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

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The gas push—pull test (GPPT) is a single-well gas-tracer method to quantify in situ rates of CH₄ 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 ≤ Sw ≤ 0.61). A series of GPPTs using He, Ne, and Ar as tracers for CH₄ 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 Sw as water in the pore space restricted diffusive gas-phase transport. Diffusional fractionation of the stable carbon isotopes of CH₄ during the extraction period of GPPTs also decreased with increasing Sw (particularly when Sw > 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 Sw (≤0.35) and underestimated recoveries at high Sw (≥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 Sw = 0.61. These data indicate that Ar is a good tracer for CH₄ physical transport over the full range of Sw studied, whereas, at Sw > 0.61, any of the tracers could be used. Greater mass recovery at higher Sw 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.

Introduction
The atmospheric abundance of the greenhouse gas, methane (CH₄), has more than doubled since the preindustrial period (1). Because CH₄ 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 CH₄ sources are being explored (2), the majority of natural and human-influenced CH₄ sources including wetlands, rice paddies, ruminants, and landfills have likely been identified (3—6). From an anaerobic source, produced CH₄ 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 CH₄ before emission to the atmosphere. Soils are estimated to be a sink for between 10 and 44 Tg CH₄/year (1). Quantification of CH₄ oxidation rates in particular subsurface environments and evaluation of influencing factors could facilitate implementation of local measures to enhance the CH₄-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 O₂ and CH₄ concentrations (7—11). Laboratory conditions, however, do not necessarily reflect field conditions, and laboratory derived rates of CH₄ 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 CH₄ oxidation (12). The GPPT was adapted from the push—pull test (PT), an aqueous tracer test that has been developed to measure rates of diverse microbial processes such as methanogenesis, sulfate reduction, and denitrification in aquifers (13). Early PTs or single-well tracer tests (SWTTs) were performed with radioactive tracers to measure aquifer properties (14, 15), later, SWTTs (frequently referred to as “huff and puff” tests) were used to estimate residual oil saturation in reservoirs (see e.g., refs 16 and 17), resident water saturation (18), and to enhance light-oil recovery (19). To date, the GPPT method has been used to determine rates of CH₄ oxidation above a contaminated aquifer (12) and in a peat bog (20), and the test is currently being investigated as a tool to measure CH₄ 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, CH₄. 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 CH₄ oxidation rates is based upon analysis of the breakthrough curves of CH₄ 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 CH₄ decreases as a result of both physical transport processes and, if methanotrophs are active, microbial CH₄ 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 (21). 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 CH₄ 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 refs 22–24. Alternatively, if CH4 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 CH4 transport in porous media is stable isotope fractionation. The slight difference in mass of the two predominant stable isotopes of carbon, 12C and 13C, results in a greater gaseous diffusion rate of 12CH4 compared to 13CH4 (23). Stable isotope fractionation of CH4 due to molecular diffusion has been shown to occur during GPPTs in the laboratory in dry porous media (26), but it is uncertain how CH4 isotope fractionation during GPPTs will be influenced by varying degrees of water saturation (Sw), as in field soils.

While CH4 oxidation occurs over a wide range of Sw, activity is greatest in the range from approximately 0.2 to 0.4 (7–9). Below this range methanotrophs suffer from desiccation and temperature fluctuations, while at higher Sw slow diffusion of gases through pore water limits CH4 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 CH4 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 CH4 (calculated from (27)), in soils with values of Sw close to one, the air relative permeability in porous media is so reduced (28) 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 (29). 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 CH4 and tracer noble gases during GPPTs in porous media for different values of Sw. Specifically, we wanted to determine (i) whether gas component transport during GPPTs is dominated by molecular diffusion over a wide range of Sw, (ii) if the cumulative mass of gas components recovered during GPPTs is influenced by Sw, (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 Sw. To this end, we performed a series of GPPTs in an abiotic laboratory system containing porous media at 0 ≤ Sw ≤ 0.61. The GPPTs were also numerically simulated. These data can aid in design and interpretation of GPPTs in the field.

Materials and Methods

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 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, θt = 0.49), and for GPPTs 7 to 12 it was packed with 0.7 to 1.2-mm diameter quartz sand (coarse sand θt = 0.43). Data for GPPTs 7 and 8 were taken from the literature (29) and were included to complete the data set. Sand of different particle sizes enabled us to attain Sw 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 Sw 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, Ch4 in the water reservoir was sparged with air to remove any dissolved CH4 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).

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 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 1). During the injection phase, a gas mixture (5.5 ± 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 ref 12). 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

FIGURE 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 Sw. 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.
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.

**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 in ref 12. The isotope ratio of the samples was calculated in reference to Vienna Pee Dee Belemnite (VPDB). Isotope values are given as δ$^{13}$C (‰) according to,

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

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 (Thermo Electron Corp., Rodano, Italy) according to ref 20. Quantification was based upon calibration by a series of standards. Gas samples were injected at room temperature and atmospheric pressure using pressure-lok syringes (Vici Precision Sampling Corp., Baton Rouge, LA).

**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 (30). 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 (31, 32) and GPPTs (29). 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 × 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.

### Results

#### 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 ($C_{\text{inj}}/C_{\text{ext}}$) versus extracted divided by injected volume ($V_{\text{inj}}/V_{\text{ext}}$). Representative breakthrough curves are shown for GPPTs with fast injection/extraction gas flow rates, GPPTs 10, 4, 12, and 6 (Figure 2 A, C, E, and G). For all 10 experimental and 2 literature (29) 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 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 × 10$^{-5}$, Ne 3.07 × 10$^{-5}$, Ar 1.86 × 10$^{-5}$, CH$_4$ 2.11 × 10$^{-5}$, at 25 °C from ref 34). 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 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 2A) and underestimated the data for high $S_w$ (Figure 2G).

#### 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$_4$ < Ar, except for GPPT 6 ($S_w = 0.61$, fast gas flow), for which Ne was slightly higher than CH$_4$ (Figure 2B, 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 $S_w = 0.35$ compared to dry conditions, whereas for $S_w > 0.35$ the cumulative mass recovered of each of the gases increased sharply with increasing $S_w$ (Figure 3). The cumulative mass recovered was also dependent upon the gas flow rate with

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**TABLE 1. Experimental Conditions and Gas Push—Pull Test Operational Conditions and Parameters**

<table>
<thead>
<tr>
<th>GPPT</th>
<th>sand type</th>
<th>$Q_{\text{water}}$ (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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<td>173</td>
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<td>482</td>
<td>37.85</td>
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<td>176</td>
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<td>0.88</td>
<td>504</td>
<td>36.22</td>
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<tr>
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<td>fine</td>
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<td>0.61</td>
<td>212</td>
<td>1.10</td>
<td>167</td>
<td>111.83</td>
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<tr>
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<td>fine</td>
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<td>729</td>
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<td>475</td>
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<td>0</td>
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<td>0</td>
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<td>720</td>
<td>0.10</td>
<td>520</td>
<td>34.88</td>
</tr>
</tbody>
</table>

* GPPT 7 and 8 were previously reported in (29). $S_w$ = water saturation [–] as measured by TDR in the vicinity of the injection/extraction location.
slow gas flow resulting in less mass recovered than tests with fast gas flow rates at equivalent water contents (Figure 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 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 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.

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 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 5).

Discussion

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 (35). 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 (29). In this work, we saw that with increasing $S_w$, and the simultaneous decrease in air pore volume, breakthrough curves of the GPPT gaseous compo-

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**FIGURE 2.** Breakthrough curves and cumulative mass recovered at injection/extraction point for CH$_4$ 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.
Porous media, therefore soils that fall within the range of 0 flow rates from one GPPT to another, different sand packs and there was some variability in gas restricted. Although the data for Figure 3 were from two away from the injection/extraction point became increasingly during aqueous PPTs (eq. of advection-dispersion, a nonsegregative transport process, contribution of gas-phase diffusion to gas-component trans-

![Figure 3](image1.png)

**FIGURE 3.** Cumulative mass of CH₄ and noble gases recovered at the end of the GPPTs performed at low and high gas-flow rates ($Q_{gas}$) as a function of $S_w$. Data from two different sand packs. Low $Q_{gas}$ range from 194 to 213 mL min⁻¹. High $Q_{gas}$ range from 685 to 789 mL min⁻¹.

s become increasingly similar (Figure 2A, 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 CH₄, Ar, and Ne is evidence that transport was advection dominated.

**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 become increasingly restricted. Although the data for Figure 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 CH₄) were close to those for Br⁻ during aqueous PPTs (13). By a $V_{sat}/V_{vap}$ of 2.5 (Figure 2B, 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.

**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 (36) 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.

**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 CH₄ and tracers due to air—water partitioning during GPPTs is inconsequential. The fraction of CH₄ 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 4). Although the Henry’s coefficients of CH₄ 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 (28) 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 C₂H₂, 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 C₂H₂ at $S_w = 0.61$. As a commonly used inhibitor of CH₄ oxidation, partitioning of C₂H₂ into the aqueous phase needs to be considered when planning inhibited GPPT as described in ref 12. Partitioning into the aqueous phase would reduce

![Figure 4](image2.png)

**FIGURE 4.** Numerical simulations of relative concentrations of CH₄ and C₂H₂ during GPPT 5 ($Q_{gas} = 212$ mL min⁻¹, $S_w = 0.61$), considering and not considering air—water partitioning. The line for CH₄ with no partitioning is not visible as it is the same as CH₄ with partitioning.
the concentration of $\text{C}_2\text{H}_2$ in the gas phase, raising the possibility that $\text{C}_2\text{H}_2$ insufficiently covers the area probed by the injected $\text{CH}_4$, thus incompletely inhibiting methanotrophic activity.

**Influence of $S_w$ on Stable Carbon Isotope Fractionation of $\text{CH}_4$ during GPPTs.** In GPPTs, microbial $\text{CH}_4$ oxidation rates may be estimated from stable carbon isotope fractionation data only if the fractionation factor due to diffusion is known (29). Here we have seen that diffusive fractionation of $\text{CH}_4$ 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 5) that at $S_w < 0.42$ diffusional fractionation of $\text{CH}_4$ 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 $\text{CH}_4$. 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.

**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 $\text{CH}_4$ 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 $\text{CH}_4$.

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 $\text{CH}_4$ 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 $\text{CH}_4$ 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.

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**Supporting Information Available**

A table listing input parameters for GPPT numerical simulations and a figure of the computational domain. This information is available free of charge via the Internet at http://pubs.acs.org

**Literature Cited**


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