Building a mechanistic biogeochemical reaction network for upscaling
Characterization of mass transport limitation between regions of hydrolysis and methanogenesis

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1 Introduction
Mechanistic models have been developed to understand longterm landfill emissions and settlement (White et al., 2004; McDougall, 2007). By finding emission/settlement controlling processes with these models, mechanistic boundary conditions can be applied in modeling to enhance predictions. In our research, we focus on finding the mechanistic biogeochemical reaction network that best describes biodegradation within landfills which is considered an important (sub)process in these models. We hope to eventually enhance predictions of longterm emissions and settlement by obtaining a mechanistically complete and fully identifiable biogeochemical reaction network.

Previously, we presented a mechanistic biogeochemical reaction network that optimally described a dataset from a lysimeter experiment in which shredded Municipal Solid Waste (MSW) was anaerobically degraded and leachate was recirculated (van Turnhout et al., 2015). Values from model parameters were taken from 'ideal experiments' published in literature, and the most uncertain parameters were optimized. All optimized parameters were identifiable and were comparable with bandwidths published in literature except for the half saturation constant of methanogenesis. Therefore in order to find a mechanistically complete network, a mass transport limitation was added to the network between regions of hydrolysis and methanogenesis following previous studies (Veeken and Hamelers, 2000; Vavilin et al., 2002). This resulted in a fully identifiable and mechanistically complete reaction network for describing the measured dataset (van Turnhout et al., 2014). This strongly suggests that this biogeochemical reaction network includes all emission controlling reactions for lysimeter scale (with recirculation), and that all rate controlling parameters are identifiable from standard emissions measurements.

In this study, we aim to validate the reaction network with an idealized experiment. We want to show that 1) rate controlling parameters are identifiable from the measured data by inverse modeling, and 2) that this network is able to predict the measured emissions in the experiment given the initial conditions. In the experiment, cabbage is used as substitute for waste, and partial pressures of $CO_2$ and $CH_4$, cumulative production of gas, Volatile Fatty Acid (VFA), $NH_4^+$ and $pH$ are measured. Different mass transport limitation between regions of hydrolysis and methanogenesis are imposed on the system. Once validated, the network can be validated for less ideal systems and eventually be used for upscaling. In this conference proceeding, we present in short the biogeochemical reaction network, our experimental set up and discuss the expected experimental results by forward modeling.

2 Methods

2.1 Biogeochemical reaction network
The mechanistic biogeochemical reaction network is presented in table 1. Hydrolysis and methanogenesis take place in separate regions. In the hydrolyzing region, cabbage is hydrolyzed into Volatile Fatty Acids (VFA), $CO_2$ and $NH_4^+$. VFA is considered as acetic acid. Also, an excess of readily available Calcite is present. Stoichiometry is taken from fully controlled lab experiments (Carducci, 2013). In the methanogenic region, VFA is converted into $CO_2$ and $CH_4$. Furthermore, bacterial decay is considered with a rate that is 5% of the growth rate (Angelidaki et al., 1999). For both regions, the main environmental inhibitions and equilibrium reactions such as speciation,
complexation, precipitation and gas-liquid partitioning are included. Regions are assumed to be perfectly mixed and gas vents when total pressure of the gas phase increases above 1 atm. Mass transport from the hydrolyzing region to the methanogenic region is calculated with equation 1 where $q$ is the flow rate in L d$^{-1}$ and $C^D$ is the concentration of compound $i$. Cabbage, Calcite and bacteria are not transported between the regions. In addition, a bleed stream with the same $q$ from the methanogenic region is considered to keep the liquid phase volume constant. Further details about the reaction network can be found in van Turnhout et al., 2015.

$$R^\text{transfer}_{\text{hyd-meth},i} = q \cdot C^D_i$$ (1)

### Table 1: Complete biogeochemical reaction network that controls emission on lysimeter scale

<table>
<thead>
<tr>
<th>Stoichiometry of total concentrations ($C_T^i$) in kinetic reactions</th>
<th>SOM</th>
<th>VFA</th>
<th>$H_2CO_3$</th>
<th>$NH_3$</th>
<th>$H_2O$</th>
<th>$CH_4$</th>
<th>$N_{meth}$</th>
<th>$H^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolyzing region</td>
<td>$R^F_{hyd}$</td>
<td>-1</td>
<td>0.36</td>
<td>0.28</td>
<td>0.1</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methanogenic region</td>
<td>$R^F_{meth}$</td>
<td>-</td>
<td>-7.86</td>
<td>-7.36</td>
<td>-0.2</td>
<td>0.6</td>
<td>7.36</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$R^F_{(decap)}$</td>
<td>0.5</td>
<td>0</td>
<td>0.2</td>
<td>-0.6</td>
<td>-1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Partial pressures ($p_i$), derived concentrations ($C^D_i$) & inhibitions ($f$)

<table>
<thead>
<tr>
<th>$p_i$</th>
<th>$C^D_i$</th>
<th>$f^\text{SL}_{R,i}$</th>
<th>$f^\text{NC}_{R,i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$(\text{meth},C^D_{\text{VFA}}V^+_{\text{FA}})$</td>
<td>$(\text{meth},C^D_{\text{VFA}}^+)$</td>
</tr>
<tr>
<td>$CO_3^2-$, $NH_3$,$H_2O$</td>
<td>$HVFA_{\text{VFA}}^-$,$VFA_{\text{VFA}}^-$,$\text{CaHCO}_3^-$,$\text{NH}_3$,$\text{Na}^+$,$\text{HCO}_3^-$,$\text{Calcite},\text{Cl}^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$OH^-$,$\text{NH}_4^+,$$CO_3^{2-},\text{CaOH}^+,$$H_2O_2,$$\text{CaVFA}^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A derived concentration is the species of a compound according to the equilibrium reactions.

The inhibitions $f^\text{SL}_{R,i}$ and $f^\text{NC}_{R,i}$ are substrate limitation and non-competitive inhibition respectively where $R$ is the reaction it inhibits and $i$ the derived or total concentrations of the inhibiting compound.

Further details about the reaction network can be found in van Turnhout et al., 2015.

#### 2.2 Experimental setup

A sketch of our laboratory set up is given in figure 1. The hydrolyzing reactor is seeded with shredded cabbage, $CaCO_3$ and additional nutrients. The methanogenic reactor is seeded with sludge from a wastewater treatment plant. All compounds in both reactors are in solution and perfectly mixed. Three pumps control the transport in and out of the reactors: 1) fresh water is transported into the hydrolyzing reactor ($F_1$), 2) liquid is transported from the hydrolyzing reactor to the methanogenic reactor ($F_2$) and 3) water is transported out of the methanogenic reactor ($F_3$). The pumping rate of all three reactors ($q$) is the same. Cabbage is retained in the hydrolyzing reactor and bacteria are retained in the methanogenic reactor by filters. The type of mass transport between the reactors can be seen as 'one way diffusion'. In both reactors p$H$, $NH_4^+$, VFA, $pCO_2$, $pCH_4$ and cumulative produced biogas are measured. Produced gas is collected and total pressure of the gas phase remains atmospheric throughout the experiment.
2.3 Prediction of experiment with biogeochemical reaction network

We predicted the outcome of an experiment with the biogeochemical reaction network. In this experiment, we first inject NaAc in the methanogenic reactor to activate the methanogens. Then after 5 days, the hydrolyzing reactor is seeded with cabbage and the pumps are switched on. Parameters we used in the model are listed in table 2.

Table 2: Parameter bandwidths, initial concentrations and environmental conditions

<table>
<thead>
<tr>
<th>Maximum rates/Henry constants</th>
<th>Initial &amp; environmental conditions</th>
<th>Hydrolyzing reactor</th>
<th>Methanogenic reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{max}}^1$</td>
<td>$K_{\text{inh}}$</td>
<td>$I$</td>
<td>$C_{T(ni)}^{(i)\text{SOM}}$</td>
</tr>
<tr>
<td>0.24</td>
<td>$1 \times 10^{-5}$</td>
<td>2</td>
<td>0.38</td>
</tr>
<tr>
<td>$\mu_{\text{max}}^2$</td>
<td>$K_{\text{H}_4}$</td>
<td>1.2</td>
<td>2.34</td>
</tr>
<tr>
<td>$K_{\text{H}_4}$</td>
<td>$K_{\text{NH}_4}$</td>
<td>0.03</td>
<td>1</td>
</tr>
<tr>
<td>$K_{\text{H}_4}$</td>
<td>$K_{\text{NH}_4}$</td>
<td>1.5 \times 10^{-2}</td>
<td>1</td>
</tr>
<tr>
<td>$K_{\text{H}_4}$</td>
<td>$K_{\text{NH}_4}$</td>
<td>7.14</td>
<td>5 \times 10^{-7}</td>
</tr>
<tr>
<td>$K_{\text{H}_4}$</td>
<td>$K_{\text{NH}_4}$</td>
<td>$2.3 \times 10^3$</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Most uncertain parameter bandwidths which may significantly influence the model results are indicated in bold. Units of maximum rates are in d^{-1}, Henry constants are in L\cdot mol^{-1}, inhibition constants are in mol\cdot L^{-1}, concentrations are in mol\cdot L^{-1}, pressures are in atm, temperature is in K, volumes are in L, and transport rates are in m\cdot s^{-1}. 1) Veeken and Hamelers, 1999. 2) estimated based on the method developed by Kleerebezem and van Loosdrecht, 2010 3) Siegrist et al., 2002 4) Meima et al., 2008 5) assumed within realistic range. 6) Atkins and de Paula, 2011. 7) Approximately 0.38 $\text{mol kg}^{-1}$ is released by 35 g cabbage in 100 ml. 8) At the beginning of the experiment 0.05 M NaAc and 0.01 M NH$_3$ is injected in the methanogenic reactor. 9) Sludge from the wastewater treatment plant is assumed to have concentrations of methanogens 10) Set in excess.

3 Results & Discussion

Expected emissions in the experiment modeled with the biogeochemical reaction network are presented in figure 2. The red and blue lines represent experiments with respectively pumping rates ($q$) of 0.0144 $\frac{L}{s}$ and 0.00144 $\frac{L}{s}$. Because of transport limitation, concentrations of $VFA$, $H^+$ and $NH_4^+$ build up in the hydrolyzing reactor. A lower transport rate results in higher concentrations. Consequently, hydrolysis becomes partly inhibited and most...
inhibited with the lowest transport rate. The cumulative produced biogas is a direct measure of the hydrolysis rate. The presence of CaCO$_3$ prevents the pH to decrease to very low values which would severely slow down the biodegradation.

In the methanogenic reactor, rates of biogas production are high during the first 5 days because of the injection of NaAc. After this period, the mass transport rate limits the supply of substrate and therefore the biogas production. The slope of the approximately linear part of the cumulative biogas curve is proportional to the mass transport rate: a lower transport rate results in a slower biogas production. Biogas production is not limited by the concentration of bacteria because all entering VFA is immediately consumed. Furthermore, we see that NH$_4^+$ concentration may build up or decrease depending on the transport rate.

Modeling of the experiment before hand helps to optimize experimental design. For instance, the model showed that addition of CaCO$_3$ would keep the duration of the experiment within reasonable lengths. It also indicated that washout of methanogens needs to be prevented to keep their activity sufficiently high. After the experiment, we want to apply inverse modeling to the measured data to test the reaction network and the identifiability of biodegradation controlling rates such as hydrolysis and mass transport. Furthermore, we want to investigate the accuracy of model prediction given the initial conditions and the uncertainty of the identified parameters. If validated for the idealized case, and shown to reproduce data on lysimeter scale we believe this network improves predictions of longterm emissions and settlement when used in upscale models. In a follow up study, it may even be tested for identification of the initial amount of solid organic material from measured data by inverse modeling.

![Figure 2: Modeled emissions for both reactors for different $q$](image)

**References**


A generic transport-reactive model for simulating microbially influenced mineral precipitation in porous medium

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1 Introduction

The spatial and temporal distribution of precipitated minerals is one of the key factors governing various processes in the subsurface environment, including microbially influenced corrosion (MIC) (Huang, 2002), bio-cementation (van Paassen et al., 2010) and sediment diagenesis (Paraska et al., 2014). The mineral precipitation not only affects the overall reaction network (Konhauser, 1997), but is also physically interconnected with the transport properties of the subsurface environment (Pintelon et al., 2012). The presence of bacteria in the subsurface greatly influences the processes of mineral precipitation (Konhauser, 1997). We apply mathematical modeling to investigate the microbially influenced mineral precipitation process under various environmental conditions. The boundary concentrations of different solutes and the distance between the boundaries are considered to have a dominant effect on the magnitude and position and width of precipitated minerals (Gebrehiwet et al., 2014).

We study the mineral precipitation induced by MIC, a process that can be interpreted as a double diffusion mixing mineral precipitation process as shown in figure 1.1. The occurrence of biocorrosion releases metallic ion from the metal surface and creates a concentration gradient of metallic ions towards the reaction region. Released metallic ions react with existing anions, for instance carbonate, and induce a concentration gradient of anions from the distant boundary to the reaction region. The concentrations of anions at the distant boundary is continuously recharged by groundwater. Meanwhile, the concentration of metallic ions at the metal surface is maintained by the metal corrosion. The concentration gradients lead to molecular diffusion from both metal surface and distant boundary towards the reaction region, and result in mineral precipitation. Two functions of bacteria are distinguished in MIC induced mineral precipitation: influence of biocorrosion and formation of biomass. The effects of bacteria in the double diffusion configuration are implicitly included in the iron corrosion boundary, and the biomass formation is explicitly employed in the reaction region as shown in Figure 1.1.

In terms of unlined landfills, the leakage of inorganic and organic pollutants can be interpreted as a diffusion boundary while the recharge of groundwater is treated as the other diffusion boundary. Similarly, the same double diffusion configuration can be applied to investigate the landfill leachate related mineral precipitation with the inclusion of microbial activities. The removal of heavy metals via mineral precipitation, on the one hand, helps to purify the contaminated groundwater and soil; on the other hand, the solid mass accumulation can be served as a clogging mechanism to reduce the leachate flow.

With the aid of our model, we obtain a more comprehensive insight into the relations between the development of microbially influenced mineral precipitation and the environment conditions.