Investigating the impact of process parameters on aeration of MSW via a mechanistic biogeochemical reaction model

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1 Introduction

Recent studies have presented aeration as a promising method to reduce emission potential of Municipal Solid Waste (MSW) within a shorter time frame than anaerobic digestion (Erses et al., 2008; Rich et al., 2008; Ritzkowski et al., 2006; Brandstätter et al., 2015). These studies show that during aeration degradable organic carbon degrades faster, ammonium concentration in leachate rapidly decreases and methane emissions are reduced. These effects are very beneficial for landfill operators. However, in order to implement and optimize this treatment method a more detailed description of the mechanistic reaction network controlling aerated degradation would be useful. For instance, a mechanistic reaction network model could provide insight in 1) the optimal flow pattern (e.g., continuous or intermittent flow) for enhanced degradation, 2) the impact of aeration on N_2O and heavy metal emissions, 3) the impact of adding carbon sources to the leachate during recirculation or 4) emission patterns after aeration (combining aerobic and anaerobic reaction networks). In general, these aspects are difficult to investigate experimentally and therefore a model would be a more efficient and faster option for investigation. In the end, the observed modeled observations can be validated by detailed targeted final experiments.

The aim of our study is to investigate previously mentioned aspects with scenario analyses via a mechanistic biogeochemical reaction network model that contains the emission controlling reactions. In order to find such a network, we apply the gray modeling toolbox developed by van Turnhout et al. (2015) on a measured dataset used in the study of Brandstätter et al. (2015). This dataset contains time series of cumulative production of CO_2, partial pressure of CO_2 and O_2, pH, NH_4^+, SO_4^{-2}, Cl^- and NO_3^- measured during aeration of columns filled with MSW. The toolbox allows to find a reaction network that optimally describes this dataset based on a set of quantitative selection criteria. Consequently, the found reaction network and investigated scenario's will be validated in lysimeter scale. In this conference proceeding, we present preliminary results about the biogeochemical reaction network that optimally describes the measured data.

2 Methods

The gray modeling toolbox developed by van Turnhout et al. (2015) allows to find a controlling mechanistic biogeochemical reaction network optimally describing the measured dataset used in the study of Brandstätter et al. (2015). Based on a set of quantitative criteria, the optimal reaction network can be selected from iterations over several reaction networks. A network is judged on the largest set of identifiable parameters, the lowest total model error and standard deviation of model error per dataset, and most optimized parameter bandwidths that fall within ranges of 'ideal experiments' published in literature. These properties are derived from the probability density distributions (pdd) resulting from parameter optimization within a Bayesian stochastic framework. The optimal reaction network has the best combination of these criteria.

Given the experimental conditions, we sketch a biogeochemical framework in which reaction networks are tested. We assume that degradation of solid organic matter (SOM) starts with a hydrolyzing step where glucose, NH_3 and H_2SO_4 are released into the leachate. Subsequently, glucose is converted into CO_2 by aerobic degradation and NH_4^+

Table 1: Parameter bandwidths, initial concentrations and environmental conditions

Maximum rates/Henry constants		Inhibitions	K_{inh}^3	l	Initial & environmental conditions			
μ_{hyd}^{max1}	**0.09 − 0.26**	$f^{SL}_{(O_2,C_{glu}^T)}$	1×10^{-3}	-	$C_{SOM_{ae}}^{T(ini)}$	3	$C_{Ca^{+2}}^{T(ini)5}$	1
$\mu_{O_2}^{max2}$	**1.49**	$f^{SL}_{(O_2,C_{NH_3}^T)}$	1×10^{-4}	-	$C_{glu}^{T(ini)}$	0	$C_{N_2}^{T(ini)6}$	-
μ_{nitr}^{max2}	**0.40**	$f^{SL}_{(nitr,C_{H_2CO_3}^T)}$	1×10^{-3}	-	$C_{H_2CO_3}^{D(ini)}$	$1\times10^{-1.9}$	$C_{Cl^-}^{T(ini)}$	0.03
μ_{denitr}^{max2}	**1.51**	$f^{SL}_{(nitr,C_{NH_3}^T)}$	1×10^{-5}	-	$C_{NH_3}^{T(ini)}$	0.028	pH	7.2
K_{H,CO_2}^4	0.03	$f^{SL}_{(denitr,C_{NO_3^-}^T)}$	**1×10^{-3}**	-	$C_{SO_4^{-2}}^{T(ini)}$	0	V_l	32
K_{H,CH_4}^4	1.5×10^{-3}				$C_{H_2O}^{T(ini)}$	55.6	V_g	30
K_{H,NH_3}^4	71.4	Stoichiometric coefficients			$C_{O_2}^{T(ini)}$	0	p_{tot}	1
K_{H,O_2}^4	0.0013	$s^3_{NH_3,hyd}$	**0.001 − 0.1**		$C_{X_{O_2}}^{T(ini)3}$	**0.001**	T	308.5
K_{H,H_2O}^4	2.3×10^3	$s^3_{SO_4^-,hyd}$	**0.001 − 0.1**		$C_{X_{nitr}}^{T(ini)3}$	**0.001**	F_{gas}^{in}	56.67
K_{H,N_2}^4	6.1×10^{-4}				$C_{X_{denitr}}^{T(ini)3}$	**0.001**	F_{water}^{in7}	0.12
					$C_{NO_3^-}^{T(ini)}$	0		

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 $\frac{L\cdot atm}{mol}$, inhibition constants are in $\frac{mol}{L}$, concentrations are in $\frac{mol}{L}$, pressures are in atm, temperature is in K, volumes are in L, and flows are in $\frac{L}{d}$. 1) Veeken and Hamelers, 1999. 2) estimated based on the method developed by Kleerebezem and van Loosdrecht, 2010 3) assumed within realistic range. 4) Atkins and de Paula, 2011.
5) Set in excess and readily available given the high alkaline potential of MSW. 6) N_2 in gas phase is set as fill up gas given the initial conditions, and N_2 in the liquid phase is set accordingly. 7) Estimated based on the dilution of Cl^-.

is converted into NO_3^- by nitrification and further reduced into N_2 by denitrification. Furthermore, bacteria are influenced by bacterial biomass decay with a maximum rate that is 5% of the growth rate and substrate limitation. Besides the biochemical reactions, all other reactions such as speciation, complexation, precipitation and mass transfer between the liquid and the gas phase are assumed to be in equilibrium. The characteristics of the main salts can be represented by Ca^{+2} and Cl^-, and an excess of $Calcite$ is assumed to be readily available given the high alkaline potential of MSW. The system is described as perfectly mixed batch because leachate was recirculated through shredded MSW. A gas flow in/out is present and a water flow in is considered to account for the dilution of the concentrations in the leachate.

Initial concentrations ($C_i^{T(ini)}$), maximum rates (μ_j^{max}), substrate limitations ($f^{SL}_{(j,C_i^{inh})}$), flows (F_{phase}^{in}), reactor temperature (T), total pressure of gas phase (p_{tot}), volume of liquid phase (V_l) and volume of gas phase (V_g) are listed in Table 1 where i represents compounds and j represents reactions. Values are taken from the measurements or from 'ideal case experiments' published in literature or estimated within realistic ranges. The most uncertain parameters that may significantly influence the model results are indicated in bold.

3   Results & Discussion

The biogeochemical reaction network we found that best describes the data is presented in Table 2. Stoichiometry is estimated following the method developed by Kleerebezem and van Loosdrecht (2010), except for the stoichiometric coefficients of NH_3. and SO_4^{-2} in the hydrolysis reaction. These coefficients were optimized and their mean values are given. Optimization indicates that hydrolysis of $1\,Cmol$ of SOM released $0.008\,mol\,NH_3$ and $0.066\,mol\,H_2SO_4$ given the reaction network.

Table 2: Kinetic reactions, inhibitions and equilibrium reactions of the reaction network

Stoichiometry of total concentrations (C_i^T) in kinetic reactions

	SOM	$C_6H_{12}O_6$	H_2CO_3	NH_3	H_2O	H^+	X_{O_2}	O_2	SO_4^{-2}	NO_3^-	X_{nitr}	X_{denitr}	N_2
R_{hyd}^F	-1	0.167	-	$\mathbf{0.008}$	-0.167	0.132	-	-	$\mathbf{0.066}$	-	-	-	-
$R_{O_2}^F$	-	-0.23	0.41	-0.2	1.01	-	1	-0.41	-	-	-	-	-
R_{nitr}^F	-	-	-1	-2.38	1.78	2.18	-	-3.35	-	2.18	1	-	-
R_{denitr}^F	-	-	0.55	-	1.01	-0.32	-	-	-	-0.32	-	1	0.059
$R_{X_{O_2}}^{F(decay)}$	-	0.166	-	0.2	-0.6	-	-1	-	-	-	-	-	-
$R_{X_{nitr}}^{F(decay)}$	-	0.166	-	0.2	-0.6	-	-	-	-	-	-1	-	-
$R_{X_{denitr}}^{F(decay)}$	-	0.166	-	0.2	-0.6	-	-	-	-	-	-	-1	-

Partial pressures, derived concentrations & inhibitions

p_i	$N_2; CO_2; NH_3; H_2O; O_2$
C_i^D	$H^+; H_2CO_3; NH_4^+; H_2O; NH_3; CO_3^{-2}; HCO_3^-; OH^-; SO_4^{-2}; HSO_4^-; Cl^-; Ca^{+2}; Calcite; NO_3^-$
f	$f_{(O_2, C_{C_6H_{12}O_6}^T)}^{SL}; f_{(O_2, C_{NH_3}^T)}^{SL}; f_{(nitr, C_{H_2CO_3}^T)}^{SL}; f_{(nitr, C_{NH_3}^T)}^{SL}; f_{(denitr, C_{SOM}^T)}^{SL}; f_{(denitr, C_{NO_3^-}^T)}^{SL}$

Stoichiometry of kinetic reactions is estimated following the method of Kleerebezem and van Loosdrecht (2010), except $s_{NH_3}^{hyd}$ and $s_{SO4^{-2}}^{hyd}$ which are optimized. Ca^{+2} and Cl^- are inert compounds.

In Figure 1, the model results (in red) with the lowest total error are presented together with the measured data (in blue). The found network can reproduce the trends of the measured emissions with reasonable accuracy. The bandwidths of its optimized parameters, listed in Table 3, are in agreement or close to values from published in literature. All parameters are identifiable indicated by the relatively low standard deviations. These results suggest that the network is close to mechanistic correctness. However, further fine tuning of the network is necessary. The discrepancy between the modeled and measured pCO_2 in the beginning of the experiment is probably caused by a fast hydrolysis step which is not included in the network. A new optimization will be performed including two hydrolysis reactions. Furthermore, the maximum rates of (de)nitrification are low suggesting that these parameters compensate for a limitation missing in the network. Interestingly, the transport of O_2 from gas to liquid phase does not seem to limit biodegradation indicated by the high values of the maximum rate of aerobic degradation.

Based on these results, we believe that the reaction network is getting close to a mechanistic complete and identified description of the system to be used for scenario analyses within reasonable accuracy. A first scenario that would be interesting to investigate is the impact of different patterns of air flow on the biological activity. For instance, intermittent flow could be preferred because of lower costs when the analysis indicates that it does not decrease the efficiency of aerobic degradation and (de)nitrification compared to continues flow. Another interesting scenario would be to investigate the emission patterns after aeration by combining identified aerobic and anaerobic reaction networks.

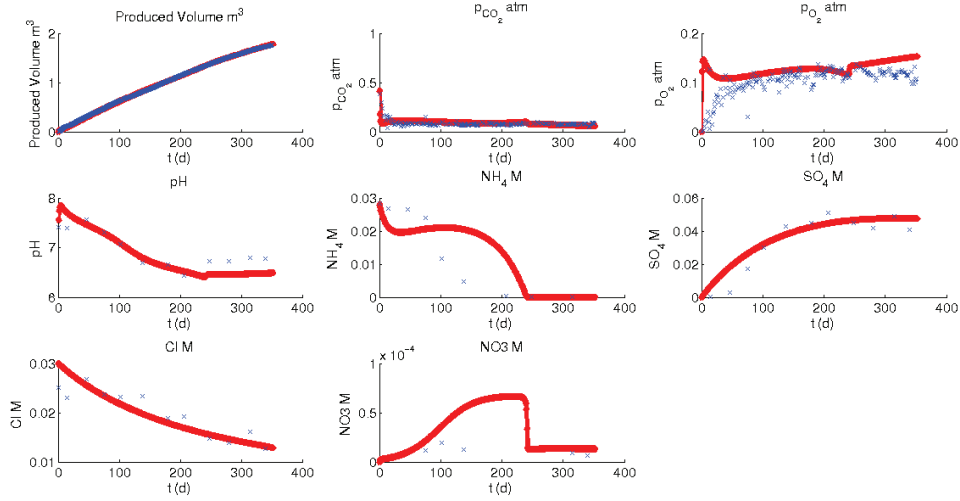Figure 1: Measured data and optimized model results

Fig 1: Modeled data is presented in red and measured data in blue. Produced volume in the top left graph is the cumulative produced volume of CO_2 in the gas phase at atmospheric pressure and $35.5\,^{o}C$ (reactor temperature).

Table 3: Mean and standard deviation of the optimized parameters

μ_{hyd}^{max}		$\mu_{O_2}^{max}$		μ_{nitr}^{max}		μ_{denitr}^{max}		$C_{X_{O_2}}^{T(ini)}$		$C_{X_{nitr}}^{T(ini)}$		$C_{X_{denitr}}^{T(ini)}$	
μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
0.0025	4×10^{-5}	4.68	0.51	0.02	0.0027	0.39	0.16	9	4.8	0.12	0.04	4.3	2.2

$s_{NH_3}^{hyd}$		$s_{SO_4^{-2}}^{hyd}$		$K_{inh,NO_3^-}^{denitr}$	
μ	σ	μ	σ	μ	σ
0.008	0.005	0.066	0.011	0.18	0.11

Units of maximum rates are in d^{-1} and units of initial concentrations and half saturation constants in mM.

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