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Theoretical Analysis of Municipal Solid Waste Treatment by Leachate Recirculation under anaerobic and aerobic Conditions

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Abstract

Long-term emissions of Municipal Solid Waste (MSW) landfills are a burden for future generations because of the required long-term aftercare. To shorten aftercare, treatment methods have to be developed that reduce long-term emissions. A treatment method that reduces emissions at a lysimeter scale is re-circulation of leachate. However, its effectiveness at the field scale still needs to be demonstrated. Field scale design can be improved by theoretical understanding of the processes that control the effectiveness of leachate recirculation treatment. In this study, the simplest and most fundamental sets of processes are distilled that describe the emission data measured during aerobic and anaerobic leachate recirculation in lysimeters. A toolbox is used to select essential processes with objective performance criteria produced by Bayesian statistical analysis. The controlling processes indicate that treatment efficiency is mostly affected by how homogeneously important reactants are spread through the MSW during treatment. A more homogeneous spread of i.e. oxygen or methanogens increases the total amount of carbon degraded. Biodegradable carbon removal is highest under aerobic conditions, however, the hydrolysis rate constant is lower which indicates that hydrolysis is not enhanced intrinsically in aerobic conditions. Controlling processes also indicate that nitrogen removal via sequential nitrification and denitrification is plausible under aerobic conditions as long as sufficient biodegradable carbon is present in the MSW. Major removal pathways for carbon and nitrogen are indicated which are important for monitoring treatment effectiveness at a field scale. Optimization strategies for field scale application of treatments are discussed.

Keywords: Municipal Solid Waste treatment, leachate recirculation, aeration, fundamental biogeochemical model, optimisation

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31 1. Introduction

32 A major challenge for this human generation is to develop treatment methods that reduce long-term
33 emissions from Municipal Solid Waste (MSW) landfills. Because landfills can emit gas and leachate for
34 hundreds of years (Belevi and Baccini, 1989), they pose a risk for human health and the environment.
35 Long-term aftercare is required which puts a burden on future generations.

36 Reduction of long-term emissions can be achieved by accelerating degradation within a waste-body
37 (Scharff et al., 2011) which is normally slow due to inhibitions and transport limitations (Kjeldsen
38 et al., 2002, Laner et al., 2011, Meima et al., 2008). Enhanced degradation leads to accelerated release
39 of carbon and nitrogen containing compounds. In the case of methane, accelerated release is also
40 economically attractive because this gas can be utilized as an energy source.

41 Treating MSW by recirculating leachate under anaerobic or aerobic conditions has shown to ac-
42 celerate emissions in experiments at a lysimeter scale (Veeken et al., 2000, Kasam et al., 2013, Erses
43 et al., 2008, Brandstätter et al., 2015a,b, Bilgili et al., 2007). By inducing (increased) water flow,
44 leachate recirculation stimulates mixing of solutes and bacteria within the waste body which removes
45 inhibitions and transport limitations for degradation (White et al., 2011). Dissolved compounds in
46 the leachate are furthermore removed by bleeding of the leachate stream. Normally, the enhanced
47 consumption of readily available electron acceptors leads to strictly anaerobic conditions.

48 In order to generate (partly) aerobic conditions, leachate recirculation can be combined with aera-
49 tion (Ritzkowski and Stegmann, 2012). This has two main advantages: aerobic degradation is generally
50 faster than anaerobic degradation (Heijnen and Kleerebezem, 1999) and ammonium can be removed
51 by oxidation to nitrogen gas via subsequently nitrification and denitrification (Bolyard and Reinhart,
52 2016).

53 Although effective in enhancing biodegradation, full-scale application of leachate recirculation or
54 aeration has not yet been proven to reduce long-term leached emissions (Benson et al., 2007, Hrad et al.,
55 2013). Apparently, the understanding of processes that control the effectiveness of these treatments is
56 insufficient and needs to be improved. We believe that a good point to start is to revisit data obtained
57 in lysimeter experiments and to distill the simplest, most fundamental biogeochemical process networks
58 that explain the measured emissions.

59 A fundamental model that is as 'simple' as possible highlights the controlling processes, reactions
60 and factors that drive (measured) emissions. It allows to identify major and minor degradation and
61 transport pathways and rate-limiting factors. Moreover, such a model provides insight in any specific
62 mass balance which is not directly measured in the context of the processes, inhibitions and limitations.
63 The challenge, however, is to identify which combination of fundamental processes are least ambiguous

64 (or subjective) and contain minimal uncertainty. We use the toolbox developed by Van Turnhout et al.
65 (2016) to find the most simplistic and best describing fundamental model; it allows to integrate several
66 environmental frameworks, quickly build different models and compare performances objectively with
67 a set of qualitative and quantitative criteria.

68 This paper presents the least ambiguous biogeochemical process networks that are responsible
69 for the emissions measured in lysimeter experiments performed by Brandstätter et al. (Brandstätter
70 et al., 2015a,b). With these networks, the processes and factors controlling the effectiveness of the
71 applied anaerobic and aerobic leachate recirculation treatment are discussed. Major and minor removal
72 pathways for carbon and nitrogen compounds are presented. Implications of the findings for full-scale
73 treatment design are given together with suggestions for improvement.

74 **2. Material & Methods**

75 *2.1. Characteristics of the lysimeter experiments*

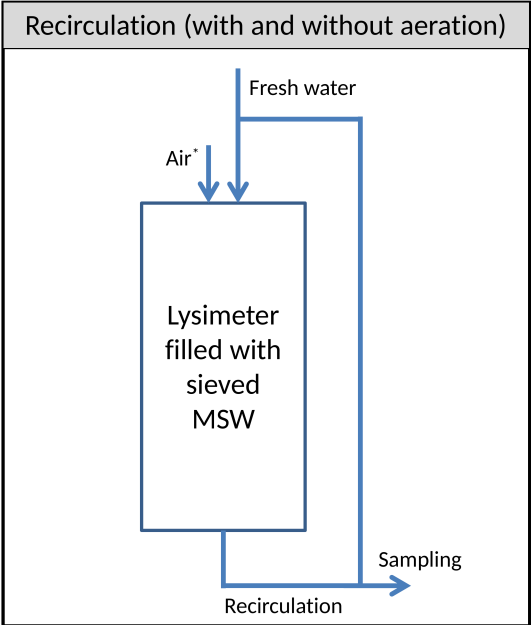
76 For this study we used the data measured in two lysimeter experiments of Brandstätter et al.
77 (2015a,b). In both experiments leachate was recirculated and the temperatures in the lysimeters were
78 kept constant ($\sim 309\text{K}$). To allow for drainage of leachate by gravity, a fine meshed grid of 8cm was
79 placed at the bottom of the reactors. Leachate removed during sampling was replaced with distilled
80 water (Aqua dest) to maintain the degree of water saturation.

81 In one experiment the conditions were anaerobic and in the other (partly) aerobic due to continuous
82 injection of air. The experiments were carried out in duplicate on MSW which was mined from a
83 landfill where operations stopped 40 years ago. The MSW was sieved to a grain size of < 20 mm. In
84 the reactors, the MSW had initially a water content of 23% and a dry bulk density of $846 \frac{\text{kg}}{\text{m}^3}$. An
85 illustration of both set-ups is presented in figure 1 and the initial and environmental conditions are
86 listed in table 1.

87 From each experiment, the following time series are used which were measured over 2.25 years:
88 cumulative produced biogas (CO_2 and CH_4), partial pressure of CO_2 , CH_4 and O_2 , pH, Biological
89 Oxygen Demand (BOD), NH_4^+ and Cl^- concentrations. One time series of each experiment was
90 used for calibration and the other for validation. The calibration dataset was used to find the least
91 ambiguous process network with the toolbox developed by van Turnhout et al. (2016). Subsequently,
92 the network was tested on the validation dataset without further parameter fitting.

93 Although the MSW was mined from a 40 year old landfill, it contained a significant percentage of
94 readily degradable organic content such as cellulose (Brandstätter et al., 2015a). This can be explained
95 by the heterogeneity of landfill bodies which can cause many types of local limitations and inhibitions
96 on the degradation of its organic content.

97 In order to arrive at a generic modeling framework, average compositions of the biodegradable frac-
 98 tion of Solid Organic Matter (SOM) of $C_6H_{10}O_5N_{0.036}$ and $C_6H_{10}O_5N_{0.032}S_{0.03}$ are used for respec-
 99 tively the anaerobic experiment and the aerobic experiment following generic principles of anaerobic
 100 digestion modeling ((Batstone et al., 2002, Reichel et al., 2007)). The fractions of nitrogen and sulfur
 101 are deduced from the fractions measured in the MSW at the beginning and the end of the experiment.
 102 Because sulfur was not significantly detected under anaerobic conditions, it was not considered in the
 103 model. Most likely, the released sulfur under anaerobic conditions was immediately converted into
 104 H_2S . For generic purposes, BOD is assumed to consist of Acetic Acid which accumulates strongest
 105 when methanogenesis is rate-limiting. The elemental composition of bacteria of $CH_{1.4}O_{0.4}N_{0.2}$ is taken
 106 from Henze et al. (1995).



* Only in case of aeration

Figure 1: Illustration of the experimental set-ups for leachate recirculation under anaerobic and aerobic conditions (Brandstätter et al., 2015a,b). The lysimeters were made of stainless steel and had a cylindrical shape with a volume of 121 L.

Table 1: Initial and environmental conditions in the duplicate experiments.

Type of experiment	Initial conditions						Environmental conditions					
	pCO_2	PO_2/PCH_4	NH_3	pH	Cl^-	V_{liquid}	$\phi_{\text{waterflow}}^{\text{in1}}$	$\phi_{\text{sampleflow}}^{\text{out1}}$	$\phi_{\text{airflow}}^{\text{in}}$	V_{gas}	$p_{\text{gas}}^{\text{tot}}$	T
	[atm]	[atm]	[M]	[-]	[M]	[L]	[L d ⁻¹]	[L d ⁻¹]	[L d ⁻¹]	[L]	[atm]	[K]
Anaerobic (calibration)	0.10	0	0.03	8	0.025	19.5	0.03	0.03	-	41.9	1	308.5
Anaerobic (validation)	0.10	0	0.03	8	0.025	19.5	0.03	0.03	-	41.9	1	308.5
Aerated (calibration)	0.41	0	0.025	7.25	0.025	21.24	0.0524	0.0483	56.67	38.8	1	308.5
Aerated (validation)	0.41	0	0.025	7.25	0.025	20.95	0.0526	0.0491	56.67	38.82	1	308.5

1) The flows of water are averaged over the entire measurement period. After the first week, the MSW reached field capacity and flows were relatively constant.

107 2.2. Selecting the least ambiguous biogeochemical process network to describe measured data

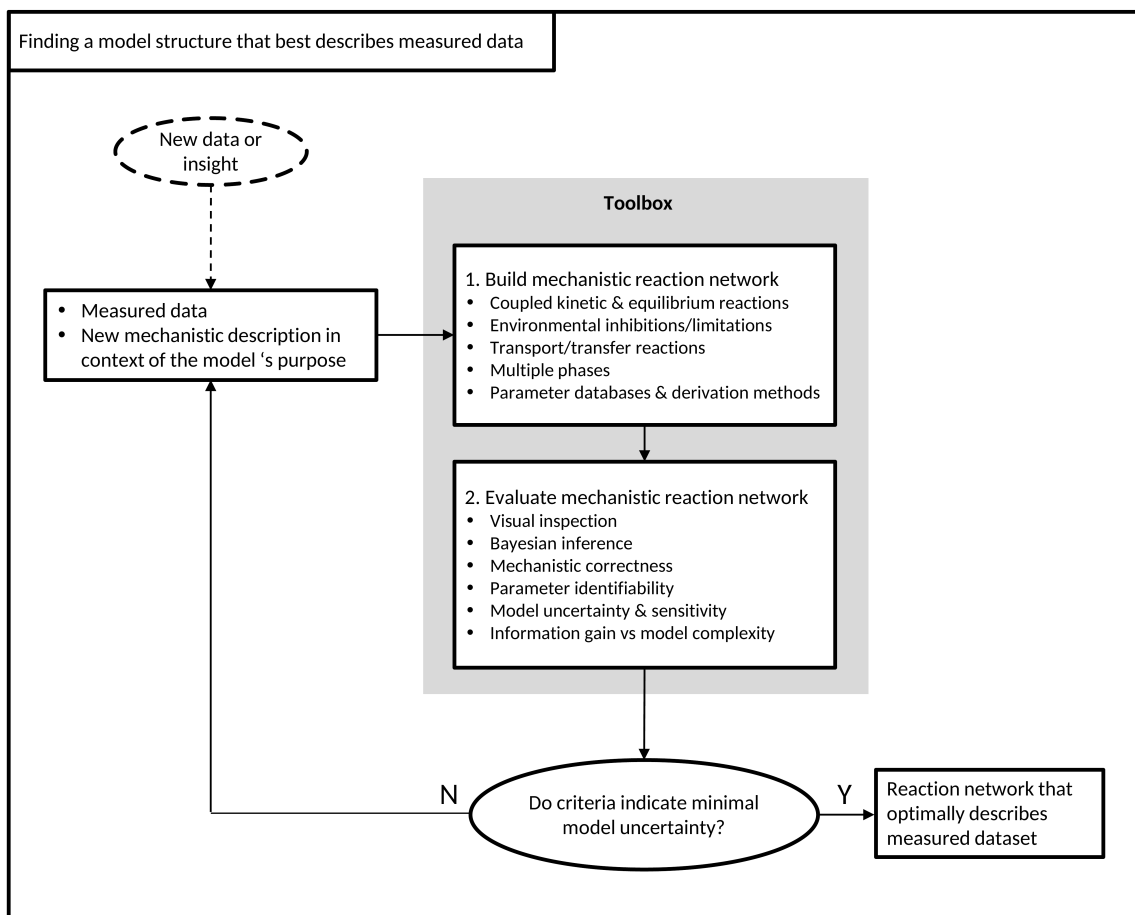


Figure 2: Iterative procedure for finding the biogeochemical process network that describes measured data with minimal ambiguity and uncertainty (van Turnhout et al., 2016). In step 1, the user manually builds the best network with the toolbox which is automatically optimized for the measured data in step 2. The user then decides if the network describes the measurements sufficiently accurate with the evaluation criteria generated in step 2. If not, the user starts another iteration and adapts the network.

108 Figure 2 shows the approach to select the least ambiguous biogeochemical process network describ-
109 ing the measured data (van Turnhout et al., 2016). First, a model structure is build to be evaluated.
110 Relevant kinetic, equilibrium, transfer and transport reactions within a multiphase environment are
111 selected together with appropriate environmental inhibitions and limitations. Fundamental param-
112 eters can be obtained from an extensive geochemical database and a method to derive biochemical
113 parameters from thermodynamic principles (Kleerebezem and van Loosdrecht, 2010). Then, the prob-
114 ability distribution functions (pdf) of the most uncertain parameters are obtained by fitting modeled
115 data to the measured data. Pdfs are obtained with a Bayesian statistical optimization method and
116 allow to evaluate the performance of the network with an extensive set of qualitative and quantitative
117 criteria. Finally, model performance is assessed with these criteria which reveals if model uncertainty
118 and ambiguity is small enough to be acceptable. If this is not satisfactory, a next iteration can be
119 started with an alternative biogeochemical process network selected by the user.

120 In this study, three criteria were used to evaluate model performance. The first is the visual fit
121 between modeled data and measured data. The second is the practical identifiability of a parame-
122 ter which is indicated by the 5% – 95% quantile range of its pdf. A smaller range means a better
123 identifiability. The third is the agreement between the 5% – 95% quantile range of a parameter and
124 its intrinsic value when measured under or estimated for non-limiting environmental conditions e.g.
125 in perfectly mixed batch reactors. The closer (all) calibrated parameter ranges agree with intrinsic
126 reference values, the stronger the evidence is that all controlling fundamental processes and limitations
127 are included in the network. The model that performs best for all three criteria has minimal ambiguity
128 and uncertainty.

129 **3. Results & Discussion**

130 *3.1. A fundamental biogeochemical reaction network for leachate recirculation under anaerobic condi-* 131 *tions*

132 Figure 4 presents the least ambiguous biogeochemical process network that describes emissions
133 during anaerobic leachate recirculation treatment. The network contains five kinetic reactions: 1)
134 lumped hydrolysis and acidogenesis with hydrolysis as rate limiting step, 2) methanogenesis, 3-4)
135 bacterial biomass decay with a maximum decay rate of 5% of the maximum growth rate (Angelidaki
136 et al., 1999) and 5) lumped nitrification and denitrification with nitrification as rate limiting step.
137 Although pure anaerobic conditions are compromised by including nitrification, it allowed to explain
138 observations in the measured data. Kinetic mechanisms and stoichiometry are listed in table 2. Also
139 a set of equilibrium reactions (i.e. speciation, complexation, precipitation and gas-liquid transfer

140 reactions) is included in the network. Corresponding species are presented in the bottom part of figure
141 4.

142 Figure 3 shows the visual agreement between the best fit of the modeled data and the measured data.
143 The uncertainty in the total model error is also indicated. Overall, the calibration and the validation
144 data sets are well described. A good description of the pH was only possible by including the set of
145 chemical/physical equilibria. The high alkalinity of leachate could be modeled with a sufficient amount
146 of readily available Calcite.

147 Only the dynamics in ammonium concentrations are not accurately described by the network which
148 indicates that fundamental processes are missing in the network. We could account for the total amount
149 of removed nitrogen in MSW by including a lumped nitrification/denitrification reaction together with
150 an intrusion flow of air. Evidence for air intrusion is given by the decrease in partial pressures of
151 methane and carbon dioxide. However it must be noted that at field scale conditions, intrusion of
152 air is most likely irrelevant. The measured data did not contain sufficient information to further fit
153 the ammonium concentrations by including additional fundamental processes. Important processes
154 could have been adsorption of NH_4^+ to the MSW as suggested by Bolyard and Reinhart (2016) and
155 autotrophic denitrification with reduced sulfur compounds as suggested by Onay and Pohland (1998).
156 Follow-up experiments should include measurements to calibrate these processes in order to identify
157 their relevance.

158 In order to evaluate the ambiguity and uncertainty of the network, we calibrated the parameters
159 with the highest uncertainty. Table 3 presents the 5% – 95% quantiles of the posterior pdfs, the
160 prior ranges and the reference values of the optimized parameters for non-limiting environmental
161 conditions. The small range of all posterior quantiles indicate that all parameters are identifiable from
162 the information present in the measured data set. Even more interesting is that, although the process
163 network is relatively simple, most calibrated bandwidths fall in the range of the reference values. We
164 believe this indicates that the process network includes most fundamental reactions and processes
165 controlling the emissions. Calibrated bandwidths of maximum rates are a bit lower than the reference
166 values presumably due to mass transport limitations in the experiments which have not been included
167 in the model.

168 The process network closely resembles the network identified for a similar type of lysimeter experi-
169 ment by van Turnhout et al. (2016). This suggests that the selected processes describe biodegradation
170 of MSW on a general level for lysimeter scale. The main difference between the networks is that we did
171 not include environmental inhibition relations because concentrations of potential inhibitors remained
172 low.

173 The calibration of the network allows to estimate the amount of organic carbon in the MSW that
174 could be removed under the experimental conditions. The mean fitted value for the initial amount of
175 biodegradable carbon ($C_{\text{SOM}}^{\text{ini}}$) of $2.3 \frac{\text{Cmol}}{\text{L}}$ or $0.018 \frac{\text{kgSOM}}{\text{kgdrywaste}}$ is comparable with the total removed car-
176 bon measured by MSW sampling. This indicates that all significant emission pathways are considered
177 in the network. For further study, it would be even more interesting to be able to predict how much
178 of SOM in the MSW can be removed under different experimental conditions. This, however, requires
179 to extend the network with processes that describe the potential of different fractions of SOM present
180 in the MSW to be hydrolyzed.

181 Because the model describes the emission controlling processes, it also indicates which phases are
182 dominant in removing carbon and nitrogen from MSW. The mass percentages of organic carbon and
183 nitrogen in the phases MSW, solutes, bacteria, sampled leachate, $\text{CO}_2(\text{gas})$, $\text{CH}_4(\text{gas})$, $\text{N}_2(\text{gas})$ and
184 $\text{NH}_3(\text{gas})$ over time are presented in figure 5. It shows that most of the organic carbon and nitrogen
185 (85% – 83%) in the MSW is unaffected by the treatment. Considering the controlling processes, the
186 main limitation seems to have been the transport of reactants e.g. oxygen or methanogenic bacteria
187 to the biodegradable fraction of MSW. The optimal network and parameter values do not indicate
188 any other severe biochemical rate limitations or inhibitions. In addition, part of the remaining carbon
189 could have been non-biodegradable. Figure 5 also shows that carbon is mainly removed via the gas
190 phase and nitrogen is mainly removed via sampled leachate. Phases such as bacterial biomass and
191 stripped ammonia contribute minimally as a final sink.

192 In order to successfully monitor the efficiency of the treatment methods at full scale, it is crucial
193 to measure the dominant final sinks of carbon and nitrogen. Inconclusive field scale results so far,
194 may (partially) be caused by incomplete monitoring. To optimize field scale application, important
195 reactants such as oxygen and methanogens should be distributed more homogeneously throughout the
196 waste-body. This could be achieved for instance by placing aeration wells or infiltration trenches closer
197 together. Important topics for further research are therefore optimization of reactant distribution and
198 monitoring of final sinks.

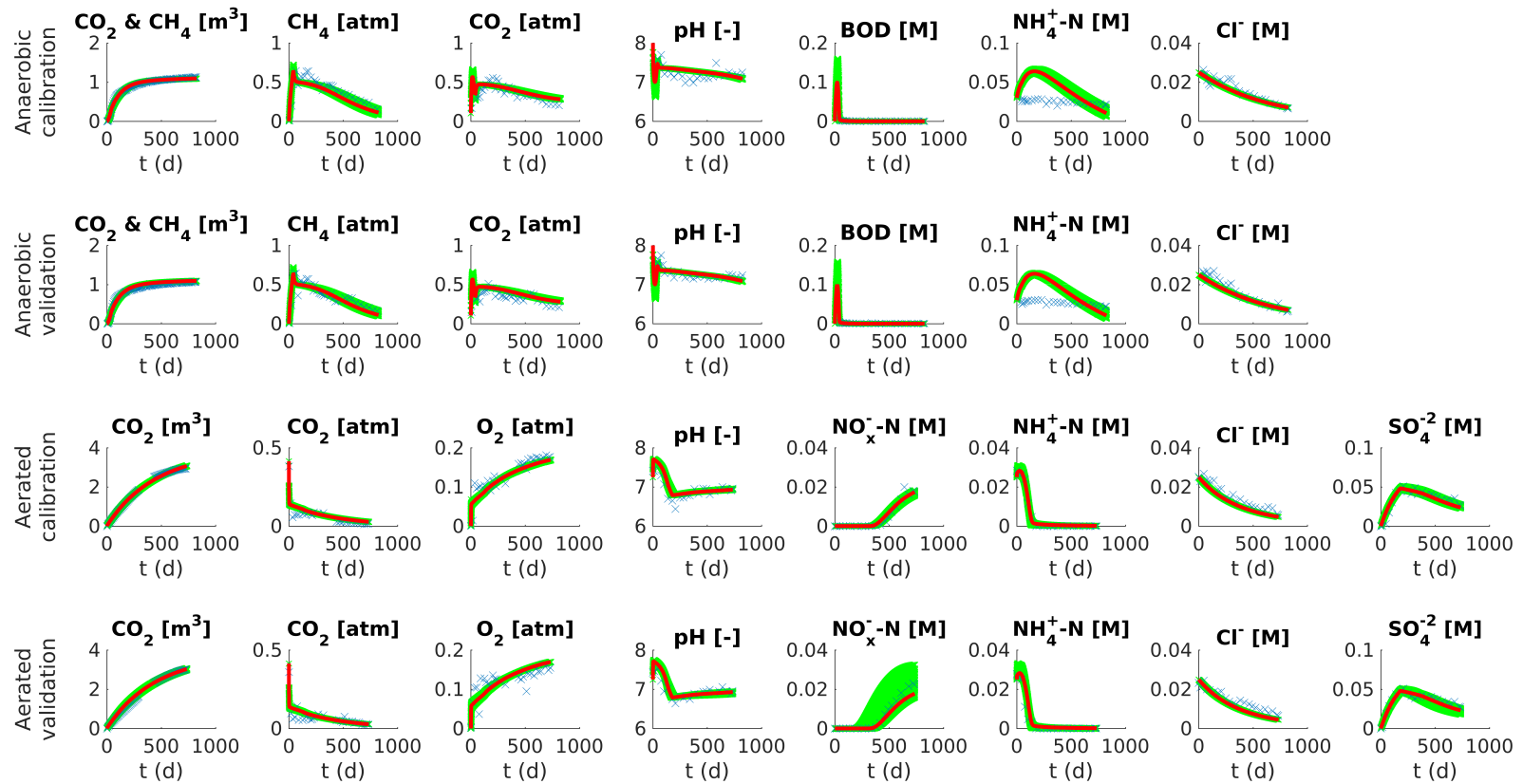
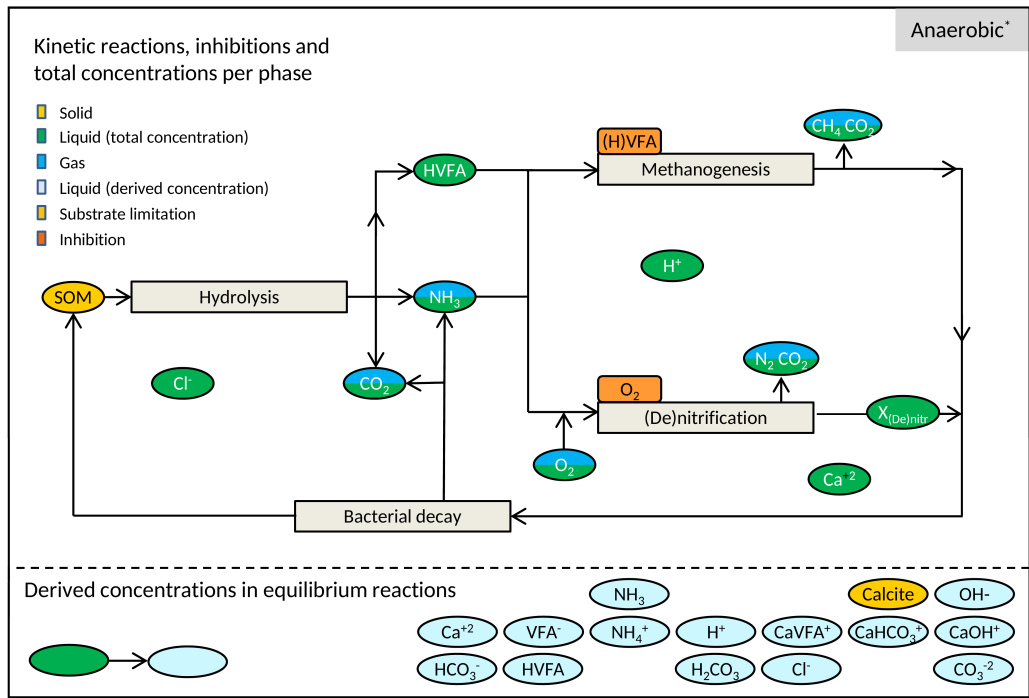
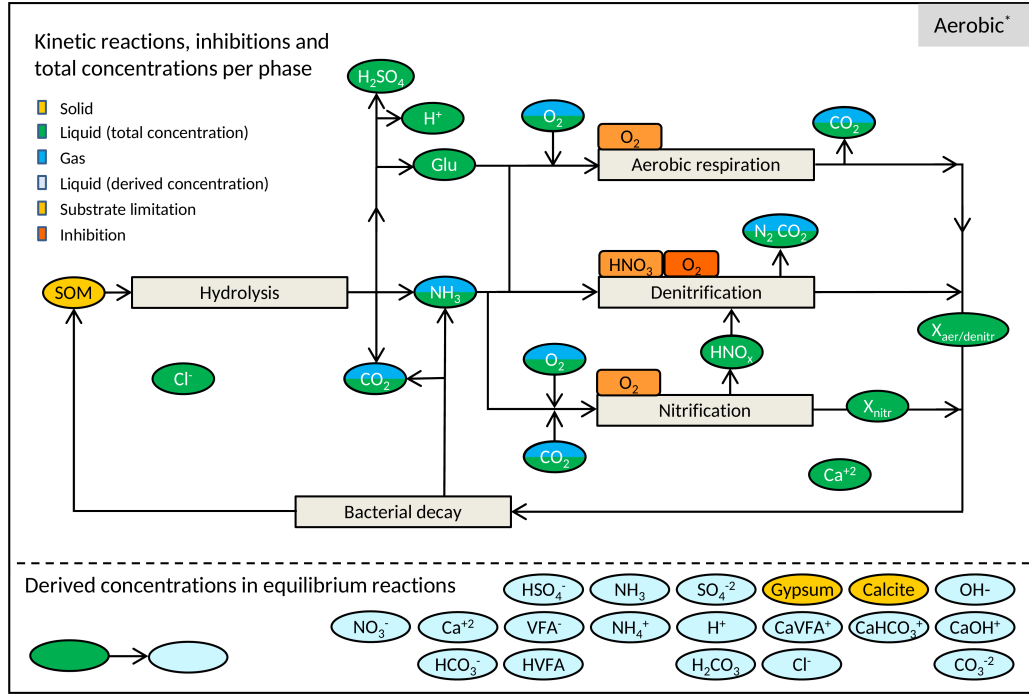


Figure 3: The visual agreement between the best fit of the modeled data (in red) and the measured data (in blue) for calibration and validation data measured during leachate recirculation under anaerobic and aerated conditions. The uncertainty in the total model error is indicated with green bandwidths surrounding the modeled data.



*with some oxygen present due to leakage



*with remaining anaerobic pockets because air is transported through preferential flow paths

Figure 4: The least ambiguous biogeochemical process networks for anaerobic (top) and aerobic (bottom) recirculation treatment on a lysimeter scale. In these schemes, gas and leachate flows that go into and out of the reactors are not included, but their values are listed in tables 1 and 3.

Table 2: Stoichiometry for the kinetic reactions in the biogeochemical process networks derived with the method from (Kleerebezem and van Loosdrecht, 2010) or deduced from the composition of MSW measured during sampling. Also the kinetic mechanisms are indicated. Parameters in bold are selected for calibration because they are highly uncertain and can significantly influence the model outcome.

Stoichiometry for the recirculation experiment under anaerobic conditions [mol]												Kinetics ^{c)}
	SOM ^{a)}	Acetic Acid	CO ₂	NH ₃	CH ₄	H ₂ O	H ⁺	X ^{b)} _{meth}	X _{(de)nitr}}	O ₂	N ₂	
Hydrolysis ^{e)}	-1	0.5	0	0.036	0	-0.172	0	0	0	0	0	$k_{\text{hyd}} \cdot C_{\text{SOM}}^T$
Methanogenesis	0	-12.91	12.41	-0.2	12.41	0.6	0	1	0	0	0	$\mu_{\text{meth}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{Ac}}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}}$
Bacterial decay ^{d)}	0	0.5	0	0.2	0	-0.6	0	-1	0	0	0	$0.05 \cdot \mu_{\text{meth}}^{\text{max}} \cdot C_X$
(De)nitrification	0	-0.12	0.39	-0.54	0	1.5	0	0	1	-0.63	0.17	$\mu_{(\text{de})\text{nitr}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{O}_2}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}}$

Stoichiometry for the recirculation experiment under aerobic conditions [mol]												Kinetics	
	SOM	Glucose	CO ₂	NH ₃	H ₂ O	H ⁺	X _{aer-denitr}}	O ₂	SO ₄ ⁻²	NO ₃ ⁻	X _{nitr}}	N ₂	
Hydrolysis	-1	0.167	0	0.032	-0.172	ν_{H^+}	0	0	0.03	0	0	0	$k_{\text{hyd}} \cdot C_{\text{SOM}}^T$
Aerobic respiration	0	-0.23	0.39	-0.2	0.99	0	1	-0.39	0	0	0	0	$\mu_{\text{aer}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{Glu}}}^{\text{SL}} \cdot f_{C_{\text{O}_2}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}}$
Nitrification	0	0	-1	-11.42	10.82	11.22	0	-21.44	0	11.22	1	0	$\mu_{\text{nitr}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{NH}_3}}^{\text{SL}} \cdot f_{C_{\text{CO}_2}}^{\text{SL}}$
Denitrification	0	-0.24	0.42	-0.2	2.62	-0.33	1	0	0	-0.33	0	0.17	$\mu_{\text{denitr}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{Glu}}}^{\text{SL}} \cdot f_{C_{\text{NO}_3^-}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}} \cdot f_{C_{\text{O}_2}}^{\text{NC}}$
Bacterial decay ^{d)}	0	0.17	0	0.2	-0.6	0	(-1)	0	0	0	(-1)	0	$0.05 \cdot \mu_{\text{aer}}^{\text{max}} \cdot C_X$

a) SOM is the biodegradable fraction of Solid Organic Matter in MSW generically modeled as $\text{C}_6\text{H}_{10}\text{O}_5\text{N}_{0.036}$ and $\text{C}_6\text{H}_{10}\text{O}_5\text{N}_{0.032}\text{S}_{0.03}$ for respectively anaerobic and aerobic conditions. b) X are species of bacteria with the elemental composition $\text{CH}_{1.4}\text{O}_{0.4}\text{N}_{0.2}$ taken from Henze et al. (1995). c) Substrate limitation factors (f^{SL}) and inhibition factors (f^{NC}) range between 0 and 1 (van Turnhout et al., 2016). Half saturation constants which are not calibrated have low values and are primarily included as switch factors. d) Bacterial biomass decay is included as a separate process for each species. e) Hydrolysis under anaerobic conditions is lumped with acidogenesis with hydrolysis being rate limiting.

Table 3: Results of the optimization: 5% – 95% quantiles of the posterior ranges. They are listed together with the prior ranges and the reference ranges measured under or estimated for non-limiting environmental conditions.

Anaerobic recirculation experiment							
	prior	posterior	reference		prior	posterior	reference
k_{hyd} [d^{-1}]	0.0005 – 0.15	0.0094 – 0.0104	0.09 – 0.26 ¹⁾	X_{meth} [mM]	0.005 – 15	0.59 – 11	0.27 – 19 ³⁾
$\mu_{\text{meth}}^{\text{max}}$ [d^{-1}]	0.01 – 3	0.04 – 0.12	0.8 ²⁾	$X_{(\text{de})\text{nitr}}$ [mM]	0.015 – 15	1.2 – 14	0.27 – 19 ³⁾
$\mu_{(\text{de})\text{nitr}}^{\text{max}}$ [d^{-1}]	0.001 – 1	0.11 – 0.96	1.4 ²⁾	$K_{\text{s},C_{\text{Ac}}^{\text{meth}}}$ [mM]	1 – 1000	5.5 – 16.7	0.03 – 420 ⁴⁾
$\phi_{\text{in,air}}$ [Ld^{-1}]	0.005 – 1.5	0.12 – 0.19	–	$C_{\text{SOM}}^{\text{ini}}$ [M]	2 – 3	2.27 – 2.33	–
Aerated recirculation experiment							
	prior	posterior	reference		prior	posterior	reference
k_{hyd} [d^{-1}]	0.00024 – 0.026	0.0021 – 0.0023	0.09 – 0.26 ¹⁾	X_{nitr} [mM]	0.09 – 110	1.1 – 2.7	0.27 – 19 ³⁾
$\mu_{\text{aer}}^{\text{max}}$ [d^{-1}]	1.2 – 121	25.6 – 118	57 ²⁾	$X_{\text{aer-denitr}}$ [mM]	7 – 800	9.5 – 35.4	0.27 – 19 ³⁾
$\mu_{\text{nitr}}^{\text{max}}$ [d^{-1}]	0.003 – 0.31	0.01 – 0.02	1.4 ²⁾	$K_{\text{s},C_{\text{NH}_3}^{\text{nitr}}}$ [mM]	0.9 – 110	1.6 – 7.1	0.04 ⁵⁾
$\mu_{\text{denitr}}^{\text{max}}$ [d^{-1}]	2 – 201	6.4 – 198	54 ²⁾	$K_{\text{i},C_{\text{O}_2}^{\text{denitr}}}$ [mM]	0.005 – 0.6	0.047 – 0.093	–
$C_{\text{SOM}}^{\text{ini}}$ [M]	5 – 7	6.2 – 6.5	–	$\nu_{\text{H}^+}^{\text{hyd}}$ [mol]	0 – 0.06	0.037 – 0.041	–

1) Veeken and Hamelers (1999) 2) Kleerebezem and van Loosdrecht (2010) 3) Nopharatana et al. (2007) 4) Meima et al. (2008) 5) Kantartz et al. (2006)

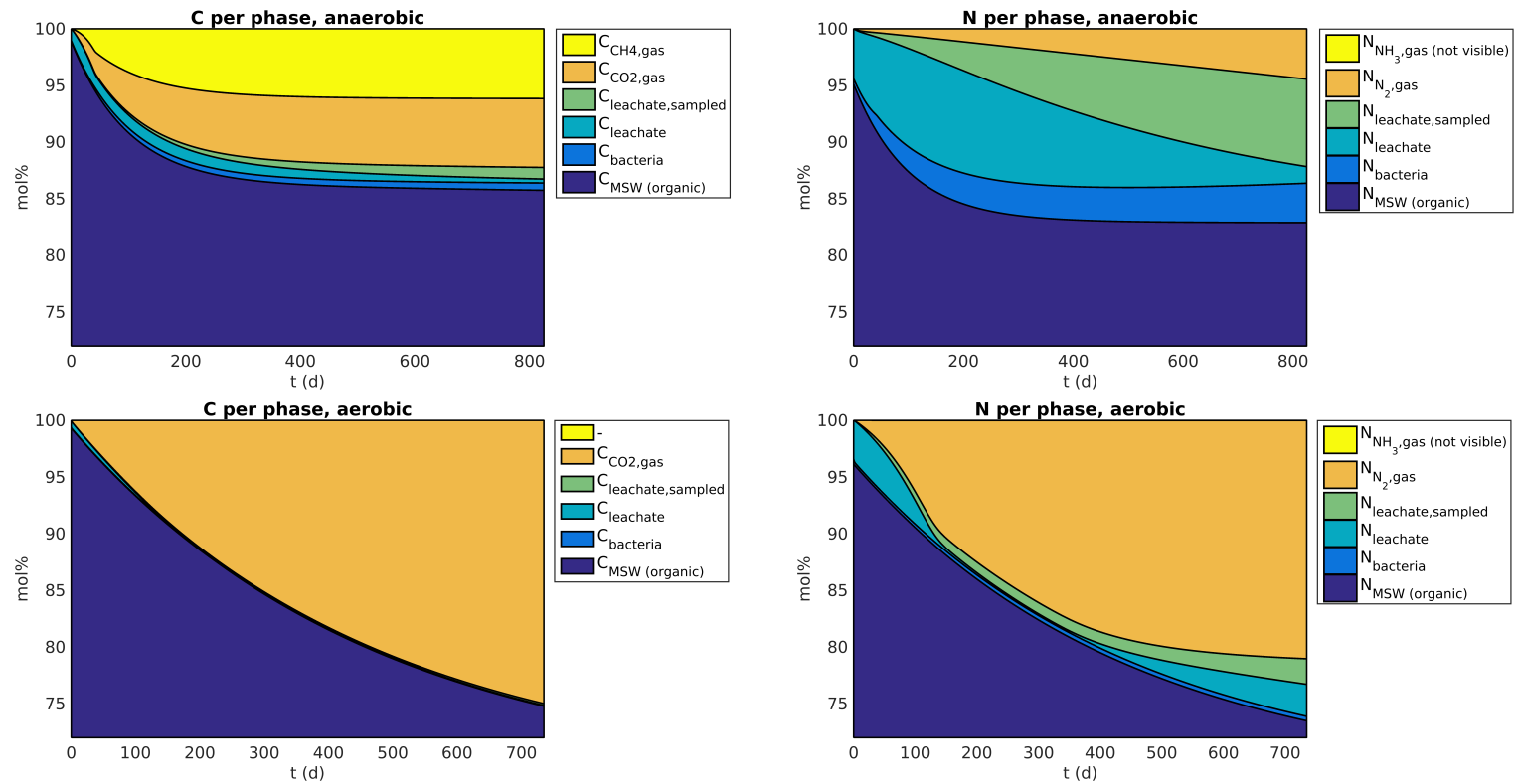


Figure 5: Modeled mass percentages of organic carbon and nitrogen in different phases during anaerobic and aerobic leachate recirculation. They indicate which phases are dominant in removing carbon and nitrogen from MSW for each treatment method.

199 *3.2. A fundamental biogeochemical reaction network for leachate recirculation under aerobic conditions*

200 Figure 4 also presents the least ambiguous process network that describes emissions during aerobic
201 leachate recirculation treatment. This network contains six kinetic reactions: 1) hydrolysis of SOM,
202 2) aerobic respiration of glucose, 3) nitrification, 4) denitrification and 5-6) bacterial biomass decay.
203 The set of equilibrium reactions is identical to that used for modeling the anaerobic experiment except
204 that sulphate speciation and gypsum precipitation are included as well. Table 2 lists the stoichiometry
205 and kinetic mechanisms.

206 The high sulfur/carbon ratio in SOM (table 2) suggests that gypsum is co-dissolved during hydroly-
207 ysis because only protein hydrolysis would give a much lower ratio. The amount of protons released
208 per sulfate (ν_{H^+}) is calibrated on the measured data and its mean calibrated value (table 3) indicates
209 mainly release of HSO_4^- . A more detailed process description of the release and conversion of sulfur
210 was not possible because the measured data was too limited. When future studies do include additional
211 measurements, it would be very interesting to extend the process description.

212 The best visual fit between modeled and measured data for aerobic treatment is presented in figure
213 3. Again all model results are in good agreement with the measured data for both the calibration
214 dataset and the validation dataset. Dynamics in measured pH and dissolved sulphate could be repro-
215 duced because of inclusion of the set of chemical equilibrium reactions.

216 The optimization results (table 3) indicate that also this network contains minimal ambiguity and
217 uncertainty. The quantile ranges of the posterior pdfs show that the identifiability of most calibrated
218 parameters is good. Only the maximum rates of aerobic respiration and denitrification have a wide
219 range with high values. This is, however, reasonable because these reactions are limited by the rate
220 of oxygen or nitrate supply. Therefore, any high value for these maximum rates gives a satisfying
221 model result. Most quantile ranges fall close to the reference values, but similar to the findings for the
222 anaerobic case, values are slightly lower due to missing mass transport limitations in the model. The
223 higher values of the initial concentration of aerobic respirators seem to compensate for a high initial
224 growth rate which was not recorded because of too large measurement intervals.

225 The consumption of ammonium (figure 3) via sequential nitrification and denitrification suggests
226 that anaerobic pockets were present in the MSW during air injection. This implies that air is trans-
227 ported through preferential flow paths which is reasonable given the strong heterogeneity of the MSW.
228 Figure 6 schematically explains how preferential flow of air leads to simultaneous nitrification and
229 denitrification. With sufficient biodegradable carbon available, the oxygen is readily consumed near
230 the preferential channels which leaves the bulk of the waste anaerobic. Nitrate that is produced in the
231 aerobic region by nitrification diffuses into the anaerobic bulk where it is utilized by denitrification. In-

232 terestingly, this mechanism only holds when sufficient biodegradable carbon is available. When carbon
 233 depletes, the oxygen penetrates deeper into the bulk of the waste violating the anaerobic conditions.
 234 This eventually leads to oxygen overtaking nitrate as oxidizer of the remaining carbon. This effect is
 235 noticeable in the measured data (figure 3) by the increase in nitrate/nitrite concentrations at the end
 236 of the experiment.

237 The inhibition of denitrification by oxygen is included in the process network with the factor:

$$238 \quad f_{C_{O_2}^T}^{NC} = \left(\frac{K_{inh}}{K_{inh} + C_{O_2}^T} \right)^6 \quad (1)$$

239 where K_{inh} is the inhibition constant and $C_{O_2}^T$ is the concentration of oxygen in the water phase. The
 240 inhibition factor $f_{denitr, C_{O_2}^T}^{NC}$ decreases from 1 to 0 as the oxygen concentration rises which indirectly in-
 241 dicates that biodegradable SOM is depleting. The main consequence of this mechanism for ammonium
 242 removal by aeration is that sufficient biodegradable carbon should be present in the MSW. Otherwise
 243 aeration will only lead to increased concentrations of nitrate/nitrite in the leachate.

244 Our mechanism that facilitates denitrification generalizes the one proposed by Brandstätter et al.
 245 (2015) (Brandstätter et al., 2015b). They propose that denitrification mainly occurred at the bottom
 246 of the reactor where leachate remained anaerobic. Although this could have amplified the presence
 247 of denitrification, we believe it is not a prerequisite for denitrification. Anaerobic regions can exist
 248 everywhere near preferential flow-paths of air because of the limited penetration depth of oxygen in
 249 water.

250 Aeration also causes a rise in temperature in waste-bodies which subsequently affects biodegrada-
 251 tion and leachate quality. Ritzkowski and Stegmann (2012) showed that temperature rise due to aera-
 252 tion can lead to enhanced ammonification, reduced nitrification and increased pH of the leachate. Our
 253 process networks for lysimeter scale do not consider the impact of temperature changes on biodegrada-
 254 tion because temperatures were kept constant throughout the experiments. However, in order to
 255 predict field scale conditions, processes should be included that describe enthalpy changes and the
 256 effect of temperature on kinetics (e.g. Arrhenius equations).

257 Figure 5 shows the mass percentages of carbon and nitrogen in different phases during both aerobic
 258 and anaerobic leachate recirculation. Clearly, more carbon is removed under aerobic conditions (\sim
 259 25%) than under anaerobic conditions (\sim 14%). This indicates that the electron acceptor (i.e. oxygen)
 260 was better mixed throughout the waste and/or the fraction of biodegradable carbon was higher. Also
 261 more nitrogen is removed under aerated conditions: \sim 27% against \sim 17%. Nevertheless, the amount
 262 of carbon and nitrogen removed is still quite small compared with the total amount in MSW. Therefore,
 263 we have the same conclusion for the aerobic recirculation treatment as for the anaerobic one: optimal

264 electron acceptor distribution throughout the waste-body at field scale is a main issue to be tackled.
 265 Figure 5 furthermore indicates that carbon and nitrogen are mainly removed via CO_2 and N_2 during
 266 aeration. These phases are therefore important to measure for monitoring treatment effectiveness at
 267 a field scale.

268 Another interesting difference between anaerobic and aerated treatment is that the hydrolysis
 269 constant is lower during aeration. Stripping of water could have caused this by decreasing the amount
 270 of water per surface area of MSW. Although hydrolysis was not intrinsically enhanced, aeration still
 271 increased the rate of hydrolysis because the fraction of biodegradable carbon in MSW was increased.
 272 An optimal treatment strategy could be to alternate anaerobic and aerobic leachate recirculation which
 273 can generate both a high hydrolysis constant and a high fraction of biodegradable carbon.

274 Adopting a different perspective (and corresponding treatment goals) on how to achieve low long-
 275 term emissions can also increase the efficiency of treatment methods. Rather than aiming to completely
 276 remove all biodegradable carbon and nitrogen in the waste body, it could be sufficient to only remove
 277 the carbon and nitrogen in the proximity of the preferential flow-paths. In the latter case, slow diffusion
 278 from the bulk of the waste and the continuing degradation in the close vicinity of the preferential
 279 pathways jointly contribute to maintaining low emission levels. Follow up studies, however, should
 280 demonstrate that settlements do not significantly influence preferential flow-paths and therefore long-
 281 term emissions. Also, it should be investigated if emissions after treatment are not only temporarily
 282 low due to limitations such as drying of the preferential flow-paths.

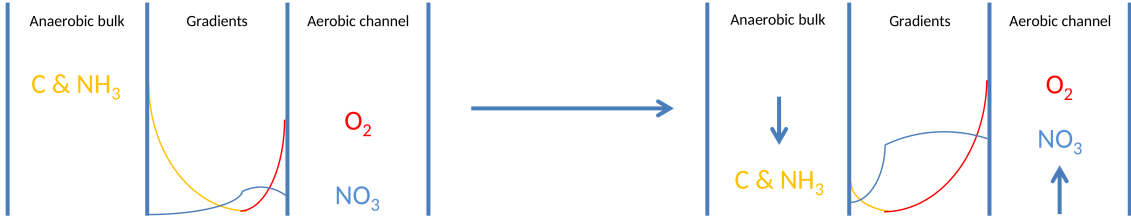


Figure 6: Illustration of the concentration gradients between aerobic and anaerobic regions in the MSW due to gas transport through preferential flow paths. When sufficient biodegradable carbon is present in the MSW, oxygen penetration is limited which leads to an anaerobic bulk where nitrate can be converted by denitrification (left). However, when the amount of biodegradable carbon becomes too small, oxygen penetrates deeper into the bulk which leads to failure of denitrification and increased nitrate concentrations (right).

283 **4. Conclusion**

284 This paper discusses factors and processes that control the effectiveness of leachate recirculation
 285 treatment under anaerobic and aerobic conditions. Fundamental process networks were found which
 286 closely reproduce the measured data from experiments at the lysimeter scale. Using qualitative and

287 quantitative criteria, we indicate that fundamental uncertainty and ambiguity in these networks were
288 small. The networks therefore represent factors and processes that control emissions of methane,
289 carbon dioxide, pH, chloride and ammonium (under aerobic conditions) sufficiently accurate. Emission
290 of ammonium under anaerobic conditions is only adequately described.

291 The effectiveness of both treatment methods is mainly controlled by how homogeneously important
292 reactants such as oxygen and methanogens are distributed through-out the MSW. Under aerated
293 conditions, a higher fraction of biodegradable carbon and nitrogen is reached and removed than under
294 anaerobic conditions: 25% compared to 14% for carbon, and 27% compared to 17% for nitrogen.
295 Interestingly, the rate constant of hydrolysis during aeration is lower than under anaerobic conditions.
296 The rate of hydrolysis is nevertheless higher during aeration because the fraction of biodegradable
297 carbon is higher.

298 Consumption of ammonium by sequential nitrification and denitrification suggests that anaerobic
299 pockets were present in the MSW during aeration. This can be explained by transport of air through
300 preferential flow-paths which is reasonable given the strong heterogeneity of the MSW. Ammonium
301 removal via N_2 is only possible when sufficient biodegradable carbon is available. Otherwise, denitri-
302 fication fails and the concentration of nitrate rises in the leachate.

303 To accurately monitor the effectiveness of treatments at field scale, the most important emitted
304 phases to measure are CO_2 , CH_4 and NH_4^+ under anaerobic conditions. For aerobic conditions, these
305 phases are CO_2 and N_2 . Gas phases, however, might be difficult to measure at field scale with current
306 techniques. Phases such as bacterial biomass and stripped NH_3 contribute minimally to carbon and
307 nitrogen removal.

308 To maximize degradation of organic matter in waste bodies at full-scale, the main challenge is to
309 maximize distribution of the electron acceptors and other reactants throughout the waste-body. This
310 could be achieved by optimizing geometry of gas wells and infiltration trenches and other operational
311 parameters. It is, however, doubtful if removal rates of carbon and nitrogen can be improved beyond
312 those observed in the lysimeter experiments where conditions were already quite optimal. A more
313 realistic goal to achieve low long-term emissions might be to remove all biodegradable carbon and
314 nitrogen in the proximity of preferential flow-paths; emissions should remain low afterwards because of
315 slow diffusion from the bulk and continuing reactivity near the flow-paths. If this is indeed a feasible
316 and stable mechanism, however, must be demonstrated in further studies.

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322 6. References

- 323 I. Angelidaki, L. Ellegaard, and B. K. Ahring. A comprehensive model of anaerobic bioconversion
324 of complex substrates to biogas. *Biotechnology and bioengineering*, 63(3):363–72, may 1999. ISSN
325 1097-0290. URL <http://www.ncbi.nlm.nih.gov/pubmed/10099616>.
- 326 D. J. Batstone, J. Keller, I. Angelidaki, S. V. Kalyuzhnyi, S. G. Pavlostathis, A. Rozzi, W. T. M.
327 Sanders, H. Siegrist, and V. A. Vavilin. The IWA Anaerobic Digestion Model No 1 (ADM1). *Water*
328 *science and technology : a journal of the International Association on Water Pollution Research*, 45
329 (10):65–73, jan 2002. ISSN 0273-1223. URL <http://www.ncbi.nlm.nih.gov/pubmed/12188579>.
- 330 H. Belevi and P. Baccini. Long-term behavior of municipal solid waste
331 landfills. *Waste Management & Research*, 7:43–56, 1989. URL
332 <http://www.sciencedirect.com/science/article/pii/0734242X89900074>.
- 333 C. H. Benson, M. A. Barlaz, D. T. Lane, and J. M. Rawe. Practice review
334 of five bioreactor/recirculation landfills. *Waste management (New York, N.Y.)*, 27
335 (1):13–29, jan 2007. ISSN 0956-053X. doi: 10.1016/j.wasman.2006.04.005. URL
336 <http://www.ncbi.nlm.nih.gov/pubmed/16766174>.
- 337 M. S. Bilgili, A. Demir, and B. Ozkaya. Influence of leachate recirculation on aerobic and anaerobic
338 decomposition of solid wastes. *Journal of Hazardous Materials*, 143(1-2):177–183, 2007. ISSN
339 03043894. doi: 10.1016/j.jhazmat.2006.09.012.
- 340 S. C. Bolyard and D. R. Reinhart. Application of landfill treatment approaches for stabiliza-
341 tion of municipal solid waste. *Waste Management*, 55:22–30, sep 2016. ISSN 0956053X.
342 doi: 10.1016/j.wasman.2016.01.024. URL <http://www.ncbi.nlm.nih.gov/pubmed/26838608>
343 <http://linkinghub.elsevier.com/retrieve/pii/S0956053X16300241>.
- 344 C. Brandstätter, D. Laner, and J. Fellner. Carbon pools and flows during lab-scale degra-
345 dation of old landfilled waste under different oxygen and water regimes. *Waste Manage-*

346 *ment*, 40:100–111, jun 2015a. ISSN 0956053X. doi: 10.1016/j.wasman.2015.03.011. URL
347 <http://linkinghub.elsevier.com/retrieve/pii/S0956053X1500152X>.

348 C. Brandstätter, D. Laner, and J. Fellner. Nitrogen pools and flows during lab-scale degradation of old
349 landfilled waste under different oxygen and water regimes. *Biodegradation*, 26(5):399–414, 2015b.
350 ISSN 15729729. doi: 10.1007/s10532-015-9742-5.

351 A. S. Erses, T. T. Onay, and O. Yenigun. Comparison of aerobic and anaerobic degradation of municipal
352 solid waste in bioreactor landfills. *Bioresource technology*, 99(13):5418–26, sep 2008. ISSN 0960-8524.
353 doi: 10.1016/j.biortech.2007.11.008. URL <http://www.ncbi.nlm.nih.gov/pubmed/18082400>.

354 J. J. Heijnen and R. Kleerebezem. *Bioenergetics of microbial growth*. 1999. URL
355 <http://onlinelibrary.wiley.com/doi/10.1002/0471250589.ebt026/full>.

356 M. Henze, P. Harremoës, J. Jansen, and E. Arvin. *Wastewater Treatment - Biological and Chemical*
357 *Processes*, 1995.

358 M. Hrad, O. Gamperling, and M. Huber-Humer. Comparison between lab- and full-scale applications of
359 in situ aeration of an old landfill and assessment of long-term emission development after completion.
360 *Waste Management*, 33(10):2061–2073, 2013. ISSN 0956053X. doi: 10.1016/j.wasman.2013.01.027.
361 URL <http://dx.doi.org/10.1016/j.wasman.2013.01.027>.

362 S. G. Kantartzi, E. Vaiopoulou, A. Kapagiannidis, and A. Aivasidis. Kinetic Characterization of
363 Nitrifying Pure Cultures in Chemostate. *Global NEST Journal*, 8(1):43–51, 2006.

364 S. Kasam, S. Syamsiah, and A. Prasetya. Effect of Leachate Recirculation on Characteristics of
365 Leachate Generation of Municipal Solid Waste from Landfill Lysimeter. *Journal of Chemistry and*
366 *Chemical Engineering*, 7:456–461, 2013.

367 P. Kjeldsen, M. Barlaz, A. P. Rooker, A. Ledin, and T. H. Christensen. Present and Long-Term
368 Composition of MSW Landfill Leachate: A Review. *Critical Reviews in Environmental Science*
369 *and Technology*, 32(4):297–336, oct 2002. ISSN 1064-3389. doi: 10.1080/10643380290813462. URL
370 <http://www.tandfonline.com/doi/abs/10.1080/10643380290813462>.

371 R. Kleerebezem and M. C. M. van Loosdrecht. A Generalized Method for Thermodynamic
372 State Analysis of Environmental Systems. *Critical Reviews in Environmental Science and*
373 *Technology*, 40(1):1–54, jan 2010. ISSN 1064-3389. doi: 10.1080/10643380802000974. URL
374 <http://www.tandfonline.com/doi/abs/10.1080/10643380802000974>.

- 375 D. Laner, J. Fellner, and P. H. Brunner. Future landfill emissions and the effect
376 of final cover installation—a case study. *Waste management (New York, N.Y.)*, 31
377 (7):1522–31, jul 2011. ISSN 1879-2456. doi: 10.1016/j.wasman.2011.02.022. URL
378 <http://www.ncbi.nlm.nih.gov/pubmed/21421299>.
- 379 J. A. Meima, N. M. Naranjo, and A. Haarstrick. Sensitivity analysis and literature review of parameters
380 controlling local biodegradation processes in municipal solid waste landfills. *Waste management*
381 *(New York, N.Y.)*, 28(5):904–18, jan 2008. ISSN 0956-053X. doi: 10.1016/j.wasman.2007.02.032.
382 URL <http://www.ncbi.nlm.nih.gov/pubmed/17499984>.
- 383 A. Nopharatana, P. C. Pullammanappallil, and W. P. Clarke. Kinetics and dynamic modelling of
384 batch anaerobic digestion of municipal solid waste in a stirred reactor. *Waste management (New*
385 *York, N.Y.)*, 27(5):595–603, jan 2007. ISSN 0956-053X. doi: 10.1016/j.wasman.2006.04.010. URL
386 <http://www.ncbi.nlm.nih.gov/pubmed/16797956>.
- 387 T. T. Onay and F. G. Pohland. In situ nitrogen management in controlled bioreactor landfills. *Water*
388 *Research*, 32(5):1383–1392, 1998. ISSN 00431354. doi: 10.1016/S0043-1354(97)00392-8.
- 389 T. Reichel, L. Ivanova, R. Beaven, and a. Haarstrick. Modeling Decomposition of
390 MSW in a Consolidating Anaerobic Reactor. *Environmental Engineering Science*, 24
391 (8):1072–1083, oct 2007. ISSN 1092-8758. doi: 10.1089/ees.2006.0230. URL
392 <http://www.liebertonline.com/doi/abs/10.1089/ees.2006.0230>.
- 393 M. Ritzkowski and R. Stegmann. Landfill aeration worldwide: concepts, indications and find-
394 ings. *Waste management (New York, N.Y.)*, 32(7):1411–9, 2012. ISSN 1879-2456. doi:
395 10.1016/j.wasman.2012.02.020. URL <http://www.ncbi.nlm.nih.gov/pubmed/22459512>.
- 396 H. Scharff, A. van Zomeren, and H. A. van der Sloot. Landfill sustainability and aftercare
397 completion criteria. *Waste management & research : the journal of the International Solid*
398 *Wastes and Public Cleansing Association, ISWA*, 29(1):30–40, jan 2011. ISSN 1399-3070. doi:
399 10.1177/0734242X10384310. URL <http://www.ncbi.nlm.nih.gov/pubmed/20921059>.
- 400 A. G. van Turnhout, R. Kleerebezem, and T. J. Heimovaara. A toolbox to find the best mechanistic
401 model to predict the behavior of environmental systems . *Environmental Modelling & Software*, 83:
402 344–355, 2016. ISSN 13648152. doi: 10.1016/j.envsoft.2016.05.002.
- 403 A. H. Veeken and B. Hamelers. Effect of temperature on hydrolysis rates of se-

- 404 lected biowaste components. *Bioresource technology*, 69:249–254, 1999. URL
405 <http://www.sciencedirect.com/science/article/pii/S0960852498001886>.
- 406 A. H. Veeken, S. Kalyuzhnyi, and H. Scharff. Effect of pH and VFA on hydrolysis of
407 organic solid waste. *Journal of Environmental Engineering*, 06:1076–1081, 2000. URL
408 <http://www.enzyme.chem.msu.ru/ekbio/article/JEE00-12.pdf>.
- 409 J. K. White, R. P. Beaven, W. Powrie, and K. Knox. Leachate recirculation in a landfill: some
410 insights obtained from the development of a simple 1-D model. *Waste management (New York,*
411 *N.Y.)*, 31(6):1210–21, jun 2011. ISSN 1879-2456. doi: 10.1016/j.wasman.2010.10.022. URL
412 <http://www.ncbi.nlm.nih.gov/pubmed/21316936>.

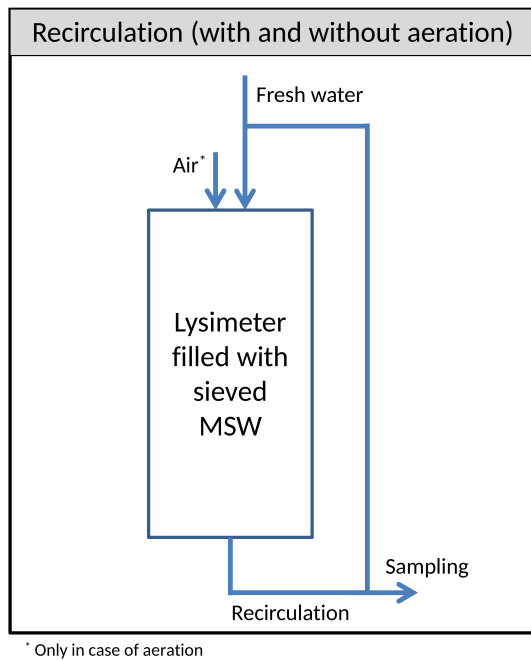


Figure 1: Illustration of the experimental set-ups for leachate recirculation under anaerobic and aerobic conditions (Brandstätter et al., 2015a,b). The lysimeters were made of stainless steel and had a cylindrical shape with a volume of 121 L. To allow for drainage of leachate by gravity, a fine meshed grid of 8cm was placed at the bottom of the reactors. Experiments were run for 2.25 years and reactor temperature was kept constant ($\sim 309\text{K}$). MSW was sieved to a grain size $< 20\text{ mm}$ and initially had a water content of 23% and a dry bulk density of $846 \frac{\text{kg}}{\text{m}^3}$.

Table 1: Initial and environmental conditions in the duplicate experiments.

Type of experiment	Initial conditions						Environmental conditions					
	p_{CO_2}	$p_{\text{O}_2}/p_{\text{CH}_4}$	NH_3	pH	Cl^-	V_{liquid}	$\phi_{\text{waterflow}}^{\text{in1}}$	$\phi_{\text{sampleflow}}^{\text{out1}}$	$\phi_{\text{airflow}}^{\text{in}}$	V_{gas}	$p_{\text{gas}}^{\text{tot}}$	T
	[atm]	[atm]	[M]	[-]	[M]	[L]	[L d ⁻¹]	[L d ⁻¹]	[L d ⁻¹]	[L]	[atm]	[K]
Anaerobic (calibration)	0.10	0	0.03	8	0.025	19.5	0.03	0.03	-	41.9	1	308.5
Anaerobic (validation)	0.10	0	0.03	8	0.025	19.5	0.03	0.03	-	41.9	1	308.5
Aerated (calibration)	0.41	0	0.025	7.25	0.025	21.24	0.0524	0.0483	56.67	38.8	1	308.5
Aerated (validation)	0.41	0	0.025	7.25	0.025	20.95	0.0526	0.0491	56.67	38.82	1	308.5

1) The flows of water are averaged over the entire measurement period. After the first week, the MSW reached field capacity and flows were relatively constant.

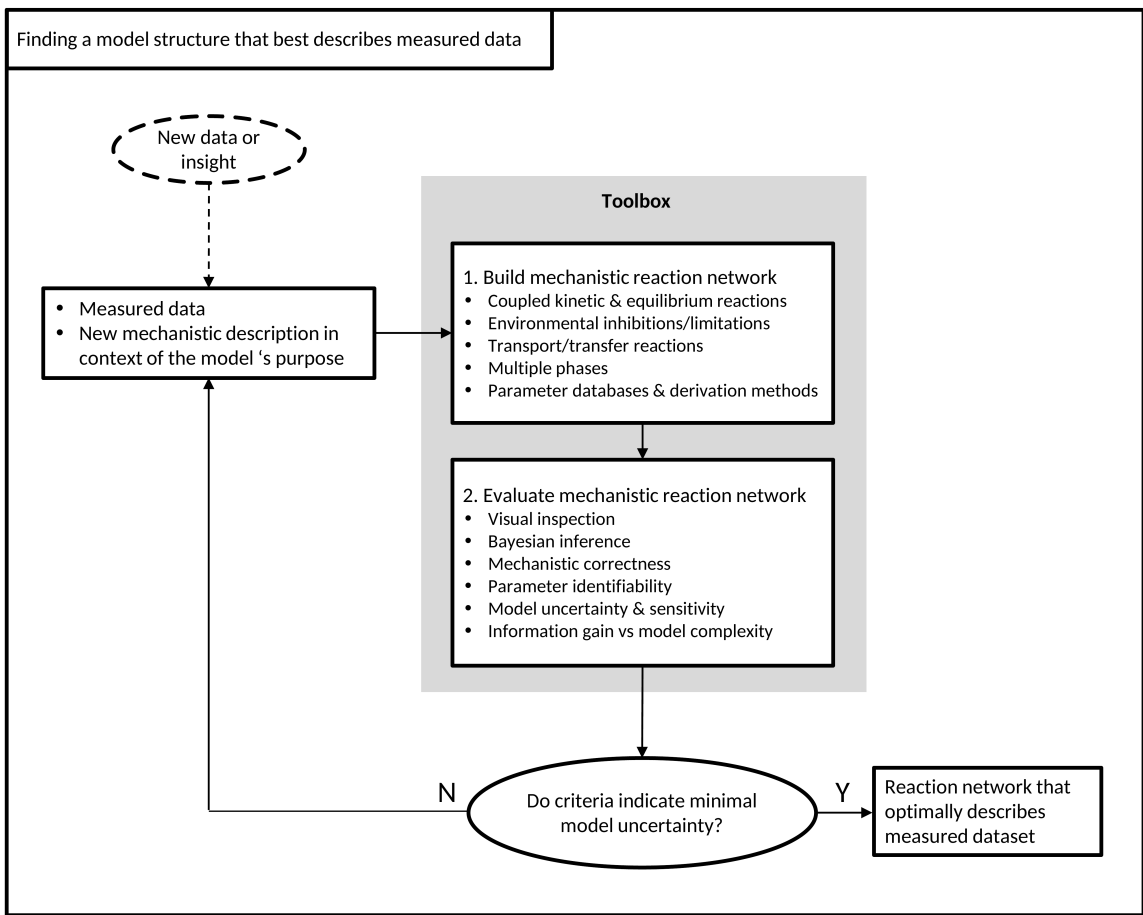


Figure 2: Iterative procedure for finding the biogeochemical process network that describes measured data with minimal ambiguity and uncertainty (van Turnhout et al., 2016). In step 1, the user manually builds the best network with the toolbox which is automatically optimized for the measured data in step 2. The user then decides if the network describes the measurements sufficiently accurate with the evaluation criteria generated in step 2. If not, the user starts another iteration and adapts the network.

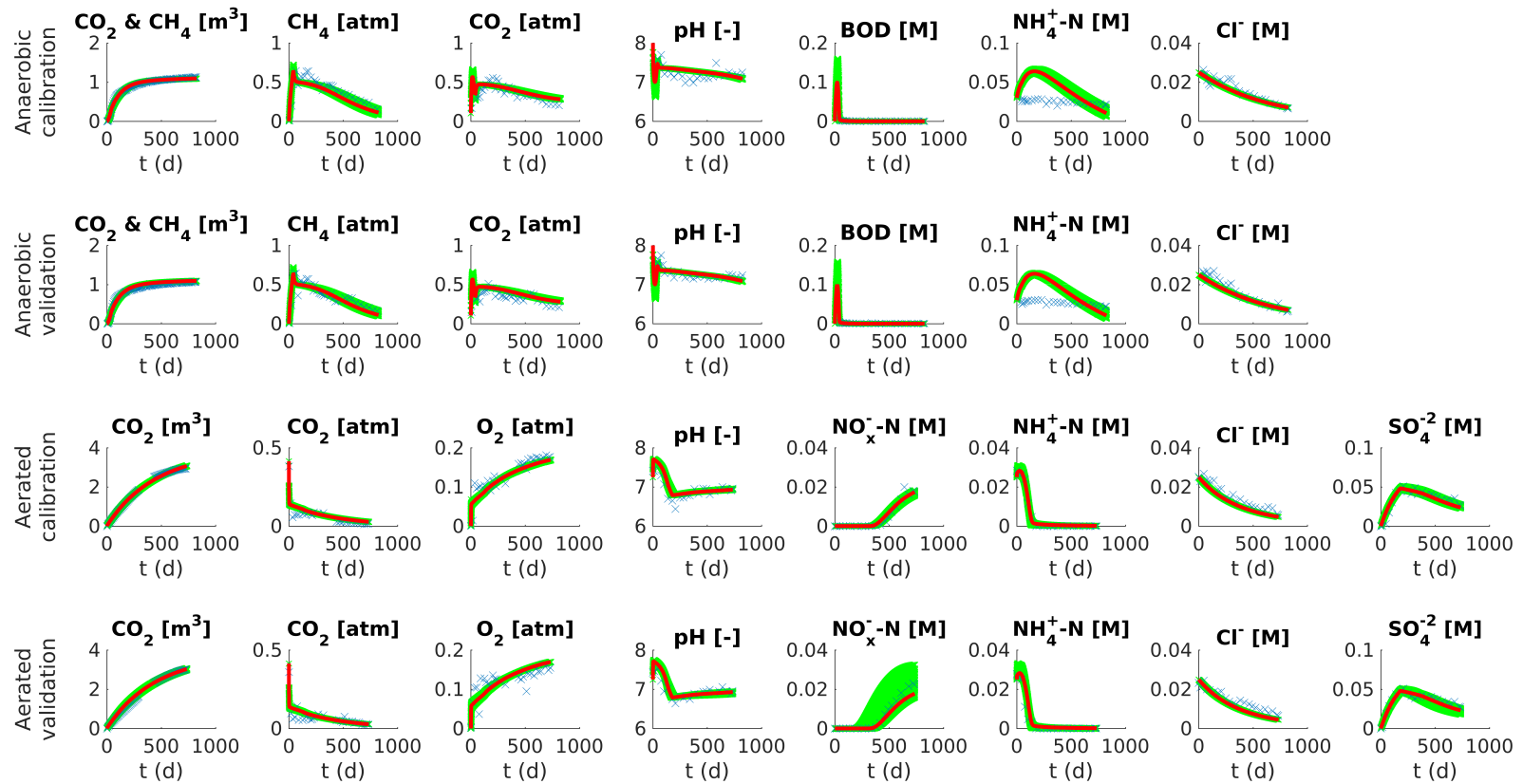


Figure 3: The visual agreement between the best fit of the modeled data (in red) and the measured data (in blue) for calibration and validation data measured during leachate recirculation under anaerobic and aerated conditions. The uncertainty in the total model error is indicated with green bandwidths surrounding the modeled data.

Table 2: Stoichiometry for the kinetic reactions in the biogeochemical process networks derived with the method from (Kleerebezem and van Loosdrecht, 2010) or deduced from the composition of MSW measured during sampling. Also the kinetic mechanisms are indicated. Parameters in bold were selected for calibration because they are highly uncertain and can significantly influence the model outcome.

Stoichiometry for the recirculation experiment under anaerobic conditions [mol]												Kinetics ^{c)}
	SOM ^{a)}	Acetic Acid	CO ₂	NH ₃	CH ₄	H ₂ O	H ⁺	X ^{b)} _{meth}	X _{(de)nitr}	O ₂	N ₂	
Hydrolysis ^{e)}	-1	0.5	0	0.036	0	-0.172	0	0	0	0	0	$k_{\text{hyd}} \cdot C_{\text{SOM}}^T$
Methanogenesis	0	-12.91	12.41	-0.2	12.41	0.6	0	1	0	0	0	$\mu_{\text{meth}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{Ac}}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}}$
Bacterial decay ^{d)}	0	0.5	0	0.2	0	-0.6	0	-1	0	0	0	$0.05 \cdot \mu_{\text{meth}}^{\text{max}} \cdot C_X$
(De)nitrification	0	-0.12	0.39	-0.54	0	1.5	0	0	1	-0.63	0.17	$\mu_{(\text{de})\text{nitr}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{O}_2}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}}$

Stoichiometry for the recirculation experiment under aerobic conditions [mol]												Kinetics	
	SOM	Glucose	CO ₂	NH ₃	H ₂ O	H ⁺	X _{aer-denitr}	O ₂	SO ₄ ⁻²	NO ₃ ⁻	X _{nitr}	N ₂	
Hydrolysis	-1	0.167	0	0.032	-0.172	ν_{H^+}	0	0	0.03	0	0	0	$k_{\text{hyd}} \cdot C_{\text{SOM}}^T$
Aerobic respiration	0	-0.23	0.39	-0.2	0.99	0	1	-0.39	0	0	0	0	$\mu_{\text{aer}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{Glu}}}^{\text{SL}} \cdot f_{C_{\text{O}_2}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}}$
Nitrification	0	0	-1	-11.42	10.82	11.22	0	-21.44	0	11.22	1	0	$\mu_{\text{nitr}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{NH}_3}}^{\text{SL}} \cdot f_{C_{\text{CO}_2}}^{\text{SL}}$
Denitrification	0	-0.24	0.42	-0.2	2.62	-0.33	1	0	0	-0.33	0	0.17	$\mu_{\text{denitr}}^{\text{max}} \cdot C_X \cdot f_{C_{\text{Glu}}}^{\text{SL}} \cdot f_{C_{\text{NO}_3^-}}^{\text{SL}} \cdot f_{C_{\text{NH}_3}}^{\text{SL}} \cdot f_{C_{\text{O}_2}}^{\text{NC}}$
Bacterial decay ^{d)}	0	0.17	0	0.2	-0.6	0	(-1)	0	0	0	(-1)	0	$0.05 \cdot \mu_{\text{aer}}^{\text{max}} \cdot C_X$

a) SOM is the biodegradable fraction of Solid Organic Matter in MSW generically modeled as $\text{C}_6\text{H}_{10}\text{O}_5\text{N}_{0.036}$ and $\text{C}_6\text{H}_{10}\text{O}_5\text{N}_{0.032}\text{S}_{0.03}$ for respectively anaerobic and aerobic conditions. b) X are species of bacteria with the elemental composition $\text{CH}_{1.4}\text{O}_{0.4}\text{N}_{0.2}$ taken from Henze et al. (1995). c) Substrate limitation factors (f^{SL}) and inhibition factors (f^{NC}) range between 0 and 1 (van Turnhout et al., 2016). Half saturation constants which are not calibrated have low values and are primarily included as switch factors. d) Bacterial biomass decay is included as a separate process for each species. e) Hydrolysis under anaerobic conditions is lumped with acidogenesis with hydrolysis being rate limiting.

Table 3: Results of the optimization: 5% – 95% quantiles of the posterior ranges. They are listed together with the prior ranges and the reference ranges measured under or estimated for non-limiting environmental conditions.

Anaerobic recirculation experiment							
	prior	posterior	reference		prior	posterior	reference
k_{hyd} [d^{-1}]	0.0005 – 0.15	0.0094 – 0.0104	0.09 – 0.26 ¹⁾	X_{meth} [mM]	0.005 – 15	0.59 – 11	0.27 – 19 ³⁾
$\mu_{\text{meth}}^{\text{max}}$ [d^{-1}]	0.01 – 3	0.04 – 0.12	0.8 ²⁾	$X_{(\text{de})\text{nitr}}$ [mM]	0.015 – 15	1.2 – 14	0.27 – 19 ³⁾
$\mu_{(\text{de})\text{nitr}}^{\text{max}}$ [d^{-1}]	0.001 – 1	0.11 – 0.96	1.4 ²⁾	$K_{\text{s},\text{C}_{\text{Ac}}^{\text{meth}}}$ [mM]	1 – 1000	5.5 – 16.7	0.03 – 420 ⁴⁾
$\phi_{\text{in,air}}$ [Ld^{-1}]	0.005 – 1.5	0.12 – 0.19	–	$C_{\text{SOM}}^{\text{ini}}$ [M]	2 – 3	2.27 – 2.33	–
Aerated recirculation experiment							
	prior	posterior	reference		prior	posterior	reference
k_{hyd} [d^{-1}]	0.00024 – 0.026	0.0021 – 0.0023	0.09 – 0.26 ¹⁾	X_{nitr} [mM]	0.09 – 110	1.1 – 2.7	0.27 – 19 ³⁾
$\mu_{\text{aer}}^{\text{max}}$ [d^{-1}]	1.2 – 121	25.6 – 118	57 ²⁾	$X_{\text{aer-denitr}}$ [mM]	7 – 800	9.5 – 35.4	0.27 – 19 ³⁾
$\mu_{\text{nitr}}^{\text{max}}$ [d^{-1}]	0.003 – 0.31	0.01 – 0.02	1.4 ²⁾	$K_{\text{s},\text{C}_{\text{NH}_3}^{\text{nitr}}}$ [mM]	0.9 – 110	1.6 – 7.1	0.04 ⁵⁾
$\mu_{\text{denitr}}^{\text{max}}$ [d^{-1}]	2 – 201	6.4 – 198	54 ²⁾	$K_{\text{i},\text{C}_{\text{O}_2}^{\text{denitr}}}$ [mM]	0.005 – 0.6	0.047 – 0.093	–
$C_{\text{SOM}}^{\text{ini}}$ [M]	5 – 7	6.2 – 6.5	–	$\nu_{\text{H}^+}^{\text{hyd}}$ [mol]	0 – 0.06	0.037 – 0.041	–

1) Veeken and Hamelers (1999) 2) Kleerebezem and van Loosdrecht (2010) 3) Nopharatana et al. (2007) 4) Meima et al. (2008) 5) Kantartz et al. (2006)

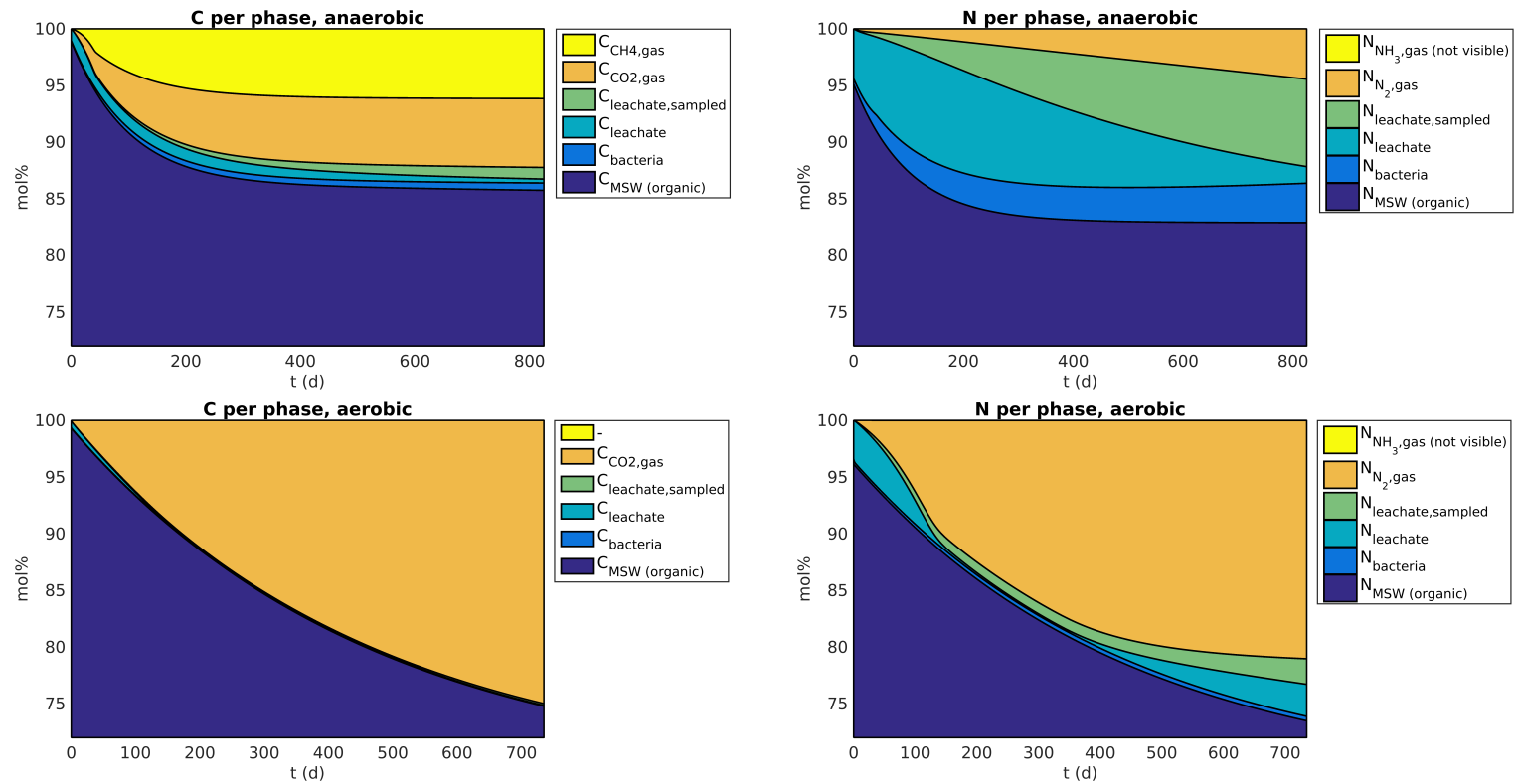


Figure 5: Modeled mass percentages of organic carbon and nitrogen in different phases during anaerobic and aerobic leachate recirculation. They indicate which phases are dominant in removing carbon and nitrogen from MSW for each treatment method.

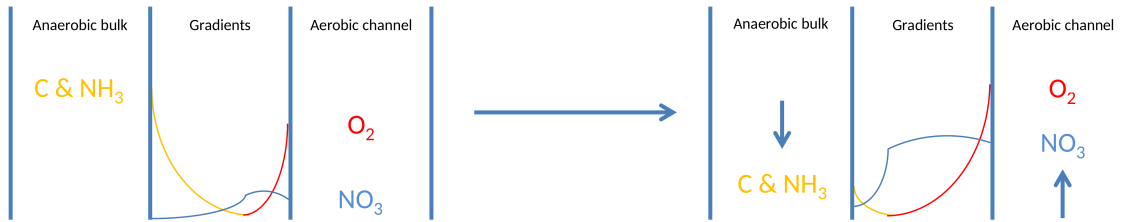


Figure 6: Illustration of the concentration gradients between aerobic and anaerobic regions in the MSW due to gas transport through preferential flow paths. When sufficient biodegradable carbon is present in the MSW, oxygen penetration is limited which leads to an anaerobic bulk where nitrate can be converted by denitrification (left). However, when the amount of biodegradable carbon becomes too small, oxygen penetrates deeper into the bulk which leads to failure of denitrification and increased nitrate concentrations (right).