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Model-based interpretation of methane oxidation and respiration processes in landfill biocovers: 3-D simulation of laboratory and pilot experiments

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HIGHLIGHTS

- 3-D model for coupled flow, transport and reactive processes in landfill biocovers.
- Interaction between methane oxidation and respiration.
- Dynamics of gas transport in multicomponent mixtures.
- Interpretation of experimental datasets in laboratory column and pilot setups.
ABSTRACT

Landfill biocovers are an efficient strategy for the mitigation of greenhouse gas emissions from landfills. A complex interplay between key physical and reactive processes occurs in biocovers and affects the transport of gas components. Therefore, numerical models can greatly help the understanding of these systems, their design and optimal operation. In this study, we developed a 3-D multicomponent modeling approach to quantitatively interpret experimental datasets measured in the laboratory and in pilot-scale landfill biocovers. The proposed model is able to reproduce the observed spatial and temporal dynamics of CH₄, O₂ and CO₂ migration in biocovers under different operating conditions and demonstrates the importance of dimensionality in understanding the propagation of gas flow and migration of gas components in such porous media. The model allowed us to capture the coupled transport behavior of gas components, to evaluate the exchange of gas fluxes at the interface between the biocover surface and free air flow, and to investigate the effects of different gas injection patterns on the distribution of gas components within biocovers. The model also helps elucidating the dynamics and competition between methane oxidation and respiration processes observed in the different experimental setups. The simulation outcomes reveal that increasing availability of methane (i.e., higher injection flow rates or higher fractions of CH₄ in the injected gas composition) results in progressive dominance of methane oxidation in the biocovers and moderates the impact of respiration.

Keywords: Landfill biocovers; multicomponent gas transport; methane oxidation and respiration; column and pilot experiments; reactive transport modeling
1. Introduction

Biodegradation of solid waste in landfills leads to the production and release of methane, which is a potent greenhouse gas with a global warming potential 28-36 times higher than that of CO₂ over 100 years (EPA, 2019). At the global level, methane emissions from landfills contribute about 8% to the anthropogenic sources of methane (Blanco et al., 2014). In Europe, recent investigations have shown that the yearly methane emissions from managed landfills is larger than 100 Mt CO₂ equivalent (EEA, 2019). Produced methane at landfill sites should be recovered and utilized as a source of energy (EU, 2018). However, the implementation of this strategy is not feasible for landfills where CH₄ quantity and quality is low. Instead, methane can be either flared or mitigated using bio-based technologies such as biowindows, landfill biofilters, landfill cover soils and compost-based biocovers (Börjesson et al., 2004; Gebert et al., 2011, 2003; Geck et al., 2016; Huber-Humer et al., 2011, 2008; Röwer et al., 2011; Scheutz et al., 2014, 2009). Landfill biocovers have been tested at the laboratory scale and in pilot scale setups where they showed a successful performance in attenuation of CH₄ emissions (Cassini et al., 2017; Mei et al., 2015; Scheutz et al., 2017; Thomasen et al., 2019). In this technology, landfills are covered by a biologically active porous medium like compost in which methanotrophic bacteria convert CH₄ to CO₂. However, in parallel, aerobic degradation of compost by a variety of microorganisms, known as respiration process, can take place in compost biocovers (Scheutz et al., 2011). Both processes compete for oxygen as the electron acceptor and generate CO₂. In immature compost, respiration can limit available O₂ and thus can hamper CH₄ oxidation. Therefore, understanding the relative importance of methane oxidation and respiration processes with respect to O₂ consumption and CO₂ generation is of pivotal importance in compost biocovers.
The interacting gas transport and biochemical processes in a compost biocover can be quantitatively described by multicomponent reactive transport models in porous media. Process-based models provide a framework that integrates flow and transport mechanisms with biogeochemical reactions and are of utmost importance to quantitatively understand reactive transport in porous media (Basirat et al., 2016; Mayer et al., 2002; Molins and Mayer, 2007; Muniruzzaman and Rolle, 2016). The main transport processes occurring in biocovers consist of diffusion and advection in a multicomponent gas mixture. Diffusive transport can be described by Fick’s law or the Maxwell-Stefan equation (Krishna and Wesselingh, 1997). In a binary system, Fick’s law formulated in terms of mass fractions can provide similar predictions to those of the Maxwell-Stefan equation (Taylor and Krishna, 1993). However, in ternary and higher-component systems, the use of Fick’s law for the description of diffusive fluxes was reported to be inadequate, particularly for diffusion-dominated transport (Fen and Abriola, 2004; Sleep, 1998; Thorstenson and Pollock, 1989). Therefore, the Maxwell-Stefan equation is a more suitable choice for the physical description of processes in landfill biocovers where multiple gas components interact.

In addition to the physical processes, biochemical reactions occurring in landfill biocovers can be incorporated into the modeling framework. In a multicomponent system, consumption or production of each component due to biochemical reactions can change the composition of the gas mixture and its main properties, resulting in a direct impact on transport mechanisms. Hence, a coupled description satisfying the dynamics between physical and reactive processes needs to be considered in the modeling framework for landfill biocovers. Reactive and conservative multicomponent transport models have been frequently used in modeling investigations of gas transport in porous media. A few examples include the simulation of CH₄, O₂ and N₂ transport in the vadose zone, modeling O₂ depletion by pyrite oxidation in unsaturated and partially-saturated porous media (Battistel et al., 2019; Binning et al., 2007;
Haberer et al., 2015a, 2015b; Molins and Mayer, 2007; Thorstenson and Pollock, 1989) and the simulation of methane oxidation in landfill soil covers (Bian et al., 2018; De Visscher and Van Cleemput, 2003; Feng et al., 2019; Im et al., 2009; Molins et al., 2008). Despite previous modeling efforts for describing gas transport in landfill covers, the impact of respiration processes on transport of gas components and methane oxidation has received limited attention (Gebert et al., 2011; Watson et al., 1997). The quantitative description of these processes, mainly taking place in compost-based landfill biocovers, is of crucial importance to interpret their complex interactions and to predict the performance of this technology.

Furthermore, previous efforts for modeling landfill biocover systems have been limited to one-dimensional descriptions (De Visscher and Van Cleemput, 2003; Molins et al, 2008). However, 3-D flow fields and non-uniform gas flow paths occur in these systems (Jury and Flühler, 1992), which affect the gas transport and the efficiency of biocovers. In addition, when the surface of a biocover is exposed to an air stream, a feedback effect between the air stream and the surface of the porous medium takes place, which influences the magnitude and direction of gas fluxes particularly at the interface between the free flow and the porous medium (Basirat et al., 2015; Davarzani et al., 2014; Jambhekar et al., 2015; Mosthaf et al., 2014; Smits et al., 2011). Incorporation of these effects in 3-D numerical simulations improves the capability to predict and interpret gas transport in landfill biocovers.

In this study, we propose a process-based modeling approach taking into account multidimensionality and coupled flow and transport effects on the propagation of gas components in biocover systems. The description includes the combined role of reactive processes simultaneously occurring in biocovers: methane oxidation and respiration. The 3-D model is applied to experimental datasets measured in laboratory columns and in a pilot-scale setup. The purpose of the investigation is to test the capability of the proposed modeling approach, based on the dynamic transport of gas components in multicomponent mixtures and
its coupling with biochemical reactions, to reproduce and quantitatively interpret the
experimental observations obtained at different scales and under different operating conditions.

2. Modeling approach

2.1 Governing equations for flow and transport in a biocover

To model flow and transport processes in a biocover, the momentum and continuity equations
for the gas mixture and transport equations for the components have to be solved. Transport in
a biocover occurs due to gas diffusion and advection. The gas diffusion of a component $i$ in
such systems can be described by the Maxwell-Stefan equation, which accounts for diffusion
driven by concentration and pressure gradients. Assuming isothermal conditions, the diffusive
flux can be written (Curtiss and Bird, 1999):

$$
\mathbf{j}_i = -\rho \omega_i \sum_{k=1}^{n} \tilde{D}_{ik} \mathbf{d}_k \quad i = 1, 2, ..., n \quad (1)
$$

where $\mathbf{j}_i$ is the total diffusive flux of the gas component $i$, $\rho$ is the density of the gas mixture,
which can be obtained by the ideal gas law ($\rho = \frac{pM}{RT}$) with $R$ being the universal gas constant
and $T$ the temperature, $\omega_i$ is the mass fraction of the gas component $i$, $n$ is the total number of
components (in this study $n=4$: CH$_4$, O$_2$, CO$_2$ and N$_2$) and $\tilde{D}_{ik}$ is the multicomponent
diffusivity. In Eq. (1), the multicomponent diffusivities ($\tilde{D}_{ik}$) are obtained from the Maxwell-
Stefan multicomponent diffusion coefficients ($D_{ik}$). The latter are the binary diffusion
coefficients of gas components, transformed to the multicomponent diffusivities ($\tilde{D}_{ik}$) through
a matrix inversion operation (Bird et al., 2007). In porous media, the effect of pores on diffusive
fluxes needs to be accounted for by introducing the effective multicomponent diffusivity
calculated as $D_{ik}^{\text{eff}} = \varepsilon D_{ik} \tau$ with $\tau$ being the tortuosity and $\varepsilon$ being the gas-filled porosity. In Eq. (1), $d_k$ is the diffusional driving force, which reads as:

$$d_k = \nabla x_k + \frac{1}{p} [(x_k - \omega_k) \nabla p]$$

(2)

where $p$ is the total pressure and $x_k$ is the mole fraction of gas component $k$, which can be calculated according to the mass fraction:

$$x_k = \frac{\omega_k \bar{M}}{M_k}$$

(3)

where $M_k$ is the molecular weight of gas component $k$ and $\bar{M}$ is the mean molar mass of the gas mixture obtained as:

$$\frac{1}{\bar{M}} = \sum_{k=1}^{n} \frac{\omega_k}{M_k}$$

(4)

In addition to diffusion, gas advection needs to be accounted for in multicomponent transport models. The gas flow in porous media can be described by a combination of Darcy’s law (momentum equation) and the continuity equation. However, to include the influence of the flow near the biocover surface, a coupled free flow and porous medium domain is considered in this model, requiring a description of the flow in both the free flow region and in the porous medium. This can be achieved by applying one set of equations throughout the entire domain without specifying explicit coupling conditions at the interface (Goyeau et al., 2003; Jamet et al., 2009; Mosthaf et al., 2011). Therefore, the Brinkman equation that combines Darcy’s law and Navier-Stokes equation in a single equation can be used as the momentum equation (Le Bars and Worster, 2006):
where the gas-filled porosity \( \varepsilon \) is assumed to be constant and spatially uniform in the biocover, \( \rho \) is the density of the gas mixture, \( \mathbf{u} \) is the velocity, \( p \) is the total pressure, \( \mu_{\text{eff}} \) is the effective gas viscosity, \( \mu_g \) is the dynamic viscosity of the gas mixture and \( k \) is the permeability of the porous medium (assumed to be isotropic in this study). The effective gas viscosity \( \mu_{\text{eff}} \) in this equation is described as \( \mu_{\text{eff}} = \frac{\mu_g}{\varepsilon} \) (Ochoa-Tapia and Whitaker, 1997). When slow gas flow velocities are considered, the inertial term (the second term on the left-hand side) can be omitted. In the porous medium subdomain, \( k \) is small and the Laplacian term (the second term on the right-hand side) becomes negligible in comparison to the last term on the right-hand side, simplifying Eq. (5) to Darcy’s law when considering steady state conditions. In the free flow subdomain, \( k \to \infty \) and \( \varepsilon = 1 \), which means that the last term on the right-hand side can be neglected and Eq. (5) simplifies to Stokes equation. The dynamic viscosity of the gas mixture in Eq. (5) depends on the mixture composition and can be obtained as (Wilke, 1950):

\[
\mu_g = \sum_{i=1}^{n} \frac{x_i \mu_i}{1 + \sum_{j=1}^{n} x_j \varphi_{ij}} \tag{6}
\]

in which \( \varphi_{ij} \) is given as (Wilke, 1950):

\[
\varphi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left( 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j^{1/2}}{M_i^{1/2}} \right) \right)^2 \tag{7}
\]

The gas flow in the porous medium is described by the momentum balance equation (Eq. (5)) and the continuity equation:
where $Q_m$ is the source and sink term.

Considering transport of different components, the mass conservation for component $i$, can be formulated as:

$$
\varepsilon \frac{\partial (\rho \omega_i)}{\partial t} + \nabla \cdot (\rho \omega_i \mathbf{u}) = R_i
$$

where $\rho$ is the density of the gas mixture, $\mathbf{j}_i$ is the diffusive flux of the gas component $i$, $\omega_i$ is the mass fraction of the gas component $i$, $\mathbf{u}$ is the velocity and $R_i$ is the source/sink term of the component $i$. As the summation of mass fractions is equal to 1, Eq. (9) can be solved for $n$-1 component and the mass fraction of $n$th component can be computed as:

$$
\omega_n = 1 - \sum_{i=1}^{n-1} \omega_i
$$

2.2 Reactive processes

The kinetically controlled reactions occurring in compost biocovers can be included in the transport equation by the source and sink term ($R_i$). The oxidation of CH$_4$ can be described by the following reaction:

$$
\text{CH}_4 + 1.5\text{O}_2 \rightarrow 0.5\text{CO}_2 + 1.5\text{H}_2\text{O} + 0.5\text{CH}_2\text{O}
$$
Double Monod kinetics can be used to simulate the consumption of both the electron acceptor and electron donor in this reaction. Therefore, the rate of methane consumption in this reaction can be written as (De Visscher and Van Cleemput, 2003; Molins and Mayer, 2007):

\[
\frac{d\omega_{CH_4}}{dt} = -V_{max} \left( \frac{\omega_{CH_4}}{\omega_{CH_4} + K_{CH_4}} \right) \left( \frac{\omega_{O_2}}{\omega_{O_2} + K_{O_2}} \right)
\]

where \( K_{CH_4} \) is the half-saturation constant of \( CH_4 \), \( K_{O_2} \) is the half-saturation constant of \( O_2 \) and \( V_{max} \) is the maximum \( CH_4 \) oxidation rate. The rate of \( O_2 \) consumption and \( CO_2 \) production in this reaction can be written according to the stoichiometry defined in (11):

\[
\frac{d\omega_{O_2}}{dt} \bigg|_{CH_4\text{ox.}} = -1.5 \frac{d\omega_{CH_4}}{dt}
\]

\[
\frac{d\omega_{CO_2}}{dt} \bigg|_{CH_4\text{ox.}} = 0.5 \frac{d\omega_{CH_4}}{dt}
\]

As the \( CH_4 \) oxidation is mediated by methanotrophic bacteria, the rate of this reaction depends on the growth and decay of bacteria. The change in the rate of this reaction is thus related to the growth and decay of biomass by:

\[
\frac{dV_{max}}{dt} = \mu_{max} \left( 1 - \frac{V_{max}}{V_{max,\text{max}}} \right) \left( \frac{d\omega_{CH_4}}{dt} \right) - (V_{max} a)
\]

where \( \mu_{max} \) is the specific growth rate of biomass, \( V_{max,\text{max}} \) is the highest value of \( V_{max} \) obtained in the biocover and \( a \) is the specific decay rate.

In addition to the methane oxidation, \( O_2 \) consumption and \( CO_2 \) production due to the respiration process need to be specified. We describe the respiration process as the zeroth-order kinetics (Scheutz et al., 2011):
The model description considers that the density and viscosity of the gas mixture are a function of the mixture composition. Furthermore, the density of the gas mixture obtained by the ideal gas law links the flow and transport equations (Eq. (5), Eq. (8) and Eq. (9)). Therefore, any temporal or spatial variation in the mixture composition due to transport of reactive processes, changes the density of the mixture and its viscosity, thereby affecting the flow field and transport behavior of the gas components. These feedback effects between the gas composition, gas flow and transport, and reactions in each time step need to be accounted for by solving the entire set of equations in a coupled manner for conservative as well as reactive transport cases. The respective equations for each case were numerically solved using the partial differential equations solver, COMSOL Multiphysics (Version 5.3a). This tool provides a flexible interface for the discretization and solution of the governing equations based on the finite element method. The flow and transport equations, completed by relevant boundary and initial conditions, were solved in the different domains considered in this study. A non-uniform tetrahedral mesh was used for the discretization of the 3-D domains, and the size of elements was varied to reach mesh-independent solutions. The mesh used for each respective 3-D geometry is show in the Supplementary Material (Figure S1).

For simulation of the reactive flow-through experiments, kinetic parameters were determined from the simulation of laboratory batch tests performed by Thomasen et al. (2019). The batch datasets were modeled with the approach outlined above, considering methane oxidation
\((V_{\text{max}} , K_{CH_4} , K_{O_2})\) and respiration \((k_{\text{resp},O_2} , k_{\text{resp},CO_2})\) kinetic constants as fitting parameters. The parameter fitting was performed in MATLAB using the \textit{lsqnonlin} function (Haberer et al., 2015a; Murray et al., 2019).

3. Benchmark and application problems

The proposed modeling approach was first benchmarked against a dataset measured in a column experiment (De Visscher et al., 1999). A 1-D reactive transport simulation was performed to capture the observed mole fractions of gases in the experiment. Model input parameters, boundary conditions as well as the simulation outcomes of this experiment are described in the Supplementary Material (Section S3 and S5).

Successively, the model was employed to quantitatively interpret conservative and reactive flow-through experiments conducted in a lab-scale compost biocover, which were run in column setups at room temperature (control column and column 1 in Thomasen et al., 2019).

In the conservative cases, a gravel-filled column with 20 cm diameter and 100 cm length was loaded with methane (5% v/v) and air (95% v/v) from a port located at the bottom of the column. Three different flow rates (5 mL/min, 25 mL/min and 50 mL/min) were sequentially tested over a period of 21 days (7 days for each flow rate). The upper part of the column hosted a port through which the column headspace was continuously flushed with a constant airflow of 109 mL/min. The gas outflow occurred through another port symmetrically located 5 cm from the air inflow port at the top of the column. This configuration in the headspace created a mixing zone in the top of the column, which provided a gas mixture similar to the atmospheric composition. The gas composition, including CH\(_4\), O\(_2\) and CO\(_2\), was continuously measured in equally spaced ports along the axis of the column. For the reactive cases, another column with the same configuration, but filled with compost was run. Similar flow rates were applied over
a period of 42 days (14 days for each flow rate) and the samples, continuously taken from an identical configuration of sampling points, were analyzed for CH\(_4\), O\(_2\) and CO\(_2\). The gas analysis in these experiments was performed using a 490 Micro GC (Agilent Technologies, USA) (Thomasen et al., 2019), allowing to reach a relative standard deviation below 0.15%.

Two batch experiments were also performed to assess the reactive processes (i.e., methane oxidation and respiration) in the compost biocover. The two batch experiments were simulated to determine the kinetic parameters of the two reactive processes. The simulation results of these experiments and the related discussions are reported in the Supplementary Material (Section S4). The detailed description of the experiment procedures is given by Thomasen et al., (2019).

Finally, the model was applied to simulate the flow-through experiments conducted in the pilot-scale compost biocover (Fjelsted et al., 2020). The pilot setup is a container with 4.85 m length, 2.4 m width and 2 m height. A distribution layer, consisting of permeable coarse gravel, is placed at the bottom of the container beneath the compost layer. The thickness of the compost layer is 1.2 m, whereas the distribution layer is thinner (0.5 m maximum height) and has a jagged surface with peaks corresponding to the locations of three gas injection lines. Such injection lines consist of hollow tubes with a diameter of 10 cm and length of 4.85 and are equally spaced (0.5 m) within the distribution layer. Three small nylon tubes were attached inside the hollow tubes for the injection of gases. A series of holes drilled on top of the three hollow tubes allowed a continuous and distributed gas release from the attached injection nylon tubes. Nine sampling ports were located in the middle cross section of the container (50 cm spacing) and each of them has six vertical measuring points spaced with 20 cm intervals. The gas composition of samples taken from these 54 points was analyzed on a regular basis for CH\(_4\), O\(_2\) and CO\(_2\). The sampling was performed using multi-port gas samples and IR Biogas 5000 (Geotechnical Instruments, Warwickshire, UK) with a detection accuracy of ±0.5 v/v %
was used for the gas composition analysis (Fjelsted et al., 2020). The pilot setup was run in two experimental campaigns in which different gas compositions with different flow rates were injected into the pilot-setup. In the first experimental campaign, air was injected at the bottom of the setup with a flow rate of 16.2 L/min. This experiment was designed to evaluate the respiration process as no methanotrophic activity was expected due to the absence of CH$_4$ in the gas composition. In the second experimental campaign, the pilot setup was loaded with CH$_4$ (8% v/v), O$_2$ (16.6% v/v) and CO$_2$ (4.2% v/v) where the flow rate was kept constant at around 17 L/min. The objective of this experiment was to assess methane oxidation in presence of active respiration. In both experimental campaigns, the setup was exposed to the atmosphere. More details of the experimental conditions, the sketch of setups as well as the model input parameters for the simulation of the column and pilot-scale flow-through experiments are presented in the Supplementary Material (Figure S1 and Table S2, respectively). Also, Table 1 provides an overview of the respective simulations performed for the lab-scale and pilot-scale experiments.
4. Results and discussion

4.1 Lab-scale setups

4.1.1 Conservative transport

The conservative flow-through experiments conducted in the gravel-filled column were simulated in a 3-D domain consisting of the porous medium and the overlying headspace in which air was recirculated. The outcomes of the 3-D simulations performed at flow rates of 5, 25 and 50 mL/min are shown in Figure 1.

The simulated streamlines in the gravel-filled portion of the column (blue lines) and in the headspace (red lines) describe the flow in the porous medium and in the free flow in the recirculation zone of the experimental setup (Figure 1a-c). The blue streamlines within the porous media are straight and parallel, whereas their pattern changes when they cross the interface and enter the headspace. This is due to the influence of the circulating flow from the top (red streamlines), which drives the blue streamlines toward the outlet of the headspace. The red streamlines show that the flow from the top creates a mixing zone in the headspace, which is affected by the magnitude of the flow from the bottom: it is larger for the lowest flow rate (5mL/min), while it shrinks when the flow from the bottom increases (25 and 50 mL/min). This impacts the migration of the gas components toward the upper part of the column, particularly near the porous medium/free flow interface. This can also be visualized by the simulated 3-D maps of CH₄ mole fractions (Figure 1d-f) that show different distribution of this gas component across the porous medium and at the interface with the free air flow. Steeper CH₄ gradients at the interface can be observed in the experiments with higher flow rates.

Figure 2a-c shows the comparison between the measured and simulated mole fraction profiles of three gas components (CH₄, O₂ and CO₂) in the column setup.
The simulated and measured mole fraction profiles agree very well particularly at the interface, where the model can capture the observed transition behavior between the porous medium and the free flow. The O\textsubscript{2} spatial profiles show a relatively constant value in the entire column for all cases since O\textsubscript{2} was supplied with a similar mole fraction from the top and bottom of the column. The simulated profile of CH\textsubscript{4} in the case of 5 mL/min flow rate shows a gradually decreasing trend, but the pattern changes to steeper curves in the upper part of the domain as the flow becomes stronger (Figure 2a-c). This can be explained by interpreting the contribution of different mechanisms controlling the CH\textsubscript{4} transport at low and high flow rates. Figure 2d-f illustrate the contribution of diffusive and advective transport to the conservative CH\textsubscript{4} displacement. In all cases, the CH\textsubscript{4} diffusive flux increases toward the top of the column, reaching the highest value at the interface. The increase in the diffusive flux of CH\textsubscript{4} is driven by the CH\textsubscript{4} concentration gradient that becomes more pronounced at the interface due to the dilution and removal of CH\textsubscript{4} from the headspace. The CH\textsubscript{4} advective flux decreases in all cases. This is caused by the reduced methane concentration in the upper part of the column, which has a direct effect on the magnitude of the advective flux ($\rho \omega_{CH_4} u$).

For the flow rate of 5 mL/min, the mechanism controlling the CH\textsubscript{4} transport in the column is mainly diffusion. The flux contribution of advection is approximately equal to the diffusion near the injection location, but the diffusive flux becomes progressively stronger toward the upper part of the column. The opposite behavior is observed for the higher flow rates, for which advection is dominant and the diffusive flux significantly increases at the top of the column, close to the interface. The dominance of advection for the higher flow rates leads to the steep curves observed in the CH\textsubscript{4} spatial profiles, while the diffusion-dominated transport for the flow rate of 5 mL/min results in the gradually decreasing CH\textsubscript{4} mole fraction toward the top of the column.
4.1.2 Reactive transport

We simulated the reactive flow-through experiments conducted in the column filled with compost considering the same 3-D geometry as for the conservative experiment. Table 2 summarizes the values of the kinetic and initial parameters obtained with a manual calibration procedure for the different reactive flow-through experiments. Furthermore, the half saturation constants of methane and oxygen (3.80 and 5.27 mmol/L, respectively) derived from the batch tests were used in the reactive transport simulations.

The simulation results for the flow-through reactive transport columns are shown in Figure 3. Panels a-c present the comparison between the measured mole fraction profiles of the three gas components and the outcomes of the reactive transport simulations at the three different flow rates.

In all cases, the model is capable of reproducing the trend and the values of the measured mole fraction profiles. At a flow rate of 5 mL/min, nearly complete methane oxidation occurs in the entire column, and the CH$_4$ mole fraction drops to as low as 0.84 % at the bottom of the column. As the flow rate increases, a higher CH$_4$ flux enters through the bottom, thereby stimulating the methanotrophic activity and resulting in higher methane oxidation. However, a relatively high CH$_4$ mole fraction is observed in the column at the higher flow rates. This indicates that although methane oxidation increases due to the higher availability of CH$_4$, the system cannot fully oxidize the high fluxes of CH$_4$ injected from the bottom of the column.

At the lowest flow rate (5 mL/min), high values of the CO$_2$ mole fractions are observed in almost the entire column, reaching approximately 18% in the bottom part. This reduces as the flow becomes stronger, but high amounts of CO$_2$ are still observed in the column. The model results suggest that the elevated CO$_2$ mole fractions at the three flow rates are mainly attributed to the respiration process, particularly at low flow rates where only a little portion stems from
methane oxidation. This can be analyzed by disentangling the contribution of the two reactive processes from the reaction term of CO$_2$ ($R_{CO_2}$). Figure 3d-f illustrates the spatial profiles and the temporal evolution of the CO$_2$ production rate by methane oxidation at the three tested flow rates. As the observed respiration process follows a zeroth-order kinetics, the values reported in Table 2 are constant in time and space, making them directly comparable with the spatially variable values computed for methane oxidation (Figure 3d-f). At 5 mL/min, even at the bottom of the column where higher CH$_4$ is available for oxidation, the production rate of CO$_2$ at steady state due to CH$_4$ oxidation is as low as 150 gCO$_2$/m$^3$·d (Figure 3a), while the production rate due to the respiration is around four times larger (604.77 gCO$_2$/m$^3$·d)). At the higher flow rates, methane oxidation increases and progressively extends through larger portion of the column. Simulated CO$_2$ production values due to CH$_4$ oxidation up to 270 gCO$_2$/m$^3$·d) at a flow rate of 50 mL/min show a consistent increase but the compost respiration rate remains higher (597.48 gCO$_2$/m$^3$·d)). Thus, these model outcomes indicate the dominance of the respiration process over the course of this experimental campaign (42 days in total). However, the higher availability of CH$_4$ induced by the higher injection flow rates can progressively shift this dominance and activate the methanotrophic bacteria in the system. Oxygen consumption is observed in all experiments, however the diffusion from the top boundary and the continuous supply of O$_2$ by injecting air from the bottom of the column prevented any oxygen limitation to the reactive processes. The maximum consumption of oxygen occurs at the bottom of the column where CH$_4$ is provided and both substrates are available for methane oxidation. The consumption rate of O$_2$ due to methane oxidation can be spatially determined similarly to Figure 3d-f. Methane oxidation is the dominant oxygen-consuming process in the high flow rate columns (25 and 50 mL/min, Figure 3e and f), whereas at the lowest flow rate (5 mL/min) the contribution of respiration to the oxygen consumption is higher.
The mole fraction profiles in these experiments are not only the outcomes of the reactive processes, but they also depend strongly on the transport mechanisms. Thus, further understanding of the observed profiles can be achieved by an interpretation of the transport mechanisms. Figure 4a-f present the simulated diffusive and advective fluxes of CH$_4$ and CO$_2$ in the three cases.

The CH$_4$ advective fluxes show a decreasing pattern toward the top of the column in all tested conditions (Figure 4a-c). The reason is that a high proportion of the CH$_4$ is oxidized prior to reaching the top, which consequently causes a decrease in the methane mole fraction and, thus, in the advective flux ($\rho \omega_{CH_4} u$) toward the interface. In the case of 5 mL/min, diffusion is the main mechanism controlling the upward CH$_4$ migration. Advection, instead, contributes more at the higher flow rates particularly in the bottom part of the column where it is clearly the dominant transport mechanism (Figure 4b and c). The simulated CO$_2$ fluxes show a different pattern, which stems from the interplay of the transport processes and boundary conditions with methane oxidation and respiration. CO$_2$ is not injected from the bottom but is produced in the column and transported upwards by the advective flux. The pattern of the advective flux is non-monotonic due to the CO$_2$ production within the reactor and its negligible concentration at the bottom and top boundaries. The buildup of CO$_2$ concentration in the column also causes interesting patterns of the diffusive fluxes that are strong and oriented upwards in the upper part of the column, close to the porous medium/free flow interface, whereas they show a reverse direction (downwards orientation) in the bottom part of the setup. The depth at which the reversal of the diffusive flux occurs shifts to the upper part of the column as the flow from the bottom becomes stronger (Figure 4e and 4f). This is due to the higher flow rates that cause the upwards movement of the zone where CO$_2$ builds up (Figure 3). Even if diffusion has a negative contribution in the lower portion of the column, the overall CO$_2$ flux remains upwards oriented since advection dominates in this part of the flow-through reactor.
4.2 Pilot-scale setup

In this section we illustrate the outcomes of 3-D simulations for the two flow-through experimental campaigns conducted in the pilot-scale biocover.

In the first experimental campaign, air was injected from the bottom of the pilot-scale setup and the top was exposed to the atmosphere. In this experiment, the injection of O₂ (electron acceptor) in the system activated the respiration process. No methane oxidation occurred since CH₄ was not injected in the system. The 3-D geometry of the pilot reactor, including the three injection lines and the distribution layer at the bottom, was defined in the model setup and the flow and transport equations were solved in this domain. Figure 5a illustrates the streamlines pattern and the computed flow velocity in the pilot-scale system.

A higher gas velocity is observed near the location of the gas injections, which becomes lower toward the upper parts of the setup. The streamlines from the central injection line follow a vertical direction to the top, whereas a lateral deviation of the flow path is observed near the two injection lines located on the sides. This affects the migration of the gas components particularly close to the injection lines. As can be better observed in the 3-D map of CO₂ mole fraction, a higher concentration of CO₂ appears to accumulate close to the side walls where the gas velocity is lower (Figure 5b). This causes a decrease in the advective flux of CO₂ (\(\rho\omega_{\text{CO}_2}u\)) and a buildup of CO₂ concentration, which is particularly pronounced (up to 5.5% v/v) in the upper part and near the side walls of the 3-D setup (Figure 5b).

The comparison between the simulated and measured mole fraction of gases is illustrated in Figure 5c. The measured mole fractions shown in this figure are extracted from the six measuring points vertically located in the center of container (x=2.5 m, y=1.2 m). The agreement between the simulated and measured values is very good. The injected flow rate in this experimental campaign is comparable to the last case of the 50 mL/min column
experiments (i.e., similar specific flow rates) and the calculated respiration rates of CO₂ in these two systems have the same order of magnitude, even though the obtained values for $k_{r,CO_2}$ in the pilot setup shows higher values (Table 2). This could be attributed to the different degree of maturation between the compost material in the two setups (Scheutz et al., 2017).

In the second experimental campaign, CH₄ (8% v/v), O₂ (16.6% v/v) and CO₂ (4.2%) were injected from the bottom of the pilot-scale setup, and methane oxidation and respiration occurred simultaneously. 3-D simulations were performed to capture the spatial distribution as well as the temporal evolution of the gas components over 33 days of this experimental campaign. Figure 6 shows the simulated spatial profiles against the experimental data taken from the nine measuring points at day 33.

Relatively high CH₄ mole fractions are observed in the entire setup after 33 days. This indicates that the injected flux of CH₄ in this experiment is greater than the capacity of the system to completely oxidize CH₄. The simulation outcomes suggest that the CH₄ surface flux emitted from the top of the setup at day 32 is almost 303 g/d, indicating a 80 percent reduction in the injected methane flux (1485 g/d) after 32 days. Relatively high CO₂ mole fractions are observed in the setup, being approximately 5% at the bottom and reaching a maximum of 6.18% in the upper portion of the setup. The model results suggest that the respiration process generates only small CO₂ amounts during the considered experimental duration. This is also quantified by the low respiration rates determined for this experimental campaign, being almost two orders of magnitude smaller than the tested flow rate of 50 mL/min in the column experiment (Table 2). Therefore, the observed CO₂ in this experimental campaign is mainly associated with the CO₂ injection and the methane oxidation. Overall, the model is able to capture the spatial distribution of the different gas components in the domain resulting from the reactive transport processes occurring in the pilot-setup.
Figure 7a-c present the 3-D map of the temporal evolution of methane in the 3-D pilot setup, considering three different times (days 12, 20 and 33) of the second experimental campaign.

The maps show the spatial variations of CH$_4$ in the pilot setup. Higher CH$_4$ mole fractions can be seen near the injection zone, which decreases radially toward the side walls of the container. This radial evolution is induced by the lateral distribution of flow toward the side walls. The comparison between observed and simulated mole fraction of gases at the three different times is shown in Figure 7d-f. The measured mole fractions shown in this figure correspond to the six measuring points vertically located in the center of pilot-setup (x=2.5, y=1.2). It can be observed that little methane oxidation occurs at the beginning but the importance of this process appears to progressively increase at later times. The CO$_2$ mole fraction profiles are relatively similar in the bottom part, but differ in the upper part in which more CO$_2$ is generated by methane oxidation on days 20 and 33. In this simulation of the 3-D pilot setup, the model shows a much lower methanotrophic activity and slower growth of the microbial population in comparison to the column experiments. For instance, in the last case of the lab-scale experiment (the most comparable to this experimental campaign) where the injected flow rate was 50 mL/min, the maximum methane oxidation rate in the column was 160 gCH$_4$/(m$^3$·d) after 10 hours, whereas this value was observed only after 16 days in this experimental campaign in the pilot-scale setup. This could be due to a longer adaptation phase of the methanotrophs resulting in slower methane oxidation rates in the pilot field conditions with respect to the higher rates observed in the more controlled and more favorable conditions (e.g., higher temperature) in the laboratory experiments.
5. Conclusions

In this study, we have proposed a 3-D multicomponent model to quantitatively describe gas transport in a domain composed of a porous medium and a free air flow and to interpret the feedback effects of different physical and bioreactive processes on gas transport in porous media. We focused on landfill biocovers and we simulated different batch and flow-through experiments conducted in laboratory and pilot-scale setups. The good agreement between the measured and simulated concentration profiles of gas components in various conservative and reactive cases demonstrates the capability of the proposed multicomponent model to quantitatively predict the spatial and temporal distribution of gas components in landfill biocovers. In analogy with recent findings in saturated porous media (Rolle et al., 2018; Ye et al., 2015), our study shows the importance of a multidimensional approach to model flow and transport processes. The 3-D description allowed us to understand the influence of non-uniform flow patterns on the propagation of gas components within the porous media. Analyzing the mechanisms controlling gas transport, we also showed that the pattern by which each gas component propagates in the multicomponent systems is coupled to the transport of all gas components in the mixture. Furthermore, the model allowed us to disentangle the relative importance of the methane oxidation and the respiration process in generation of CO2 and consumption of O2 and to quantify the kinetic rates of these two biochemical processes in the laboratory and pilot-scale setups. For instance, the ratio between the generated CO2 due to methane oxidation and respiration in the column-setup reached a maximum of 0.25 when the methane influx was 7.8 g/(m²·d), whereas this ratio increased to almost 0.45 when methane influx was ten times higher (almost 78 g/(m²·d)). The simulations showed that the dynamics of these two biochemical processes, their spatial distribution, and their CO2 production depend on the availability of CH₄, the abundance of methanotrophs, and the interplay with the governing transport mechanisms of advection and diffusion.
The modeling tool developed in this study can be applied to optimize the design of landfill biocovers. For instance, the gas injection rates, as well as the location and pattern of injection points, can be simulated to achieve the best performance of the system. Similarly, the model can be used to determine optimal injection strategies (e.g., composition of the injected gas, oxygen content, flow velocities etc.) that ensure the enhancement of methane oxidation and its dominant role with respect to compost respiration. Also, the model can be further extended to non-isothermal conditions by adding an energy balance equation to account for seasonal temperature variations during long-term operation. Finally, we envision further development and application of the proposed modeling approach to describe gas transport in physically and chemically heterogeneous unsaturated porous media in which spatially distributed permeability, degradation rates and geochemical reactions (Battistel et al., 2019; Fakhreddine et al., 2016; Jung et al., 2011) control the transport, consumption and production of different gases and volatile compounds.
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31


<table>
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<tr>
<th>Test</th>
<th>Problem</th>
<th>Description of key features</th>
</tr>
</thead>
</table>
| 1    | Benchmark problem (De Visscher and Van Cleemput, 2003) | - 1-D reactive transport of CH₄, O₂, CO₂ and N₂ in a soil cover  
- Injection of CO₂ (50 % v/v) and CH₄ (50 % v/v) at the flow rate of 7 mL/min  
- The respiration process was not considered |
| 2    | Lab-scale biocover (Thomasen et al., 2019): conservative experiment | - 3-D conservative transport of CH₄, O₂, CO₂ and N₂ in a gravel-filled column  
- Injection of CH₄ (5 % v/v) and air (95 % v/v) at the flow rates of 5, 25, 50 mL/min  
- Circulation of air at the flow rate of 109 mL/min in the headspace of column  
- The total simulation time was 21 days (7 days for each flow rate) |
| 3    | Lab-scale biocover (Thomasen et al., 2019): reactive experiment | - 3-D reactive transport of CH₄, O₂, CO₂ and N₂ in a compost-filled column  
- Injection of CH₄ (5 % v/v) and air (95 % v/v) at the flow rates of 5, 25, 50 mL/min  
- Circulation of air at the flow rate of 109 mL/min in the headspace of column  
- Concurrent methane oxidation and respiration  
- The total simulation time was 42 days (14 days for each flow rate) |
| 4    | Pilot-scale biocover (Fjelsted et al., 2020): the first experimental campaign | - 3-D reactive transport of O₂, CO₂ and N₂ in a compost-filled container  
- Injection of air at the flow rate of 16.2 L/min  
- Methane oxidation was not considered in the simulations as CH₄ was not injected  
- The total simulation time was 8 days |
| 5    | Pilot-scale biocover (Fjelsted et al., 2020): the second experimental campaign | - 3-D reactive transport of CH₄, O₂, CO₂ and N₂ in a compost-filled container  
- Injection of CH₄ (8 % v/v), O₂ (16.6 % v/v) and CO₂ (4.2 % v/v) at the flow rate of 17 L/min  
- Concurrent methane oxidation and respiration  
- The total simulation time was 33 days |
Figure 1. Simulated streamlines in the column headspace (red lines) and biocover (blue lines) at flow rates of 5, 25 and 50 mL/min (a-c). Simulated 3-D maps of CH$_4$ mole fractions at day 7 for the conservative transport cases at the same flow rates of 5, 25 and 50 mL/min (d-f).
Figure 2. Spatial profiles of the measured versus simulated gas mole fractions at day 7 for the conservative transport cases at flow rates of 5, 25 and 50 mL/min (a-c). Contribution of advective and diffusive fluxes to the conservative transport of methane at the same flow rates of 5, 25 and 50 mL/min (d-f). The zero on the y-axis corresponds to the interface between the porous medium and the free flow.
Table 2. Kinetic parameters fitted to the lab-scale and pilot-sale flow-through experiments

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Lab-scale</th>
<th>Pilot-scale</th>
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<td></td>
<td>5 mL/min</td>
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<td>$V_{\text{max}}$</td>
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<td>$a$</td>
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<tr>
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<td>[gO$_2$/(m$^3$·d)]</td>
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<tr>
<td>$k_{r, CO_2}$</td>
<td>[gCO$_2$/(m$^3$·d)]</td>
<td>604.8</td>
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*a This fitting parameter denotes the initial value for Eq. (15)

b From Amaral and Knowles (1995)
Figure 3. Spatial profiles of measured versus simulated gas mole fractions at day 14 for the reactive transport cases at flow rates of 5, 25 and 50 mL/min (a-c). Spatial and temporal distribution of the CO₂ production rate due to methane oxidation at the flow rates of 5, 25 and 50 mL/min (d-f).
Figure 4. Contribution of advective and diffusive fluxes to the reactive transport of CH$_4$ (a-c) and CO$_2$ (d-f) at flow rates of 5, 25 and 50 mL/min at day 14.
Figure 5. (a) Simulated streamlines and gas velocity in the pilot-scale setup, (b) Simulated 3-D map of the CO₂ mole fraction and (c) spatial profiles of the measured versus simulated gas mole fractions after 8 days of the first experimental campaign in which air was injected into the setup and only respiration occurred in the system. As in the visualization of the lab-scale results, the zero on the y-axis (panel c) corresponds to the interface between the porous medium and the atmosphere.
Figure 6. Spatial profiles of observed and simulated gas mole fractions at the nine sampling points in the 3D pilot setup. The profiles are taken at day 33 of the second experimental campaign in which CH₄, O₂ and CO₂ were injected into the system with a flow rate of 17 L/min from the bottom of the pilot container.
Figure 7. Simulated 3-D maps of CH₄ mole fraction at day 12, 20 and 33 during the second experimental campaign (a-c). Spatial profiles of the simulated versus measured gas mole fractions at the center of pilot-scale setup at corresponding day 12, 20 and 33 of the experimental campaign (d-f).