vertical profile samplers, GPPT location, gas domes and gas collection pipes were positioned accurate to a scale of ± 1 cm using a base station at a known fixed location (Figure 5-2).

**Figure 5-2.** Contour plot of the relatively flat area of the Lindenstock landfill-cover soil showing locations of sampling equipment and permanent installations. Also shown is the approximate Eddy covariance footprint. Footprint isolines and numbers (in bold) denote equal percentage of flux footprint weight with respect to the point of maximum contribution. EC tower = eddy covariance tower.

### 5.3.3 Flux Chamber Measurements

A total of 16 static chambers (31 cm diameter x 17 cm height above soil surface) were installed permanently on the landfill (Figure 5-2). The chambers consisted of a base collar (inserted 5 to 10 cm into the ground) that was fitted with a detachable lid for 30-minute incubation periods, during which time three gas samples were taken with a syringe. Gas samples were injected into pre-evacuated sample vials which were quantified for CH₄ concentration by gas chromatography and calibrated against a set of external standards. Methane fluxes were calculated by linear regression of concentrations against sampling time; the correlation coefficient of the linear regressions was generally > 0.95 except for fluxes close to zero. On
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each of the five sampling dates, all chambers were measured over two 30-minute incubation periods.

5.3.4 Eddy Covariance Measurements

The mobile eddy covariance system used here was described in full detail by Eugster and Plüss (Eugster & Plüss, 2010). In short, the system consisted of a closed-path fast methane analyser (DLT-100, Los Gatos Research Inc., Mountain View, CA, U.S.A.) using off-axis integrated cavity output spectroscopy (ICOS). The inlet of the 6.7 m intake hose (10 mm inner diameter) was attached below the sensor head of a three-dimensional ultrasonic anemometer-thermometer (Gill R2A, Solent, U.K.) with a measurement height of 1.60 m above the soil surface (1.30 m above the aerodynamic displacement height). A strong vacuum pump (BOC Edwards XDS-35i) was used to maintain the high flow rate required for 20 Hz sampling for eddy covariance fluxes (flow rate of 140 L min$^{-1}$ at ca. 190 hPa cell pressure in the 0.408 L optical cell). Data acquisition was fully digital via two serial data communication lines (RS-232) attached to an embedded computer system with in-house data acquisition software running under the Linux operating system. All raw data were collected and saved at full resolution and were processed off-line with the eth-flux software (see Mauder et al., 2008) following the concept used in an earlier application for N$_2$O flux measurements with a different gas analyzer (Eugster et al., 2007). In short, the following steps were involved in data processing: (1) wind vectors were rotated to align the co-ordinates with the mean streamlines for each averaging interval (see below); (2) a second rotation was applied to achieve zero mean vertical wind speed; (3) the time lag between the wind speed measurements and the CH$_4$ data was determined from the cross-correlation between vertical wind speed and CH$_4$ time series using a narrow search window centered at the lag estimated from flow rate and volume of intake hose, filter, and optical cell; (4) the two time series were shifted according to this time lag and covariances were then computed; (5) finally, the CH$_4$ flux was determined from the covariance by converting
measured units of ppm m s$^{-1}$ to µg CH$_4$ m$^{-2}$ s$^{-1}$ using ambient pressure and air temperature readings performed at the same location. This procedure was used to compute CH$_4$ fluxes that integrate over 5, 10, 30, and 60 minutes. The system was powered with a 9 kW gasoline power generator and was only operational during the daytime when other field work was carried out.

### 5.3.5 Soil-Gas Profiles and Radon Measurements

On each sampling day, soil-gas samples were collected from previously installed 1.5 mm i.d. stainless-steel needles positioned at approximately 15, 40, 60, and 100 cm depth at eight locations in the cover soil (Figure 5-2). Syringes fitted with a luer lock valve were flushed twice with sample prior to injecting 5 mL of sample into 13-mL N$_2$-flushed vials. A manometer (Keller AG, Winterthur, Switzerland) was used to measure the pressure of the vials before and after sample addition and the change in the pressure was used to calculate the dilution of the soil-gas sample. Profile samples taken immediately prior to each GPPT experiment were quantified for CH$_4$ by GC-FID and O$_2$ and CO$_2$ by GC-TCD (Urmann et al., 2005).

To quantify CH$_4$ fluxes from the soil-concentration data, the effective diffusion coefficient of CH$_4$ was estimated from Rn concentration profiles and surface-flux measurements (Dorr et al., 1983). All $^{222}$Rn measurements were performed by alpha spectroscopy employing a Durridge Rad7 Radon detector (Durridge Co., Inc., Bedford, MA, USA). Using the instrument’s “sniff” mode, $^{222}$Rn concentrations (in units of Bq m$^{-3}$) were quantified based on detection of alpha particles emitted from decaying $^{218}$Po atoms, a progeny of $^{222}$Rn. Before each measurement, the instrument’s 700-mL detection cell was purged with 5 L of air, and the instrument was left to equilibrate in this state for at least 15 min. For each profile measurement, 5 L of soil gas drawn from a sampling needle was pumped through the instrument at a flow rate of 1 L min$^{-1}$ to load the detection cell with the sample. Following a 5-min equilibration period, $^{222}$Rn concentration in the gas sample was determined as the average concentration obtained from four consecutive 5-min-long measurement intervals. The detection limit of the instrument
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is 10 Bq m\(^{-3}\). A total of six vertical \(^{222}\text{Rn}\) soil-gas concentration profiles were measured during the two-week campaign (two profiles each at locations B, C, and G (Figure 5-2)). Using a similar procedure, \(^{222}\text{Rn}\) surface-flux measurements were conducted, two each in flux chambers 2, 12, and 14, located adjacent to depth profiles B, C, and G. For \(^{222}\text{Rn}\) surface-flux measurements, flux chambers were closed for time intervals ranging from 0 to 160 min.

5.3.6 Gas Push-Pull Tests

Five GPPTs were performed as described earlier (Gómez et al., 2009) at the designated location (Figure 5-2) at 30 cm depth in the soil using a previously installed injection/extraction rod (Gómez et al., 2009). On each occasion, approximately 24.8 ± 0.4 L of a gas mixture containing ca. 8 % CH\(_4\), 17 % O\(_2\), and 25 % of each the inert tracer gases: helium (He), neon (Ne) and argon (Ar), was pumped into the cover soil using a gas-flow controller and a mass-flow meter (Urmann et al., 2005). The average injection flow rate was 770 mL min\(^{-1}\). Following a transition time of ca. 0.5 min during which the direction of the pump was reversed, gas was extracted from the same location (10.3 ± 0.05 L) at an average flow rate of 500 mL min\(^{-1}\). Samples were collected in 20-mL vials containing the drying agent CaO and sealed with butyl rubber septa and metal crimp caps. Sample bottles were flushed with at least 500 mL of sample using an inflow and an outflow needle. Sample methane concentrations were measured by GC-FID and noble gases were quantified by GC-TCD (Gómez et al., 2009).

5.4 Results

5.4.1 Surface CH\(_4\) Concentrations

Throughout the study period and over much of the surface area of the cover soil the concentration of CH\(_4\) at the soil surface was below the detection limit of 1 μL L\(^{-1}\), which is below the average atmospheric CH\(_4\) concentration of approximately 1.8 μL L\(^{-1}\), and therefore indicative that the cover soil was functioning as a sink for atmospheric CH\(_4\) (Figure 5-3). Areas
where the CH\(_4\) concentration was substantially higher than the atmospheric concentration were also common with most of the hot spots having CH\(_4\) concentrations greater than 15000 µL L\(^{-1}\) located around gas collection pipes and gas domes, especially those located close to the coordinates 623500/260500 and 623525/260515 (easting/northing on Swiss map grid). With increasing distance from the gas pipes or domes the CH\(_4\) concentration decreased although the surface area of the cover soil that was influenced by the hot spots was different on each sampling day. Surface CH\(_4\) concentrations were especially high on all days close to 623495/260495 where the closed outlets of several gas collection pipes are located. The size and direction of the CH\(_4\) plume around these pipes varied over the study period.

### 5.4.2 Flux Chamber Measurements

On the five sampling days the majority of the chambers indicated that the soil was a net sink for atmospheric CH\(_4\) with near surface methanotrophs oxidizing CH\(_4\) from the chambers at rates as high as 380 µmoles CH\(_4\) m\(^{-2}\) d\(^{-1}\) (Figure 5-3). On July 4, 8 and 10 few or none of the chambers detected small positive fluxes (emissions) of CH\(_4\) from the cover soil. In contrast, on both July 15 and 17 large positive CH\(_4\) fluxes were measured from the cover soil into chambers 2 and 7. Most of the chambers were relatively consistent in both the direction of the CH\(_4\) flux and the magnitude of the rate of the CH\(_4\) flux over the five day experimental period, with the exception of the few chambers that measured small emissions only on July 4 or 10 and the chambers 2 and 7 which changed from uptake to emitting CH\(_4\) on July 15 and 17. Based upon the chamber measurements, the area of the landfill-cover soil tested was estimated to be a net sink for atmospheric CH\(_4\) (Figure 5-4A), oxidizing CH\(_4\) at a median rate of -46 µmol m\(^{-2}\) d\(^{-1}\) (Note that the extreme values measured on July 15 and 17 were omitted from Figure 5-4A to better visualize the general trend over the entire experimental period).
Figure 5-3. CH₄ concentration measured at the surface of the landfill-cover soil (left) and CH₄ fluxes calculated from flux chambers on the corresponding experimental date (right).
5.4.3 Eddy Covariance Flux Measurements

In contrast to the estimates of CH$_4$ flux from chamber measurements, estimates from eddy covariance measurements show that on four of the five sampling days the probed surface area (the flux footprint area) was a net source of CH$_4$ to the atmosphere (Figure 5-4B). Only on July 10 was the cover soil a comparatively small net sink for atmospheric CH$_4$ (Figure 5-4B) with an interquartile range of fluxes from -590 to -7600 µmol CH$_4$ m$^{-2}$ d$^{-1}$ (median of -3300 µmol CH$_4$ m$^{-2}$ d$^{-1}$).

On all measurement dates except July 10 and 15, there were quite a few excursions towards higher CH$_4$ concentrations (Figure 5-5). Due to the skewed distribution of values, calculation of parameters based on a normal distribution, such as mean fluxes and standard deviations, are not very useful.

Figure 5-4. Estimated CH$_4$ fluxes from (A) chamber and (B) eddy covariance measurements for each experimental date. Boxes represent 25, 50 (median), and 75 percentile; whiskers represent maximum and minimum values. Extremely high positive chamber CH$_4$ flux values from flux chambers 2 and 7 on July 15th and 17th were excluded from (A). Eddy covariance flux measurements based on 30-minute intervals are taken from Eugster and Plüss (Eugster & Plüss, 2010). Note the different scales of the vertical axes in the two panels.
5.4.4 Soil-Gas Profiles

The soil-gas concentration profiles varied both by location in the cover soil and from one sampling day to the next. Representative CH$_4$ concentration profiles are shown for the five experimental dates for location G (Figure 5-6A), the closest profile sampling point to the location where GPPTs were performed. At location G the trend for the concentration of CH$_4$ in the gas samples to decrease from high concentrations at 100 cm depth to close to atmospheric concentrations at 60 cm depth was observed on all sampling days. However, the CH$_4$ concentration at 100 cm depth varied widely from day to day, ranging from 6 μL L$^{-1}$ to 46000 μL L$^{-1}$. While not visible due to the scale of the figure, CH$_4$ concentration gradients from 60 to 15 cm depth show that on three of the five study dates the upper 60 cm of the cover soil was also a sink for atmospheric CH$_4$. 
Figure 5-6. CH$_4$ concentrations in soil-gas profile samples taken from location G on each of the sampling dates (A) and the CH$_4$ to CO$_2$ ratios for each of the samples. CO$_2$ concentrations for July 15$^{th}$ were not measured. Note the discontinuous x-axes.

Estimates of CH$_4$ flux at the soil surface were calculated for each profile sampling location on each experimental date using the CH$_4$ concentration gradient of the profile samples taken from 15 and 60 cm depth and the mean effective CH$_4$ diffusion coefficient (Table 5-2). The mean effective CH$_4$ diffusion coefficient ((6.5 ± 3.5) x 10$^{-3}$ cm$^2$ s$^{-1}$) was calculated from radon profile and flux measurements (not shown) and the diffusion coefficient of CH$_4$ in air at 293K (Dorr et al., 1983). Most of the CH$_4$ flux estimates from the profile samples fall within the range of -40 to +20 µmol m$^{-2}$ d$^{-1}$. Only location G on July 15 shows slightly higher emissions, and location D on July 15 and 17 had large emissions.

Oxygen concentrations of the profile samples decreased with increasing depth in the cover soil but were consistently above 5 % (v/v) at all locations and all depths except on July 15$^{th}$ and 16$^{th}$ where at sampling location D and F there was at some depths only between 2 and 4 % O$_2$ (not shown). Profiles of the ratio of CH$_4$ to CO$_2$ were similar to the CH$_4$ profiles however, in all profiles CH$_4$:CO$_2$ was lowest at 60 cm depth and increased both closer to the surface and deeper within the cover soil (Figure 5-6B).
5.4.5 Gas Push-Pull Tests

The breakthrough curves for CH$_4$ and the noble gases during the extraction phase of each GPPT were plotted as relative concentration (C*) versus extracted divided by injected volume ($V_{ext}/V_{inj}$). As the breakthrough curves for all GPPTs were similar, only that for GPPT1 is shown as a representative plot (Figure 5-7A). For all GPPTs the C* of CH$_4$ for the first extraction phase sample was between the C*s of Ne and He, thereafter the breakthrough curve of CH$_4$ decreased rapidly relative to the tracer gases, and by $V_{ext}/V_{inj}$ of approximately 0.5, the C* of CH$_4$ was below that of He. Throughout the remainder of the extraction phase the C* of CH$_4$ continued to decrease relative to the noble gases and no influence from the background CH$_4$ in the cover soil on the breakthrough curves was detected.

![Figure 5-7. Breakthrough curve for CH$_4$ and noble gases for extraction phase samples for GPPT 1 performed on July 4 (A) and the plot for determination of the first-order rate constant (k) for CH$_4$ oxidation calculated using Ar as the nonreactive tracer (B). The k value was calculated as the negative slope of the linear regression (solid line) of the data points that showed a linear relationship.](image)

Apparent first-order rate constants (k) for CH$_4$ oxidation during GPPTs were estimated from the fit of a regression line to the natural logarithm of C* of CH$_4$ divided by C* of Ar plotted against residence time (Figure 5-7B). As Michaelis-Menten kinetics were evident from the curvature of the graphs, only the points at the end of the extraction time that showed a linear
relationship were used to calculate the $k$ values. Over the study period the $k$ values ranged from 10.0 to 15.8 h$^{-1}$ (Table 5-2).

Table 5-2. Volumetric water content of the landfill-cover soil as measured by TDR and apparent first-order rate constants ($k$) for CH$_4$ oxidation calculated for each GPPT.

<table>
<thead>
<tr>
<th>Date</th>
<th>Volumetric water content (m$^3$ soil-water m$^{-3}$ soil)</th>
<th>First-order rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Depth below soil surface (m)</td>
<td>GPPT No.</td>
</tr>
<tr>
<td></td>
<td>0 – 0.3</td>
<td>0.3 – 0.6</td>
</tr>
<tr>
<td>4 July</td>
<td>0.22</td>
<td>0.32</td>
</tr>
<tr>
<td>8 July</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>10 July</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>15 July</td>
<td>0.30</td>
<td>0.34</td>
</tr>
<tr>
<td>17 July</td>
<td>0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>Mean</td>
<td>0.24</td>
<td>0.31</td>
</tr>
</tbody>
</table>

$^a$ $k$ values are reported with their 95% confidence interval

5.5 Discussion

On a landfill surface, emissions of CH$_4$ can be highly variable in both space and time and have been reported to vary over seven orders of magnitude from less than 0.0004 to 4000 g CH$_4$ m$^2$ d$^{-1}$ (Bogner et al., 1997). At the Lindenstock landfill the median daily CH$_4$ flux estimated using flux chambers indicate that the landfill-cover soil surveyed was not a net emitter of landfill-produced CH$_4$ but was in fact a net sink for atmospheric CH$_4$ (Figure 5-4A). The large emissions detected at only two of the 16 chambers on July 15$^{th}$ and 17$^{th}$ reflect the heterogeneity of the site and were likely due to the higher soil moisture content after several days of rain (July 15$^{th}$, Table 5-2) and the sharply decreasing atmospheric pressure (July 17$^{th}$, Figure 5-1). Soil moisture has been related to emissions and Gebert & Groengroeft (Gebert & Grongroft, 2006)
reported higher landfill-gas emissions during periods of decreasing atmospheric pressure due to a relative increase in the landfill-gas pressure indicating additional gas advection from the waste body to the soil surface. The sink strength of the Lindenstock landfill-cover soil for atmospheric CH₄ (maximum chamber measurement -380 µmol m⁻² d⁻¹) was comparable to maximum negative flux values calculated using chambers at other landfills (Boeckx et al., 1996, Bogner et al., 1995) and twice as high as values calculated for a non-landfill soil (Ball et al., 1997).

In contrast to the chamber results, the median daily CH₄ flux estimated using eddy covariance measurements showed CH₄ emissions occurring on four out of the five sampling days (Figure 5-4B). Even on the day where mostly net uptake was found (10 July; see Figure 5-4B) the eddy covariance fluxes were more than an order of magnitude larger than chamber fluxes. Lohila et al. (Lohila et al., 2007) compared eddy covariance estimates of CH₄ fluxes above a landfill with chamber estimates and reported higher variability in the chamber measurements, but overall good agreement between the two methods. In contrast, Börjesson et al. (Borjesson et al., 2000) compared chamber flux measurements with those from a tracer-gas micrometeorological technique and found that estimates from chambers were more than four time lower than those measured using the tracer-gas technique. At the Lindenstock landfill, CH₄ hot spots were identified around gas domes and pipes where chambers could not be deployed. The landfill gas emitted from these hotspots therefore contributes to CH₄ flux estimates from eddy covariance measurements but not to those from flux-chamber measurements. These differences in flux footprint areas of eddy covariance and chamber measurements may be the key factor explaining the differences in fluxes. However, it should be noted that the short periods of eddy covariance flux measurements during daytime periods only do not allow for a more detailed statistical analysis. As Eugster and Plüss [15] noted, the rather episodic bursts with higher CH₄ concentrations observed at this site (data not shown, but see [15]) are indicative of event-driven CH₄ release processes. The frequency of occurrence of such events and their flux magnitude may thus easily bias any comparison between eddy covariance and chamber flux.
measurements. Thus, these differences should not primarily be considered an indicator for the quality of flux measurements, but as an indicator for processes with spatial and temporal scales that are not resolved by chamber flux measurements.

The soil-gas profiles in this study indicate that the zone of maximum oxidation for the landfill-derived CH$_4$ was at about 60 cm depth below the surface (Figure 5-6). The texture of the cover soil and the relatively dry summer conditions permitted O$_2$ to diffuse deeply into the soil where it could facilitate CH$_4$ oxidation. Reductions in CH$_4$:CO$_2$ are a rough indicator that CH$_4$ oxidation has occurred. As the Lindenstock landfill-gas from the waste prior to migration through the cover soil has a CH$_4$:CO$_2$ ratio of approximately 1.6 and the values at 1 m depth were less than 0.003, CH$_4$ oxidation has presumably occurred even at depths greater than 1 m. On two dates extremely high emissions were quantified at profile sampling location D. While even higher values have been reported (Borjesson et al., 2000), flux calculations from profile samples should be considered with reservations. Bogner et al. (Bogner et al., 1995) compared fluxes calculated from profile samples with those from chamber measurements and found that profile estimates were 50% higher. One concern when calculating fluxes from profile samples is that the calculation assumes that soil transport properties and porosity are constant over the depth of the profile. Another concern is that soil diffusivity has been shown to fluctuate due to precipitation (Ball et al., 1997) and seasonally and therefore, rather than using an average value for the entire study as was done here, effective diffusion coefficients should be measured each time profile samples are taken (Kusa et al., 2008). More frequent measurement of the radon concentration of the soil-gas may be restricted by the time required per measurement.

In contrast to the fluctuations in the calculated above- and below-ground fluxes, the GPPTs indicate that below the surface of the cover soil the methanotrophs oxidized the landfill-produced CH$_4$ at a relatively constant rate (Table 5-2). In contrast to a previous field campaign at the Lindenstock landfill, calculation of rate constants from GPPTs was not adversely influenced by high background CH$_4$ concentrations (Gómez et al., 2009). Background CH$_4$
concentrations and first-order rate constants were in general lower than at the same location in the previous study. This could be due to differences in the climatic conditions between the two years or to a reduction in CH$_4$ production as the landfill ages.

Due to the heterogeneity of both landfill-cover soils and landfill waste, CH$_4$ fluxes from landfills are both temporally and spatially difficult to quantify. Additional variability in flux estimates arises from the effect of climatic factors such as precipitation, temperature and pressure fluctuations on gas transport and methanotrophic activity. Therefore measurements from one day are likely to be different from the next, and measurements from one year are likely to be different from the following. Each of the methods examined provides valuable and unique information concerning the fate of CH$_4$ in a landfill-cover soil which when combined, gives a glimpse into the complex dynamics of the landfill.

The choice of method to employ in a study of CH$_4$ dynamics in a landfill-cover soil depends upon the question being asked. If, for example, the goal is to quantify net greenhouse-gas emissions from a landfill-cover soil, then the eddy covariance method would be the appropriate selection as it includes any CH$_4$ that bypasses the cover-soil in quantification of fluxes and can be run continuously if needed. If the goal is to evaluate the effectiveness of a cover soil to oxidize atmospheric CH$_4$ or to evaluate the heterogeneity in soil-atmosphere fluxes across the landfill-cover soil surface, relating fluxes to local soil parameters, then flux chamber measurements should be employed. And, finally, if the goal is to quantify CH$_4$ oxidation rates within the cover soil then GPPTs may be the method of choice. As is the case for all field studies, a combination of several techniques results in more robust conclusions.

5.6 Acknowledgements

We thank F. Heeb, R. Cho, F. Ugolini, and S. Liebner for assistance in the field. We also thank R. Sauter (Forestry Department, Liestal). The financial support for this research was provided by Grant No. 200021-103619 from the Swiss National Science foundation. The DLT-
100 analyzer was purchased from funds received from ETH Scientific Equipment grant 0-43350-07 to Werner Eugster and Josef Zeyer, and by funds from Alfred Wüest and Carsten Schubert (EAWAG Kastanienbaum).

5.7 References


Chapter 5: Comparison of Methods to Assess the Fate of Methane in a Landfill-Cover Soil


Discussion
6.1 Evaluation of field methods to quantify landfill methane dynamics

6.1.1 Gas Push-Pull Tests

In this work we explored the gas push-pull test (GPPT) as a tool to quantify in situ rates of CH$_4$ oxidation in the cover soil of a landfill. Initially, GPPTs were performed in an abiotic laboratory tank that simulated an open system to examine the physical transport properties of CH$_4$ and the tracer noble gases during GPPTs (chapters 2 and 3), thereby providing tools for improving the design and interpretation of GPPT field experiments.

6.1.1.1 Gas transport during GPPTs

During GPPTs gas transport may occur in the form of molecular diffusion, advection or partitioning into- or out of- the water phase. Additionally, mechanical dispersion and sorption to solid particles could be taken into account, however, mechanical dispersion was previously calculated to be negligible under most GPPT conditions because gas pore-velocity decreases rapidly away from the injection point due to the spherical velocity field, and sorption of CH$_4$ and noble gases to solid particles was considered negligible (Gonzalez-Gil et al., 2007). GPPTs performed in an abiotic laboratory tank at water saturations ($S_w$) that might be expected in landfill cover soils, $S_w<0.61$ m$^3$ m$^{-3}$, showed that the relative importance of molecular diffusion during GPPTs decreased with increasing water saturation and injection/extraction gas flow rate. With increasing $S_w$ and faster gas flow rate, gas component transport became more advection dominated as evidenced by increasing similarity in the breakthrough curves of CH$_4$ and the tracer gases. This would suggest that high gas flow rates should be employed to assure similar transport, however, this may lead to unacceptably short contact time between reactant gases and microorganisms. Air-water partitioning was shown to be inconsequential over the range of $S_w$ and gas-flow rates studied. An understanding of gas component physical transport during GPPTs in media with different degrees of $S_w$ is needed for selection of an appropriate gas tracer.
6.1.1.2 Selection of a tracer

The choice of an appropriate tracer gas to be used in field GPPTs is an important consideration because if the tracer has similar transport properties as the reactant, then simplified methods to interpret breakthrough curves and calculate rates of microbial kinetics can be applied (Snodgrass & Kitanidis, 1998, Haggerty et al., 1998, Schroth & Istok, 2006). The best possible tracer to quantify rates of CH$_4$ oxidation during GPPTs would have the same physical transport behaviour as CH$_4$, but would be non-reactive so that any difference between the breakthrough curves of the two gases could be attributed to microbial consumption of CH$_4$. An additional option is to use CH$_4$ itself from a subsequent inhibited GPPT as a nonreactive tracer.

In contrast to an earlier field study in which Ne was found to be the most suitable tracer for CH$_4$ during GPPTs (Urmann et al., 2005), in the laboratory tank Ar was determined to be the best tracer over the range of $S_w$ studied. At $S_w \geq 0.61$, any of the tracers investigated (He, Ne, Ar) could be suitable due to the advection-dominated gas transport. The difference between this laboratory study and the previous field study is that the laboratory tank was equipped with gas vents to simulate an open system, whereas in the previous field study GPPTs were performed inside a well casing that partially restricted gas transport.

6.1.1.3 Stable carbon isotope analysis of CH$_4$ during GPPTs

The relative contribution of advective versus diffusive gas transport also had a strong influence on stable carbon isotope fractionation during GPPTs. Strong isotopic fractionation due to diffusion could potentially mask any fractionation due to oxidation in environments where CH$_4$ oxidation rates are low. However, in environments where CH$_4$ oxidation rates are typically high, such as landfill-cover soils, stable carbon isotope analysis of GPPT samples can be used as an additional tool to verify that CH$_4$ oxidation is microbially mediated. To distinguish isotopic fractionation due to microbial activity from fractionation due to diffusion,
two sequential GPPTs can be performed with the second GPPT containing an inhibitor of CH$_4$ oxidation in the injection gas mixture. Potential inhibitors of CH$_4$ oxidation (commonly used inhibitors include acetylene, ethylene and methyl fluoride) should first be tested on the soil of interest to determine the efficacious concentration for the desired degree of inhibition (Chan 2001). The results of the two sequential GPPTs can be used in mathematical models to estimate the in situ fractionation factor due to CH$_4$ oxidation. Typically, CH$_4$ oxidation fractionation factors used to calculate the fraction of CH$_4$ oxidised from landfill-cover soil vertical gas profile samples or chamber emissions are from laboratory incubations (Liptay et al., 1998). As even small variations in fractionation factor estimates have a large influence on calculation of the fraction of CH$_4$ oxidised as it passes through the cover soil, in situ estimates would give the most accurate estimates of CH$_4$ oxidation (Chanton & Liptay, 2000).

6.1.1.4 GPPTs in a landfill-cover soil

After examining the transport of CH$_4$ and tracer gases in detail, two field campaigns were performed in the cover soil of the Lindenstock landfill, one in the summer of 2007 (chapter 4) and the other in the summer of 2008 (chapter 5). The in situ CH$_4$ concentration was shown to have a strong influence on calculations of CH$_4$ oxidation kinetics. When background CH$_4$ concentrations were relatively low (i.e. < 1000 µL L$^{-1}$ rather than 200,000 µL L$^{-1}$) first order rate constants for CH$_4$ oxidation could be reproducibly calculated. However, when in situ CH$_4$ concentrations were higher, possibly due to changes in atmospheric pressure (Czepiel et al., 2003, Gebert & Groengroeft, 2006) or following precipitation events (McBain et al., 2005), intrusion of the background CH$_4$ into the soil volume being probed by the GPPT resulted in underestimation of the first-order rate constant for CH$_4$ oxidation. This could possibly restrict the use of GPPTs in winter months when CH$_4$ concentrations in landfill-cover soils are typically higher (Borjesson & Svensson, 1997). Quantitative means for background correction are available (Yang et al., 2007), but they rely
upon the assumption that background concentrations are constant, which was not the case
during the two field study periods at the Lindenstock landfill.

The GPPT is a useful option for quantifying rates of CH\textsubscript{4} oxidation in landfill-cover
soils because the use of a tracer gas with similar physical transport properties to CH\textsubscript{4} removes
the need to use laboratory determined values such as CH\textsubscript{4} turnover rates or isotopic
fractionation factors. GPPTs could be used as a tool to monitor methanotrophic activity at a
specific location over time or to evaluate the effect of different treatments on the rate of in situ
CH\textsubscript{4} oxidation. Scaling up of GPPT results to calculate CH\textsubscript{4} oxidation rates for a larger area
has not yet been considered, however it is expected that CH\textsubscript{4} oxidation rates will be highly
variable due to the soil and waste heterogeneity and therefore many sampling points would be
required.

Quantification of CH\textsubscript{4} oxidation in landfill-cover soils is one of the major uncertainties
in global models to estimate CH\textsubscript{4} dynamics, and it has recently been reported that the default
value of 10\% for the fraction of CH\textsubscript{4} oxidized as it passes through the cover soil is an
underestimation (Chanton et al., 2009).

6.1.2 Soil-air concentration profiles

The depth of maximum methanotrophic activity can be identified using soil-air
concentration profiles. This is important for determining where to place the injection rod for
GPPTs or deciding at which depth soil samples should be collected for laboratory incubations.
The ease of taking soil-air samples and the low cost make profile sampling a popular tool,
however, the use of profile data to calculate fluxes or CH\textsubscript{4} oxidation rates has several
drawbacks. Landfill-cover soils are highly heterogeneous in terms of both soil and gas
composition, therefore profile air-samples, which are point samples, will have widely varying
gas-component concentrations reflecting the non-steady state conditions of the system. In
addition, soil macroporosity including cracks and earthworm burrows and soil layering have a
significant influence on gas movement in porous media (Lange et al., 2009). This heterogeneity in gas component concentration will be reflected in the estimates of CH$_4$ oxidation rates or fluxes as was seen in this work for the different sampling locations and dates.

6.1.3 Flux chambers

Like the soil-air sampling method, flux chambers are inexpensive and easy to use and have the advantage of being capable of measuring fluxes into- or out of- the soil surface. While chambers are appropriate tools to quantify differences in flux between soil types or treatment plots, extrapolation of flux chamber measurements to larger areas may lead to underestimation or overestimation of fluxes. Because chambers only capture fluxes across the soil surface on which they are placed, failure to place chambers on areas of high flux such as cracks or fissures in the cover soil may lead to underestimation of fluxes. Conversely, fluxes may be over estimated if only a few chambers are deployed and randomly selected sampling locations are disproportionately located over hot spots (Janssens et al., 2000).

Several researchers have noted that when CH$_4$ fluxes for a landfill-cover soil are calculated only a few chambers may be responsible for most of the flux due to the inherent heterogeneity of the cover soil and any differences in the CH$_4$ production capacity of the waste (Chan & Parkin, 2001, Borjesson et al., 2000). High variability in individual chamber flux measurements results in high variance in estimates of average fluxes, therefore requiring deployment of many chambers for reliable estimates (Borjesson et al., 2000). In this work 16 chambers were installed and the variance was estimated to be approximately 100% for each sampling date. Bogner et al. (1997) suggested that more than 100 chambers be used to reduce variance to an acceptable level and Börjesson et al. (2000) calculated that more than 4610 chambers would be needed to estimate fluxes within 10% for a 3 ha site.
6.1.4 Eddy covariance

In contrast to flux chambers, estimates of CH$_4$ fluxes from landfill-cover soils using eddy covariance are strongly influenced by CH$_4$ emissions through cracks in the cover soil or, as in this work, through preferential flow paths alongside gas domes or gas sampling pipes.

While eddy covariance has proven to be a useful tool for measuring fluxes over large relatively homogeneous surfaces, such as lakes (Anderson et al., 1999) or crops (Verma et al., 2005), its use to quantify fluxes over landfill-cover soils has only been explored in a handful of studies (Lohila et al., 2007, Laurila et al., 2005, Rinne et al., 2005). It would be especially advantageous to use eddy covariance to measure fluxes above landfill-cover soils during winter months when deployment of chambers is challenging due to frozen soil and presence of snow.

A handicap concerning the use of eddy covariance over landfill-cover soils is due to the extremely heterogeneous emissions. As was seen in this thesis, mean flux estimates can vary greatly from one day to the next possibly due to changing wind directions that slightly move the footprint.

6.1.5 CH$_4$ emission measurements

An additional tool that has been used to detect hot spots of CH$_4$ emissions and leaks around gas installations on landfill cover soils is a field-portable flame-ionization detector to quantify CH$_4$ with a bell probe. The probe is placed on the soil surface where it measures the CH$_4$ concentration in the uppermost soil layer at the landfill surface. When geographic coordinate readings (e.g. using the Global Positioning System - GPS) are additionally collected, the spatial distribution of hot spots and areas of low CH$_4$ emissions can be visualized.
6.2 Method selection

Selection of a method to be used to study CH$_4$ dynamics in a landfill-cover soil depends upon the question being asked. If, for example, the goal is to quantify net greenhouse-gas emissions from the landfill-cover soil, then the eddy covariance method would be appropriate as it includes any CH$_4$ that bypasses the cover-soil in quantification of fluxes and can be run continuously if needed. If the goal is to evaluate the effectiveness of a cover soil to oxidize atmospheric CH$_4$ or to evaluate the heterogeneity in soil-atmosphere fluxes across the landfill-cover soil surface, relating fluxes to local soil parameters, then flux chamber measurements should be employed. And, finally, if the goal is to quantify CH$_4$ oxidation rates within the cover soil then GPPTs may be the method of choice. As is the case for all field studies, multiple lines of evidence through a combination of several techniques results in more robust conclusions.

6.3 Considerations for landfill-cover design to reduce CH$_4$ emissions

6.3.1 Soil type

The hydrology of landfill waste is controlled to a large extent by the cover soil. The composition and thickness of the cover soil and the vegetation influence evapotranspiration and downward percolation of precipitation (USEPA, 2003). Because of their low hydraulic conductivities, clay soils have frequently been selected as cover soil material to reduce water infiltration into waste. The hydraulic properties of soils selected for use as landfill-cover soils are, however, determined for compacted laboratory soil samples, therefore the hydraulic properties may be very different from soils exposed to environmental conditions (Benson et al., 2007). During periods of wetting and drying, freezing and thawing, root growth and earthworm movement, the hydraulic properties of the soil changes thereby changing the hydrology and creating cracks that allow water to infiltrate the waste. Cracks in the clay soil
also serve as preferential flow paths for emission of CH$_4$ from the waste, bypassing transport through the cover soil and thereby circumventing the possibility for consumption by methanotrophs. These changes over time in the hydraulic properties of cover soils can be reduced by selecting soils that are coarser in texture, have lower clay content and do not swell or shrink (Benson et al., 2007).

In addition to cracking after wetting and drying, clay soils also tend to retain water longer than coarser soils and have widely been used as covers for mine waste to maintain a high degree of water saturation and prevent O$_2$ infiltration thereby preventing formation of sulphuric acid (Yanful & Catalan, 2002). When used as landfill-cover soils, this property is not optimal in terms of providing the best conditions for CH$_4$ oxidation. As moisture content rises during and after precipitation events the soil pores in the fine textured soil rapidly become water-saturated thereby effectively sealing the cover soil and reducing its gas permeability (Boeckx et al., 1997). Selection of a coarse soil with high porosity and high gas permeability will ensure that the cover soil is a zone for dynamic mixing of landfill gas with the air; it will allow deeper penetration of O$_2$ into the cover soil possibly resulting in oxidation of a greater fraction of the landfill-produced CH$_4$. Soil texture is also an important factor when considering oxidation of atmospheric CH$_4$ by landfill-cover soils as it has been shown that CH$_4$ oxidation increases with gas diffusivity at the soil surface (Ball et al., 1997).

An alternative to the traditional landfill cover system is the capillary barrier system. It is constructed over the landfill waste by first installing a layer of coarse material (capillary block) on a slope followed by a layer of fine material (capillary layer). Under unsaturated conditions the moisture is retained in the fine layer by capillary forces and can be removed by evapotranspiration or by lateral transport down the slope in the fine soil above the interface (Morris & Stormont, 1997). The combination of a capillary barrier with an additional coarse-textured cover layer for maximum CH$_4$ oxidation could be a possible solution to the problem.
of how to optimise CH$_4$ oxidation while preventing water infiltration to the waste body (Berger et al., 2005).

A number of studies have been performed to evaluate the CH$_4$ oxidising capacity of different cover soil materials. Stern et al. (2007) evaluated the CH$_4$ oxidizing capacity of a biocover composed of pre-composted garden waste over a layer of crushed glass and found that CH$_4$ emissions were reduced relative to control cells due to longer retention of CH$_4$ in the moist soil under the compost. Biocovers also serve to insulate underlying soil during cold months in so doing keeping CH$_4$ oxidation rates relatively constant year round (Huber-Humer et al., 2008).

### 6.3.2 Soil moisture

In addition to influencing the gas permeability of the cover soil, soil moisture also influences methanotrophic activity. Maximum methanotrophic activity occurs at a soil moisture content that allows rapid gas-phase diffusion of O$_2$ into the cover soil, while at the same time is sufficiently moist to prevent desiccation and physiological stress to the methanotrophs (Berger et al., 2005). Laboratory studies have been performed with different-textured landfill cover soils at different water contents to determine the optimum range of water content for methanotrophs to consume CH$_4$ (Table 6-1).
Table 6-1: Optimum volumetric soil moisture content for CH$_4$ oxidation in landfill-cover soils

<table>
<thead>
<tr>
<th>Soil texture</th>
<th>Optimal volumetric soil moisture content (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>10</td>
<td>(Park et al., 2005)</td>
</tr>
<tr>
<td>Sand mixed with clay</td>
<td>11</td>
<td>(Whalen et al., 1990)</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>15.6 – 18.8</td>
<td>(Boeckx et al., 1996)</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>15 - 20</td>
<td>(Park et al., 2004)</td>
</tr>
<tr>
<td>Sandy clay loam</td>
<td>15.7</td>
<td>(Czepiel et al., 1996)</td>
</tr>
<tr>
<td>Loam</td>
<td>15.4</td>
<td>(Stein &amp; Hettiaratchi, 2001)</td>
</tr>
<tr>
<td>Loamy sand</td>
<td>18 - 24</td>
<td>(Scheutz &amp; Kjeldsen, 2004)</td>
</tr>
</tbody>
</table>

To ensure maximum CH$_4$ oxidation, landfill management practices could be implemented to maintain cover soil moisture within the optimal range for gas permeability and microbial activity especially in arid climates.

### 6.3.3 Soil nutrient content

In addition to water content, the nutrient status of the cover soil could be optimized through fertilizer amendment, as in particular nitrogen concentrations have been shown to influence CH$_4$ oxidation rates (Boeckx et al., 1996). In extensive studies of the effect of different nitrogen fertilizers on oxidation of atmospheric CH$_4$, it was concluded that addition of ammonium, urea, green manure (alfalfa) and mineral nitrogen fertilizer inhibited methanotrophic activity (Le Mer & Roger, 2001). In contrast, addition of organic manure, nitrate or NaNO$_3$ did not inhibit CH$_4$ oxidation (Le Mer & Roger, 2001), and more recently it was shown that growth of methanotrophs in a rice soil was stimulated by addition of an ammonium-based fertilizer (Bodelier et al., 2000). Addition of ammonium fertilizers to soils raises the problem of competitive inhibition of the methane monooxygenase (mmo). Because
the mmo can also convert ammonia to nitrate, the presence of ammonia will reduce the amount of mmo available for CH$_4$ (Bodelier et al., 2000). Therefore, monitoring of the nitrogen status of landfill-cover soils could ensure the optimal methanotrophic activity.

6.4 Seasonal fluctuations in landfill methane dynamics

Our experimental field campaigns were both preformed in the summer months when warm temperatures and moderate soil moisture provided the most favourable conditions for CH$_4$ oxidisers. Other researchers have investigated the variability of landfill-cover soil CH$_4$ emissions throughout the year (Table 6-2). In well-constructed landfills the waste is well insulated from fluctuations in atmospheric temperatures and infiltration of water into the waste is regulated, therefore production of CH$_4$ can be assumed to be relatively stable throughout the year. Landfills with poorly constructed cover soils that are either too thin or have cracks (e.g. the clay soil in Table 6-2) may be strongly influenced by climate and changes in CH$_4$ emission rates throughout the year could be due to changes in the rate of CH$_4$ production.

<table>
<thead>
<tr>
<th>Soil Texture</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy loam</td>
<td>-</td>
<td>19.5</td>
<td>472.5</td>
<td>189.2</td>
<td>(Boeckx et al., 1996)</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>1800</td>
<td>250</td>
<td>3100</td>
<td>1400</td>
<td>(Borjesson &amp; Svensson, 1997)</td>
</tr>
<tr>
<td>loam</td>
<td>-0.12</td>
<td>-0.12</td>
<td>-6.0</td>
<td>2.4</td>
<td>(Borjesson et al., 1998)</td>
</tr>
<tr>
<td>Sandy loam</td>
<td>718</td>
<td>1450</td>
<td>7870</td>
<td>-</td>
<td>(Borjesson et al., 1998)</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>31.4</td>
<td>55.5</td>
<td>47.9</td>
<td>262</td>
<td>(Borjesson et al., 1998)</td>
</tr>
<tr>
<td>Sand with clay</td>
<td>20111</td>
<td>18884</td>
<td>-</td>
<td>-</td>
<td>(Kallistova et al., 2005)</td>
</tr>
<tr>
<td>Mulch</td>
<td>33,000</td>
<td>60,000</td>
<td>100,000</td>
<td>98,000</td>
<td>(Chanton &amp; Liptay, 2000)</td>
</tr>
<tr>
<td>Clay</td>
<td>1,600,000</td>
<td>1,700,000</td>
<td>370,000</td>
<td>1,200,000</td>
<td>(Chanton &amp; Liptay, 2000)</td>
</tr>
</tbody>
</table>

- not measured
In well-constructed landfills seasonal fluctuations in CH$_4$ emissions are likely due to the influence of climate on CH$_4$ oxidation rates in the cover soil (Chanton & Liptay, 2000). Temperature also influences CH$_4$ emission rates from landfill-cover soils by reducing evapotranspiration and methanotrophic activity at lower temperatures (Tanthachoon et al., 2008, Einola et al., 2007). Use of artificial heating in the cover soil has been explored as a means to maintain CH$_4$ oxidation during the winter in cold climates where methanotrophic activity has been shown to cease in the winter (Zeiss, 2006). Local climates that have a season in which it rains more may have greater CH$_4$ emissions during the rainy months due to reduced air permeability of the cover soil.

6.5 Questions for future research

Recent legislation in Switzerland dictates that municipal waste can no long be directly dumped in Swiss landfills (FOEN, 2009). This decision was made with the aim to prevent contamination of ground water from landfill leachates and to adopt a process that could be turned off within a few hours in the case of an incident (FOEN, 2009). Instead of direct dumping, waste is first incinerated and then only the non-burnable incinerator waste is deposited onto landfills and therefore problems concerning generation of CH$_4$ from organic matter will no longer be of such importance in Switzerland. Only the current landfills will have to be monitored as they age and approach natural conditions. Incinerator wastes will introduce new problems such as generation of H$_2$ and the risk of explosion, and although incinerated wastes will generate less gas than non-incinerated waste, they may also contribute to global warming because landfill gas recovery will likely be less efficient in landfills with low or variable CH$_4$ production (Manfredi et al., 2009).

In other European countries, such as Great Britain, and also in the United States, landfilling is still the preferred method for disposal of wastes. It would benefit these and other countries that don’t incinerate waste if landfill-cover design was investigated in terms of
predicted global warming in the specific local area. As landfills generally have lifetimes of thirty years or more, changes in the local climate over that period could have an influence on the ability of the landfill-cover soil to prevent water infiltration to the waste and CH$_4$ emissions to the atmosphere. This is especially important for landfills in areas that are likely to become drier, thereby changing the gas permeability of the cover soil (USEPA, 2003).

In terms of the GPPT, future research into separating the influence of the background CH$_4$ concentration from the GPPT-injected CH$_4$ could be explored to enable use of the GPPT even when background CH$_4$ concentrations are very high.

6.6 References


Appendix 1

In Situ Quantification of Methane Oxidation in Soils using Gas Push–Pull Tests

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Published in International Congress Series (2006) 1293, 42–45
A.1 Abstract

The Gas Push–Pull Test (GPPT) is a tool for measuring in situ soil processes including methane oxidation. To quantify methane oxidation, methane and non-reactive gases selected based on transport behaviour similar to methane, were injected into soil above a petroleum hydrocarbon contaminated aquifer and gas samples were extracted over time. The rate of loss of methane was compared to the loss of tracer gases and differences in the concentrations were attributed to microbial activity. To further support the evidence for microbial methane consumption, tests were also performed under conditions of inhibited microbial activity.

A.2 Introduction

The atmospheric concentration of the greenhouse gas methane (CH$_4$) is strongly influenced by soils which can act as either a source or a sink. Methane oxidizing microorganisms are ubiquitous in soils and are potentially the largest biological sink for CH$_4$. Biological CH$_4$ oxidation largely occurs at the aerobic–anaerobic interface of diverse anaerobic environments such as peat bogs (Morris et al. 2002), rice field soils (Damgaard et al. 1998), landfills (Czepiel et al. (1996), the unsaturated zone above contaminated aquifers (Urmann et al. 2005), and as recently reported, in cattle slurry storage surface crusts Petersen et al. 2005). Current field methods mainly focus on surface gas flux measurements, which only describe net geochemical changes and do not give direct in situ turnover rates of CH$_4$ oxidation and production. The latter are required to better interpret, and eventually predict future net CH$_4$ fluxes into the atmosphere. Hence, there is a need to develop and implement robust methods for the in situ measurement of microbial activities in soil and associated rates of gas transformation.

We developed the Gas Push–Pull Test (GPPT) to assess microbial processes in soils with a particular emphasis on CH$_4$ oxidation. The GPPT method is based on the quantification
of reactant (CH₄) consumption from the soil gas phase. The test consists of the injection of a gas mixture of CH₄ and tracer gases into the soil followed by extraction of a blend of soil air and the injected gas mixture. During the GPPT, CH₄ can be oxidized by indigenous microbes. Microbial CH₄ conversion is quantified by comparing the concentrations of extracted CH₄ versus extracted tracer gases. Several key issues needed to be resolved to determine whether the GPPT may be a valuable tool for the quantification of microbial activities in soils. A first issue is the selection of appropriate tracer gases. In an ideal situation, the tracer gas and the reactant gas should have similar transport characteristics. Under these conditions, the difference in the breakthrough curves of the tracer and reactant gas can be strictly attributed to microbial conversion and microbial activity can thus be quantified (Haggerty et al. 1998). The identical transport characteristics of the gases can be further confirmed if the same reactant/tracer gas mixture is injected at the same location but when the soil is biologically inactive (e.g. sterile or inhibited). Then the extraction breakthrough curves of the tracer and reactant gas will coincide. We implemented the GPPT in a numerical simulator and investigated which inert gas(es) could be suitable tracer(s) for CH₄. Once an understanding of the behaviour of tracer and reactant gases was gained, the next step was to apply the GPPT in the field. For this purpose, it was decided to run the test in the vadose zone above a petroleum hydrocarbon contaminated aquifer located in Studen, Switzerland. Large amounts of CH₄ are produced in the anaerobic zone of the aquifer and hence high CH₄ oxidation activities can be expected in the overlying aerobic zones.

A.3 Materials and methods

To determine which gases to use as non-reactive tracers of CH₄, the GPPT was implemented in a numerical simulator. Simulations from dry to various soil water contents were performed. For the field applications of the test, we designed and constructed a completely gas-tight “gas flow controller” (GFC), which allowed controlled injection and
extraction of gases into and out of the soil. Two GPPTs were performed in the vadose zone above the contaminated Studen aquifer at 2.6 – 2.7 m depth, where substantial methanotrophic activity was suspected. In each of the two GPPTs, we injected 30L of a gas mixture containing about 3.2vol.% Ne and 20vol.% Ar as non-reactive tracers, as well as 3.3vol.% CH$_4$ and 16.5vol.% O$_2$ as reactants in N$_2$ at a flow rate of ~0.6L/min. Immediately after injection, we began extracting a total of 90L of gas mixture/ambient soil gas at a flow rate of 0.52L/min. Total test duration was ~4.0h. The two GPPTs differed from each other in that ~2vol.%C$_2$H$_2$ was additionally co-injected during GPPT2 as a specific inhibitor of methanotrophic activity. Methane was measured with a gas chromatograph (GC) equipped with a Hayesep N column and an FID detector. Conversely, Ne, Ar and O$_2$ were measured with a GC equipped with a molecular sieves column and a TCD detector. The latter equipment was specifically modified to allow the measurement of Ar in the presence of O$_2$ (Hofer & Imboden 1998).

A.4 Results

The transport of gases during a GPPT, assuming 1.7g/cm$^3$ soil bulk density and a solid–aqueous phase partition coefficient of 0.002 (mg/kg soil)/(mg/m$^3$ water) were simulated to determine which gases might be suitable non-reactive tracers for CH$_4$ (Figure A-1). The curves that most closely mirror the CH$_4$ curve were those of the noble gases Ne and Ar. These were selected to be used as non-reactive tracers.
Figure A-1. (a) Simulated recovery fractions for diverse trace gases and methane. Total, air-filled, and water-filled porosity are 0.45, 0.35, and 0.10, respectively. (b) Simulations considering different water-filled porosities. At very high water-filled porosity values (i.e. 0.3), we can expect similar breakthrough curves for Ne and CH₄.

For the two GPPTs performed above, the contaminated aquifer in Studen (GPPT1 and GPPT2), the relative concentrations, \( C^* \) (concentration measured during extraction divided by the injection concentration), of Ne, Ar, and CH₄ declined during the extraction phase of both GPPTs as a consequence of dilution of the injected gas mixture with ambient soil gas (Figure A-2).

Figure A-2. Breakthrough curves for Ar, Ne and CH₄ obtained during the extraction phase of (a) GPPT1 and (b) GPPT2. Acetylene (not shown) was co-injected during GPPT2. Note that Ar concentrations in this figure were corrected for Ar contained in ambient soil gas. A modified version of these panels was published in Urmann et al. (2005).
In both tests, relative concentrations of Ne and Ar were nearly identical throughout the extraction phase. Concentrations of CH$_4$ were substantially smaller than Ne or Ar concentrations during GPPT1 indicating CH$_4$ consumption, presumably due to microbial activity (Figure A-2a). Conversely, CH$_4$ concentrations were nearly identical to Ar and Ne concentrations during GPPT2 (test with C$_2$H$_2$ inhibitor, Figure A-2b). Thus, these results demonstrate that observed CH$_4$ consumption during GPPT1 was due to microbial activity. Results from GPPT2 also indicated that Ne, Ar and CH$_4$ were transported in a similar fashion during the tests (except for microbial conversion of CH$_4$). This is important as it is a prerequisite for the application of a simplified method to compute first-order rate coefficients of microbial activities (here CH$_4$ oxidation) from push–pull test data (Haggerty et al. 1998). As expected, the rate coefficient of CH$_4$ oxidation during GPPT2 was ~0 as a consequence of the inhibition of methanotrophic activity using C$_2$H$_2$, whereas the rate coefficient for GPPT1 indicated a CH$_4$ half-life of 0.32h during the test (Figure A-3).

Figure A-3. Determination of first-order rate coefficients for CH$_4$ oxidation. Values of k are obtained from the slope of a straight line fitted to experimental data plotted as ln(C*CH$_4$/C*Ne) vs. $t^*$, the time since the end of gas injection. Computation details can be found elsewhere (Urmann et al. 2005).
A.5 Discussion

GPPTs can be conducted under virtually undisturbed soil conditions. The GPPT could be used to assess and monitor CH$_4$ oxidation activities in diverse natural and managed soils, and thus aid in the understanding of CH$_4$ and CO$_2$ fluxes in these environments. This preliminary study indicates that GPPTs may be a valuable tool for the quantification of microbial activities in the vadose zone. Further research is needed to investigate the capabilities and limitations of this tool.

A.6 References


Curriculum Vitae

December 28, 1972  Born in Sheffield, United Kingdom

1986 - 1990  High school in Cincinnati, Ohio USA

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Acknowledgements

Thank you Professor Josef Zeyer for accepting me into the Environmental Microbiology group and for giving me the opportunity to work on this project.

Thanks to Prof. Dani Or and Dr. Werner Eugster and Prof. Martin Schroth for being thesis co-examiners, and to Prof. Ruben Kretzschmar for chairing the thesis examination.

Special thanks to Prof. Martin Schroth who has been an excellent guide during my time at ETH. Your support and encouragement have been invaluable.

Special thanks also to Dr. Graciela Gonzalez-Gil for sitting next to me during the first two years of my PhD and for showing me how to be a researcher.

Many people have assisted me in field and laboratory research. Among them I would like to thank Peter Oester from Oester Messtechnik, Thun for teaching us about landfills in Switzerland; Dr. Rolf Siegwolf and Dr. Matthias Saurer from PSI for assistance with stable carbon isotope measurements; and Hanspeter Läser for his Plexiglas creations.

Thanks to current and previous environmental microbiology group members for talks, companionship and cooperation in the field. I am very grateful for the support system provided by fellow PhD students and Postdocs.

Finally, I would like to thank my family. Thanks to my parents for all the help with the kids, thanks to Flo, Evan and Vera for keeping me firmly grounded in the present and thanks to Luis for sharing your kindness and wisdom.