TU Delft

Gray box modeling of MSW

Revealing its dominant (bio)chemical mechanism

A.G. van Turnhout, T.J. Heimovaara, R. Kleerebezem

Overview presentation

Introduction

What is the gray box model

Results

What can we simulate and what are the limits

Outlook

How to design follow up experiments

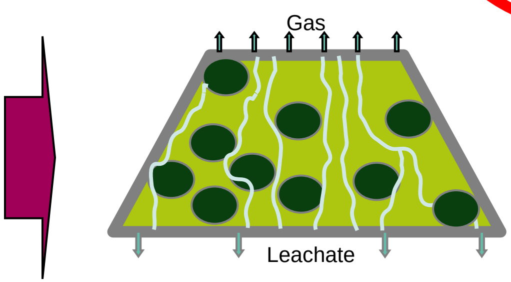
Model applications

The Gray box model

How to measure the (average) emission (potential)?

The Gray box model

Our approach



Water pocket (Biochemistry)
A.G. van Turnhout

Preferential flow (Transport)
S. Baviskar

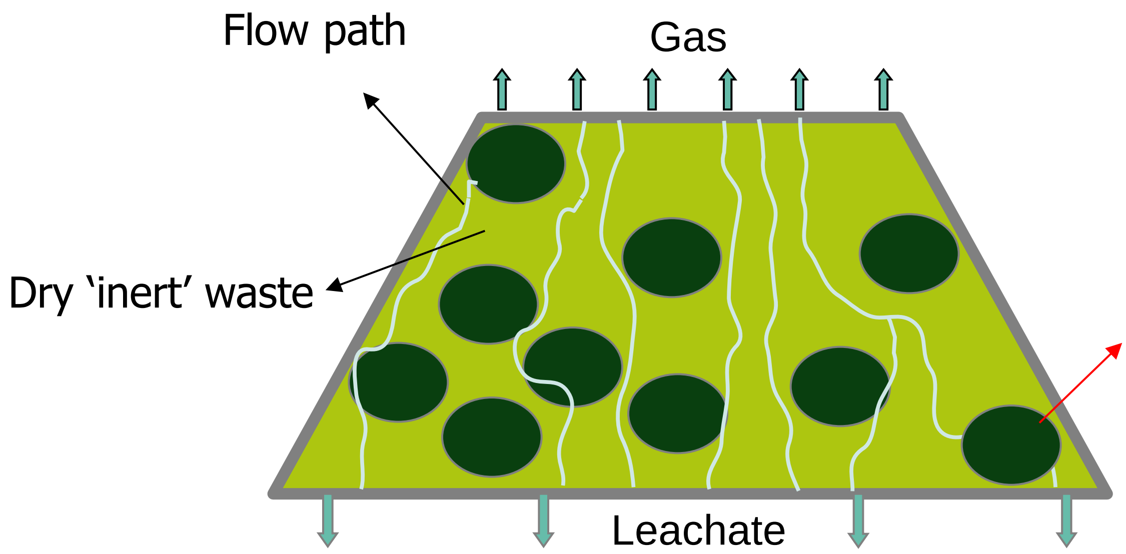
Coupled model
A. Bun

Parameter information (Geophysics)
L. Konstantaki

The Gray box model

Our hypothesis:

Most of the organic degradation takes place in water pockets



Important source term for biogas, leachate compounds

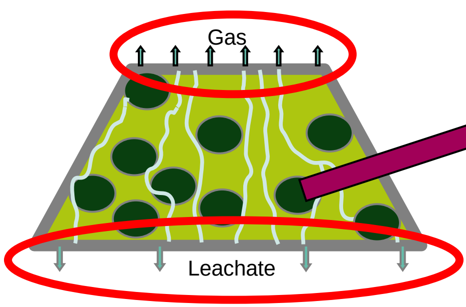
The Gray box model

Insight in treatment effects on degradation kinetics

Insight in processes/inhibitions controlling degradation

Extrapolate or inverse data

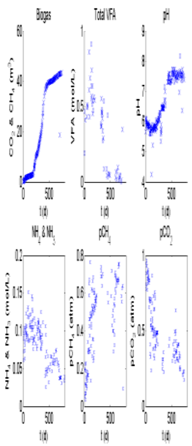
Water pocket



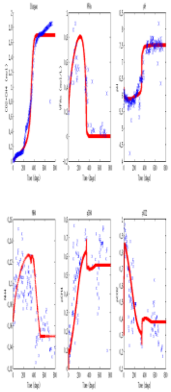
Column experiment

Shredded Municipal Solid Waste
(R. Valencia 2008)

Data

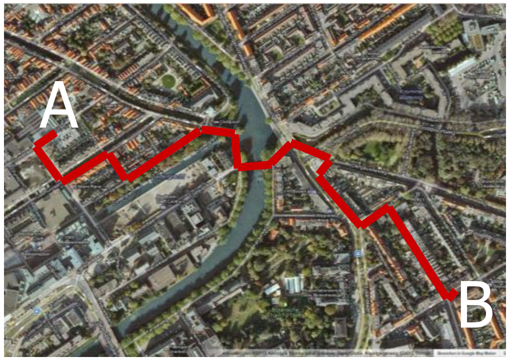


Numerical model



The Gray box model

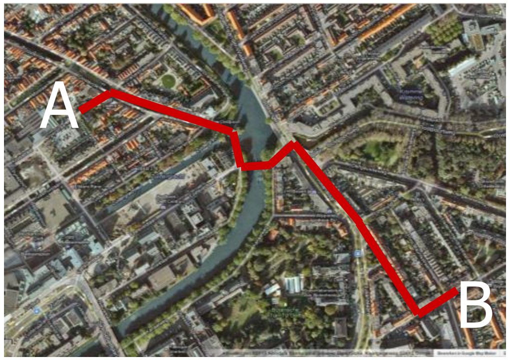
White box
(many parameters)



Black box
(few parameters)

Water pocket:
Many different
reactions

Gray box
(optimized parameter set)



The Gray box model

Where to simplify the model?

Model only the relative slow dominant reactions other processes are considered constant or in equilibrium

1. Hydrolysis and Methanogenesis kinetics
2. Sulphate reduction
3. Mass transfer from liquid to gas kinetics
4. First order Ammonium oxidation

INCLUDING

Accurate calculation of chemical and physical equilibrium

Essential to include because kinetics of processes are very sensitive to environmental conditions

The Gray box model

1. Lumped hydrolysis (inhibited by pH and VFA) — Kinetics

CxHyOzNi + H2O → VFAx+ NH3 + X(ace) + CO2

2. Methanogenesis (inhibited by pH, NH3 and H2S) — Kinetics

VFAx + NH3 → CH4 + CO2 + X(meth)

3. Sulfate reduction (inhibited by H2S) — Kinetics

H2SO4 + NH3 → H2S + CO2 + X(sulph)

4. Mass transfer from liquid to gas — Kinetics

pCO2 = H x C*   Rate constant = kla → f(Vg/Vl)

5. Ammonium oxidation — Kinetics

First order relation → k(NH3)

6. Chemical & Phase equilibrium — Equilibrium

Specific concentrations → pH, [HCO3-], [VFA-]   C(s) ↔ C(aq)

The Gray box model

Model parameters

Initial conditions
(Measurements)

T	p
Vl	Vg
% Inerts	Ci(hyd)
Ci(H2CO3)	Ci(VFAx)
Ci(CH4)	Ci(NH3)
Ci(SO4)	Ci(H+)
Ci(H2S)	

Semi-fundamental Parameters
(Peer review literature)

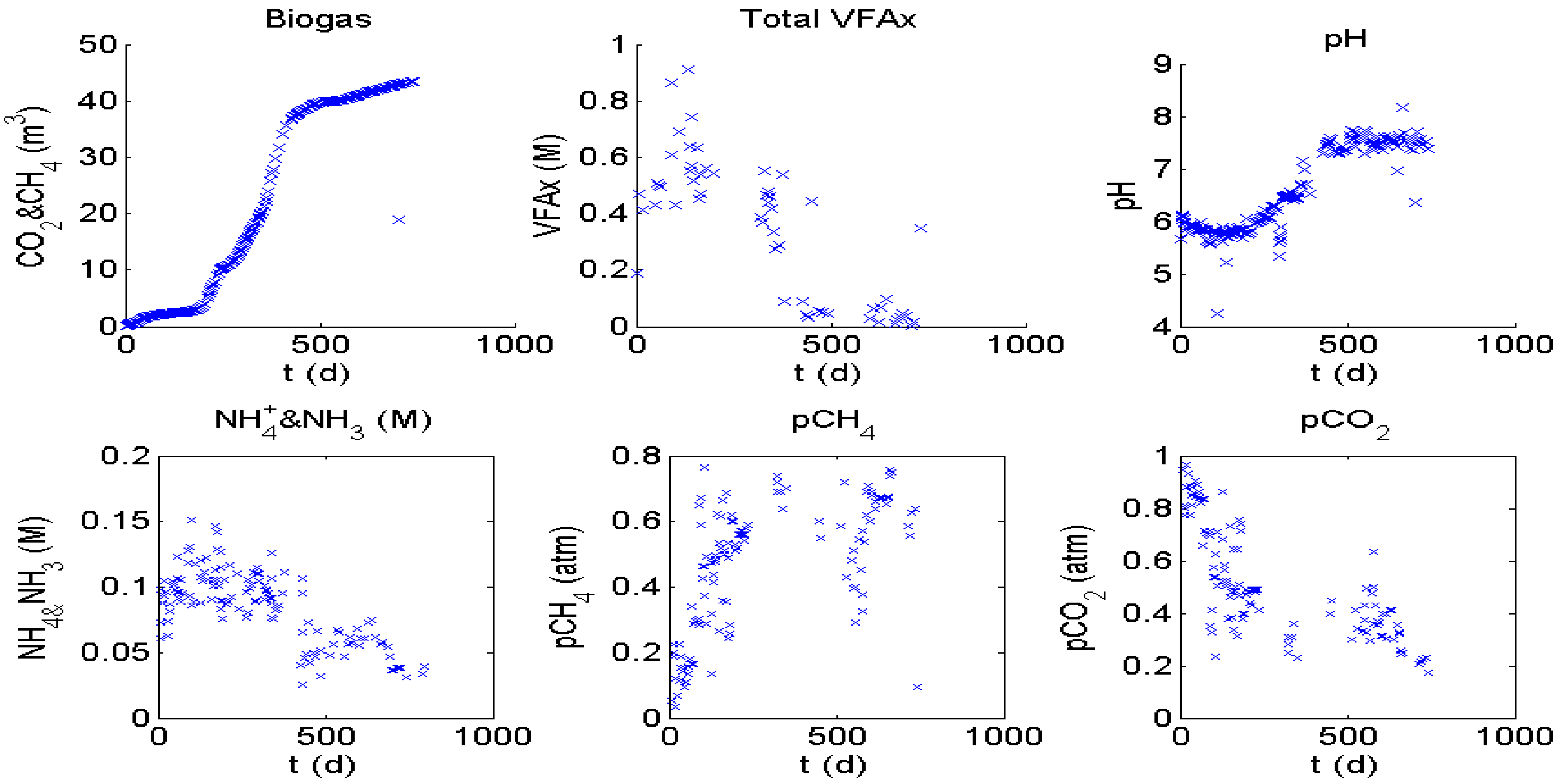
k(hyd)	qsmax(meth)
qsmax(sulph)	Ks(meth)
Ks(sulph)	Ki(pH,hyd)
Ki(pH,meth)	Ki(VFA,hyd)
Ki(NH3,meth)	Ki(H2S,meth)
Ki(H2S,sulph)	

Unknown Parameters
(fitted to data)

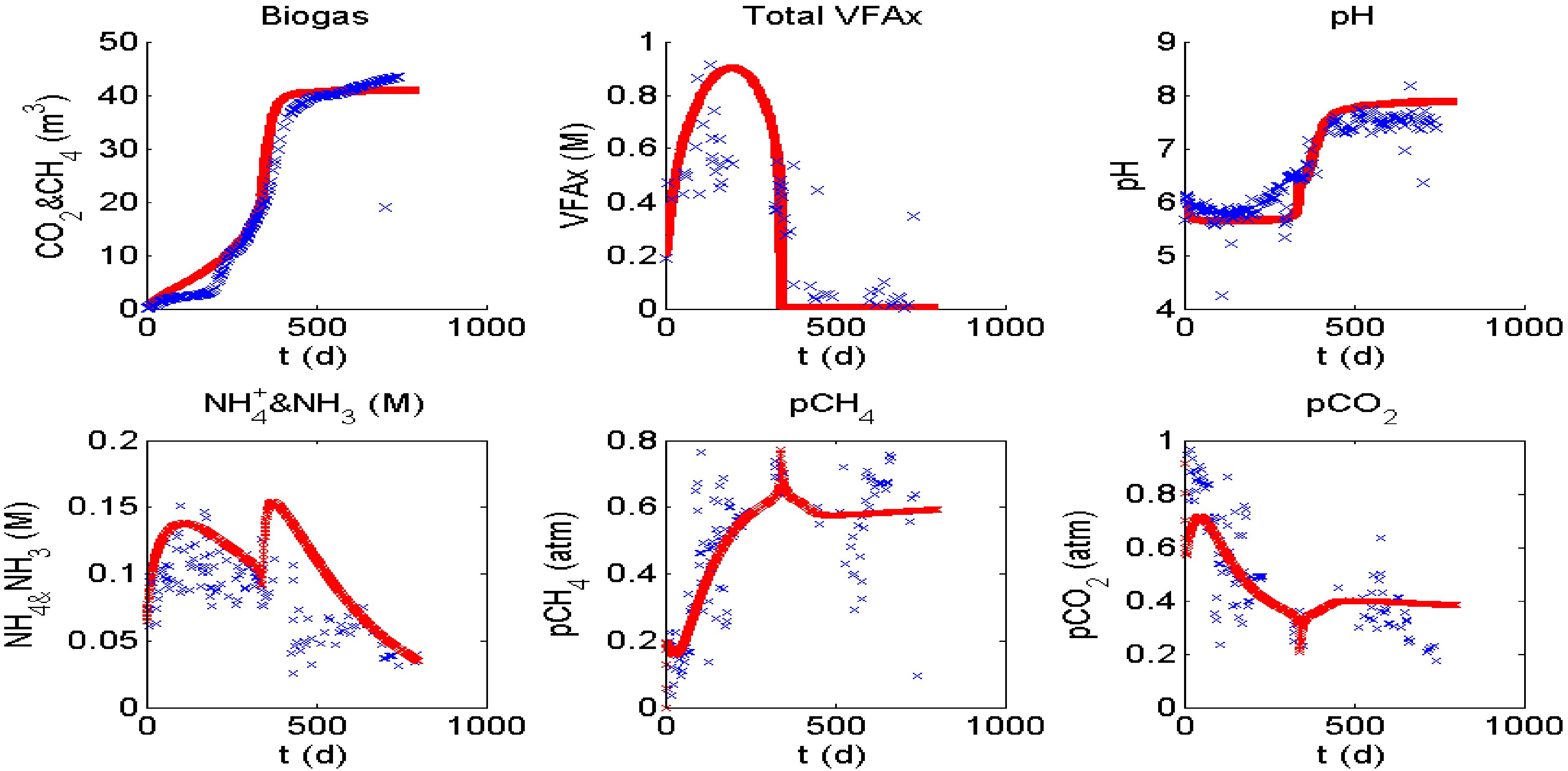
k(NH4)	kla
Ci(Xmeth)	Ci(Xsulph)

Fitted with SLS & Bayesian Statistics within realistic ranges

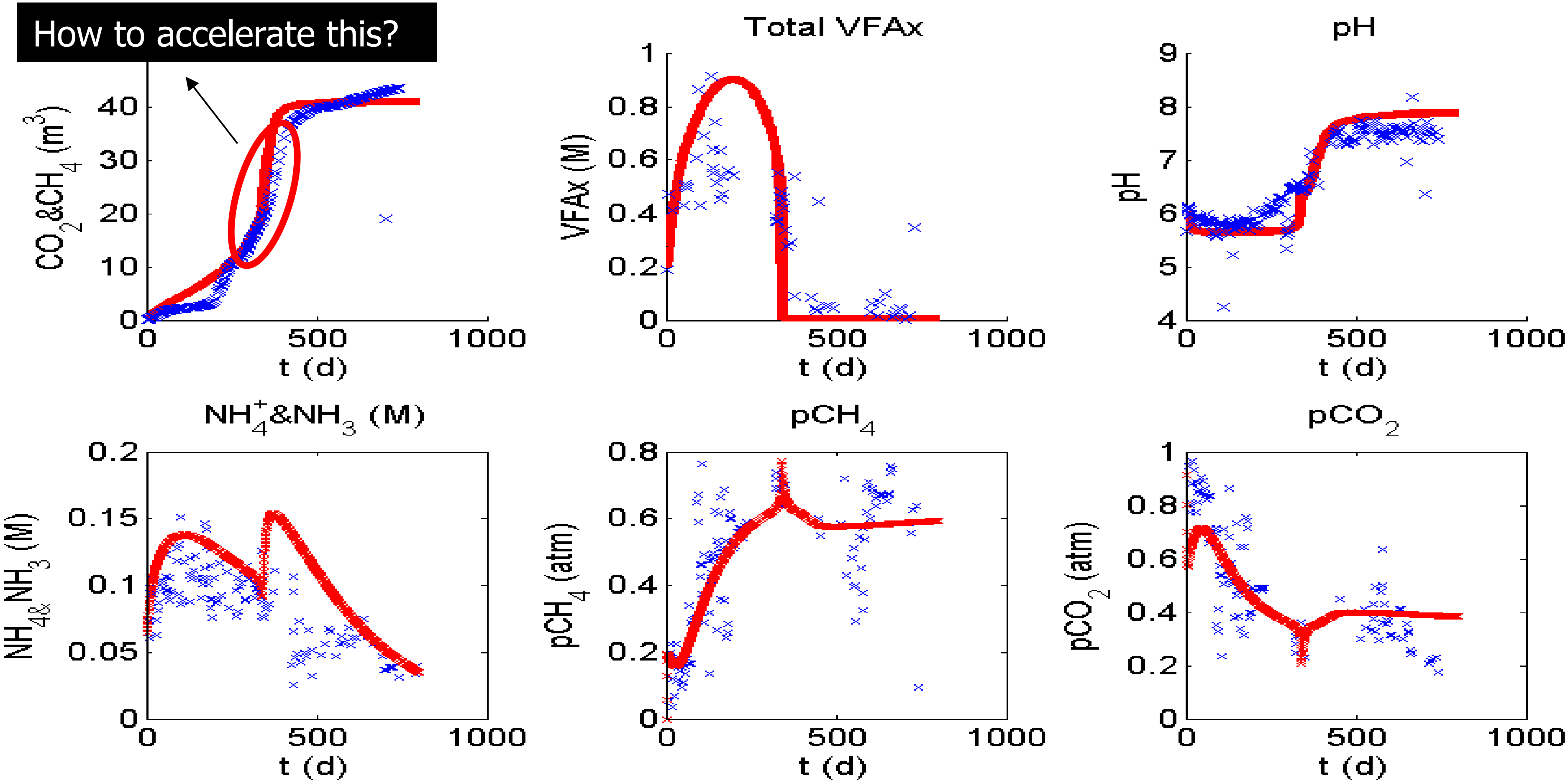
Results


Biogas
CO_2&CH_4 (m^3)
t (d)
Total VFAx
VFAx (M)
t (d)
pH
pH
t (d)
NH_4^+&NH_3 (M)
$NH_{4\&}NH_3$ (M)
t (d)
pCH_4
pCH_4 (atm)
t (d)
pCO_2
pCO_2 (atm)
t (d)

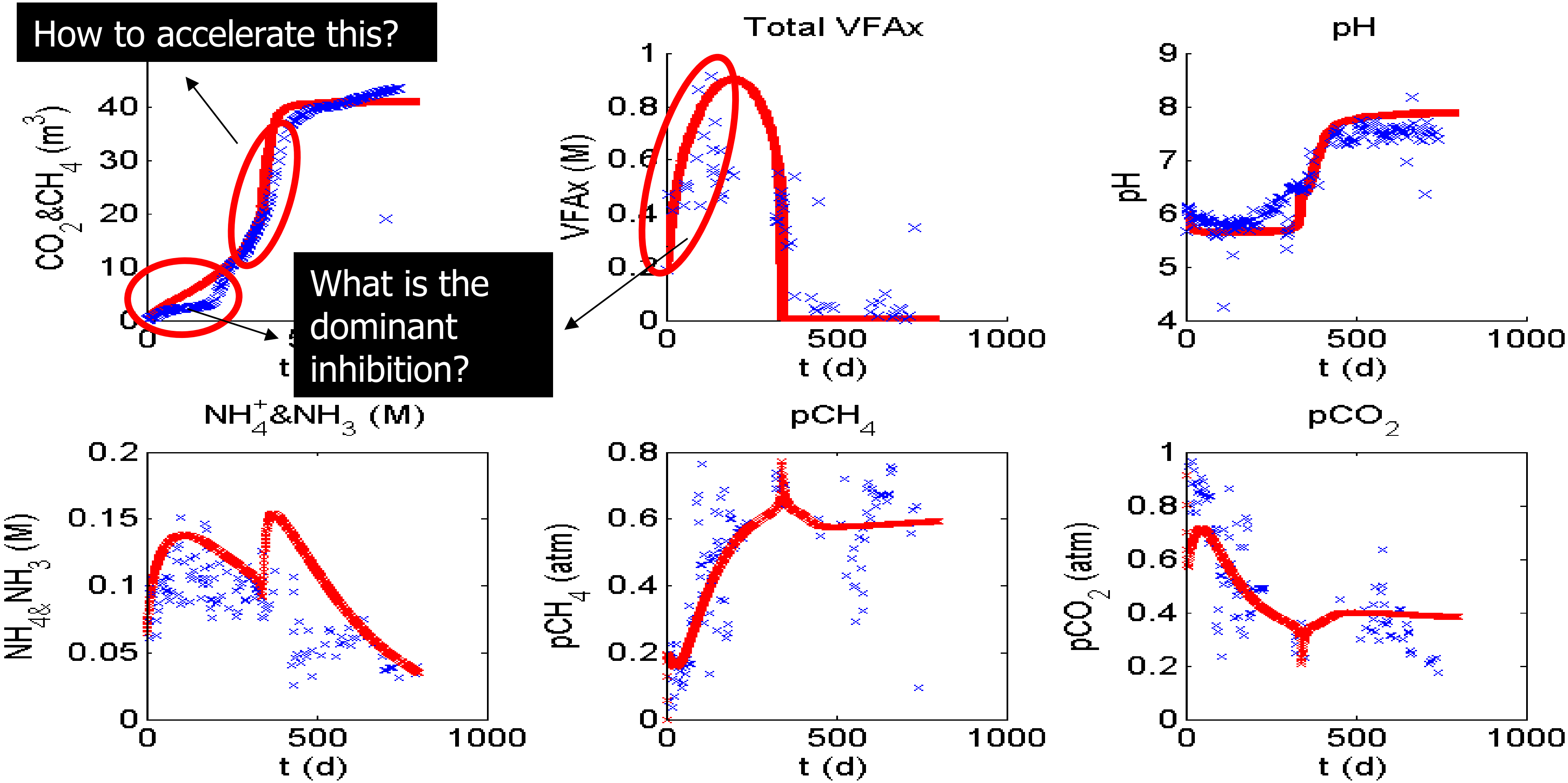
Results


Biogas
CO_2&CH_4 (m^3)
t (d)
Total VFAx
VFAx (M)
t (d)
pH
pH
t (d)
NH_4^+&NH_3 (M)
$NH_{4\&}NH_3$ (M)
t (d)
pCH_4
pCH_4 (atm)
t (d)
pCO_2
pCO_2 (atm)
t (d)

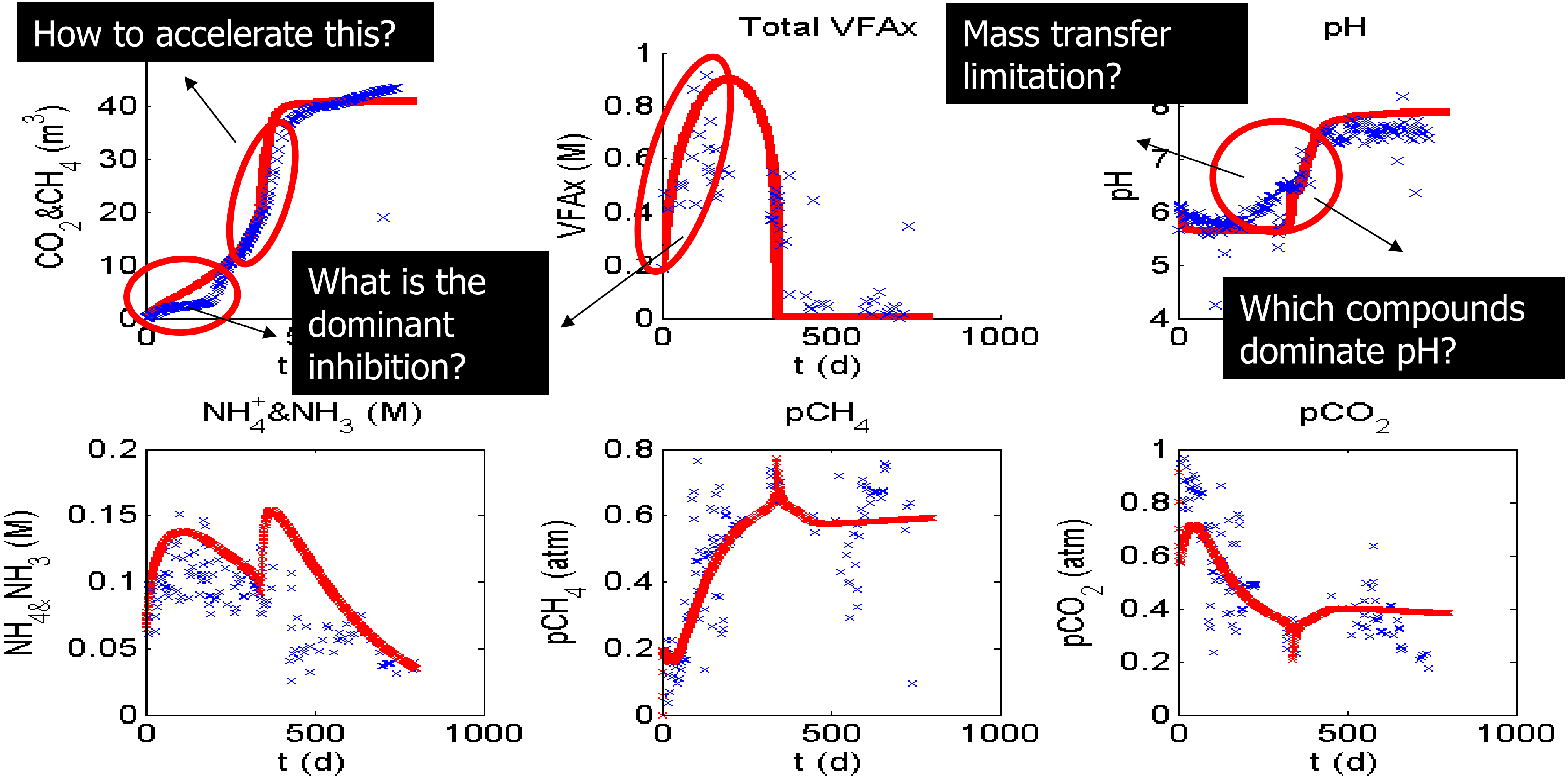
Results


How to accelerate this?
CO_2&CH_4 (m^3)
t (d)
Total VFAx
VFAx (M)
pH
NH_4^+&NH_3 (M)
$NH_{4\&}NH_3$ (M)
pCH_4
pCH_4 (atm)
pCO_2
pCO_2 (atm)

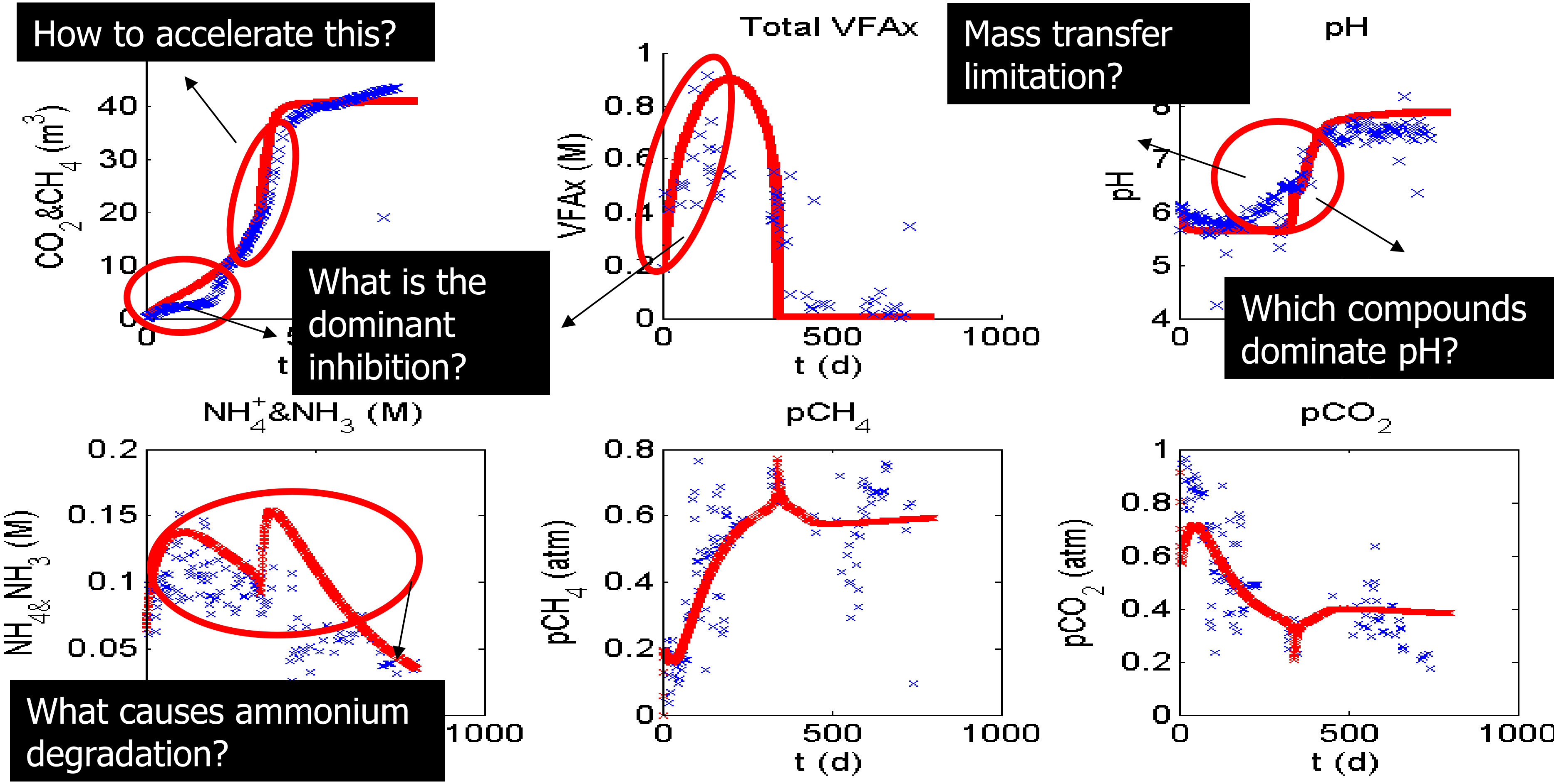
Results


How to accelerate this?
What is the dominant inhibition?
CO_2&CH_4 (m^3)
Total VFAx
VFAx (M)
pH
NH_4^+&NH_3 (M)
$NH_{4\&}NH_3$ (M)
pCH_4
pCH_4 (atm)
pCO_2
pCO_2 (atm)
t (d)

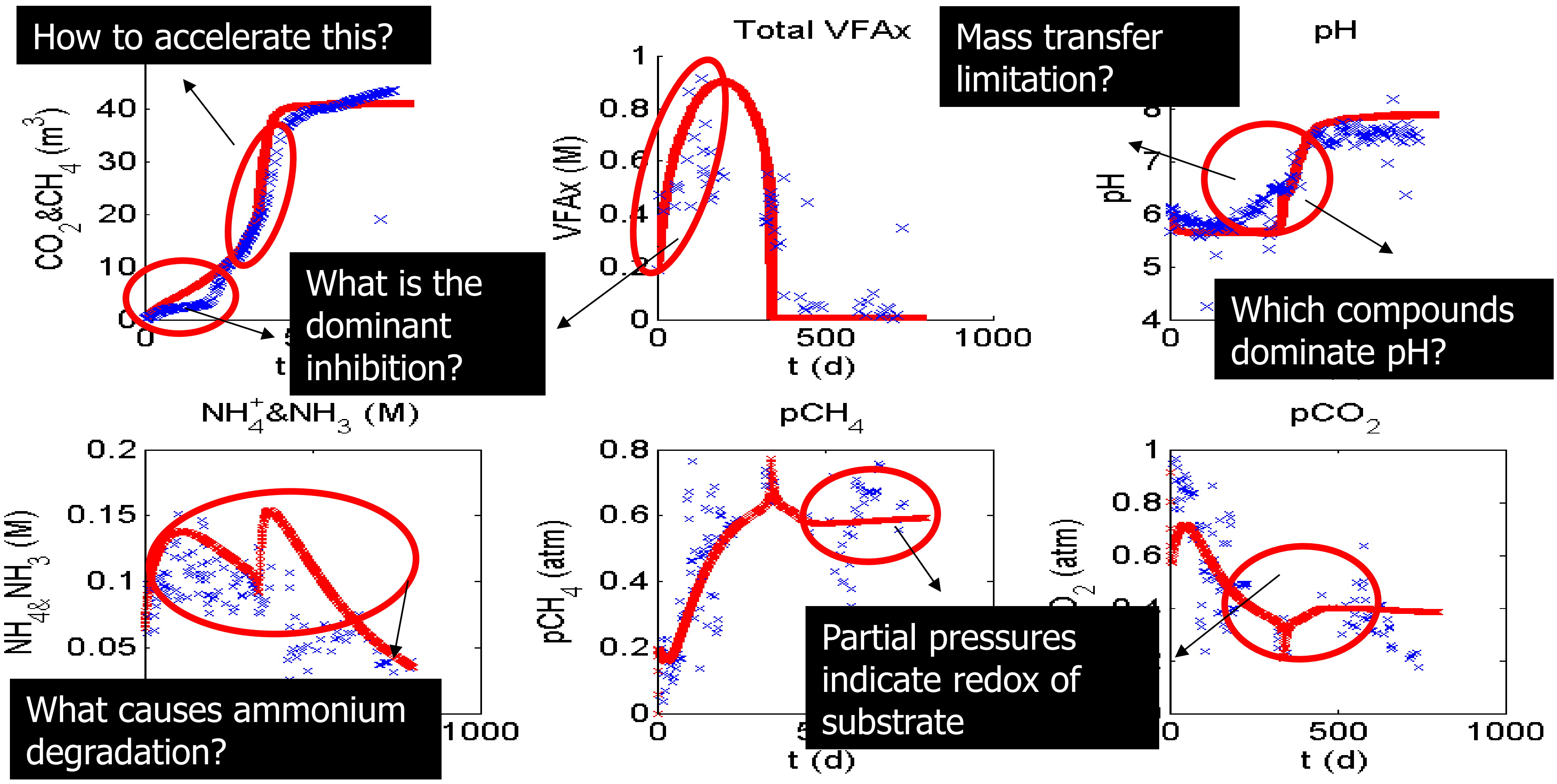
Results


How to accelerate this?
Total VFAx
Mass transfer limitation?
pH
What is the dominant inhibition?
Which compounds dominate pH?
CO2&CH4 (m3)
VFAx (M)
t (d)
NH4+&NH3 (M)
pCH4
pCO2
NH4&NH3 (M)
pCH4 (atm)
pCO2 (atm)
0
500
1000

Results


How to accelerate this?
CO_2&CH_4 (m^3)
Total VFAx
VFAx (M)
Mass transfer limitation?
pH
What is the dominant inhibition?
Which compounds dominate pH?
t (d)
NH_4^+&NH_3 (M)
$NH_{4\&}NH_3$ (M)
What causes ammonium degradation?
pCH_4
pCH_4 (atm)
pCO_2
pCO_2 (atm)
0
500
1000

Results


How to accelerate this?
What is the dominant inhibition?
Mass transfer limitation?
Which compounds dominate pH?
What causes ammonium degradation?
Partial pressures indicate redox of substrate
CO_2&CH_4 (m^3)
Total VFAx
VFAx (M)
t (d)
pH
NH_4^+&NH_3 (M)
NH_4&NH_3 (M)
pCH_4
pCH_4 (atm)
pCO_2

Results

Model parameters

Initial conditions
(Measurements)

T	p
Vl	Vg
% Inerts	Ci(hyd)
Ci(H2CO3)	Ci(VFAx)
Ci(CH4)	Ci(NH3)
Ci(SO4)	Ci(H+)
Ci(H2S)	

Semi-fundamental Parameters
(Peer review literature)

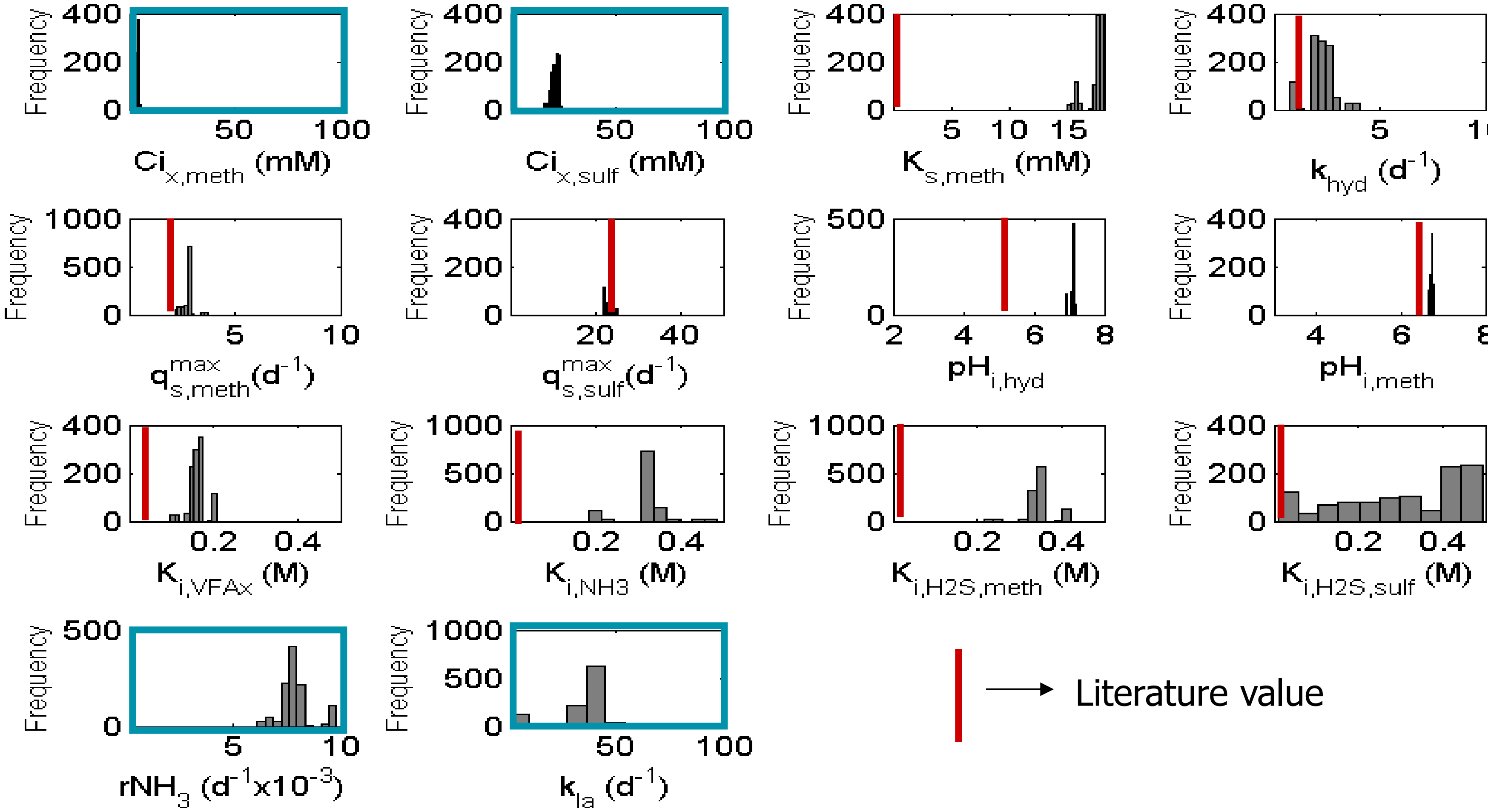
k(hyd)	qsmax(meth)
qsmax(sulf)	Ks(meth)
Ks(sulf)	Ki(pH,hyd)
Ki(pH,meth)	Ki(VFA,hyd)
Ki(NH3,meth)	Ki(H2S,meth)
Ki(H2S,sulf)	

Unknown Parameters
(fitted to data)

k(NH4)	kla
Ci(Xmeth)	Ci(Xsulf)

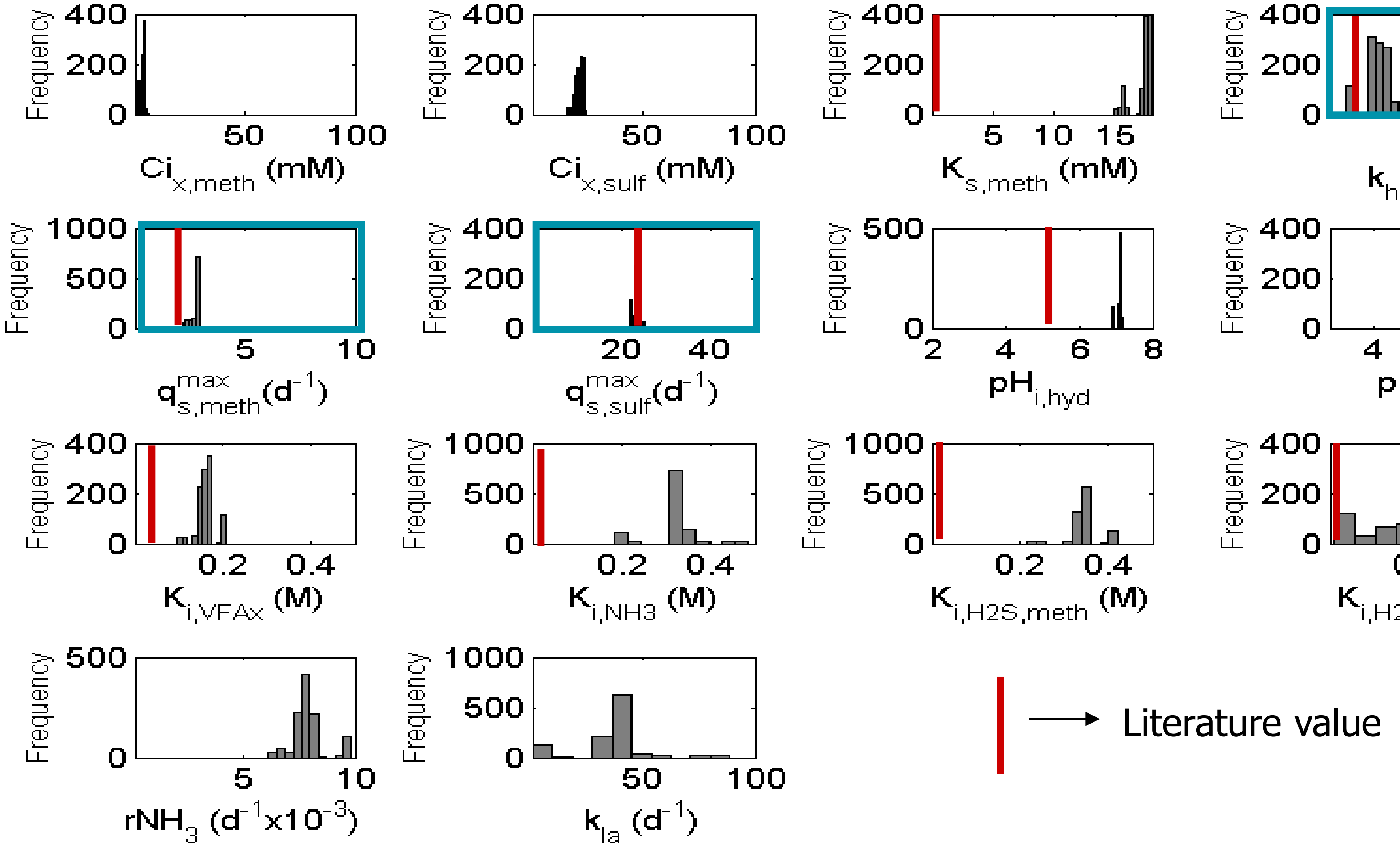
Fitted with SLS & Bayesian Statistics within realistic ranges

Results

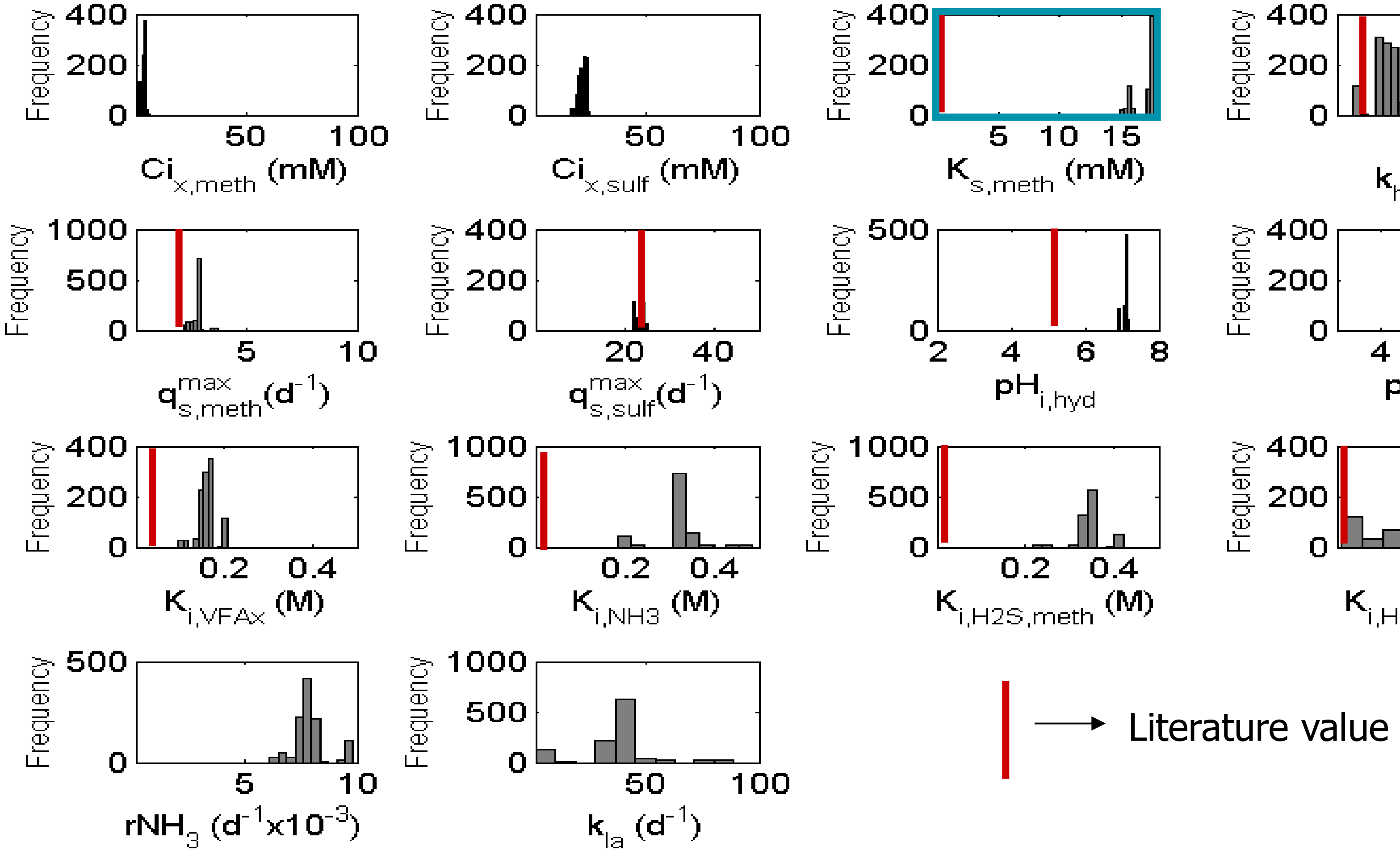


Frequency
400
200
0
50
100
Ci x,meth (mM)
Ci x,sulf (mM)
5 10 15
K s,meth (mM)
k hyd (d-1)
1000
500
q max s,meth (d-1)
q max s,sulf (d-1)
20 40
pH i,hyd
pH i,meth
0.2 0.4
K i,VFAx (M)
K i,NH3 (M)
K i,H2S,meth (M)
K i,H2S,sulf (M)
rNH3 (d-1x10-3)
k la (d-1)
Literature value

Results

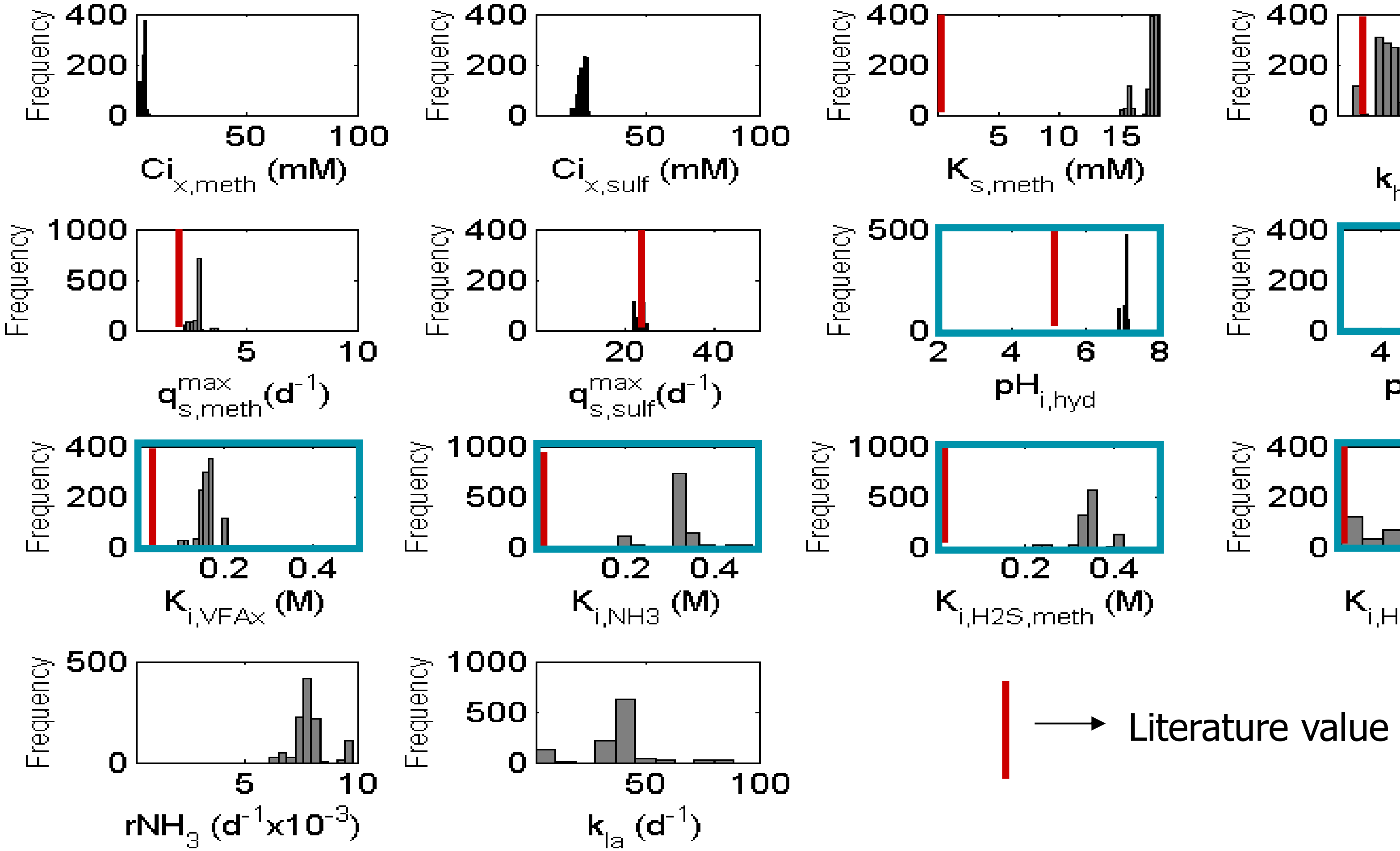

Frequency
400
200
0
50
100
$Ci_{x,meth}$ (mM)
$Ci_{x,sulf}$ (mM)
5
10
15
$K_{s,meth}$ (mM)
k_{hyd} (d^{-1})
1000
500
$q^{max}_{s,meth}$ (d^{-1})
20
40
$q^{max}_{s,sulf}$ (d^{-1})
2
4
6
8
$pH_{i,hyd}$
$pH_{i,meth}$
0.2
0.4
$K_{i,VFAx}$ (M)
$K_{i,NH3}$ (M)
$K_{i,H2S,meth}$ (M)
$K_{i,H2S,sulf}$ (M)
rNH_3 (d^{-1}x10^{-3})
k_{la} (d^{-1})
Literature value

Results



Frequency
Ci x,meth (mM)
Ci x,sulf (mM)
K s,meth (mM)
k hyd (d-1)
q max s,meth (d-1)
q max s,sulf (d-1)
pH i,hyd
pH i,meth
K i,VFAx (M)
K i,NH3 (M)
K i,H2S,meth (M)
K i,H2S,sulf (M)
rNH3 (d-1x10-3)
k la (d-1)
Literature value

Results


Frequency
Ci x,meth (mM)
Ci x,sulf (mM)
K s,meth (mM)
k hyd (d-1)
q max s,meth (d-1)
q max s,sulf (d-1)
pH i,hyd
pH i,meth
K i,VFAx (M)
K i,NH3 (M)
K i,H2S,meth (M)
K i,H2S,sulf (M)
rNH3 (d-1x10-3)
k la (d-1)
Literature value

Results

What do we see?

1. Generally the gray box model simplifies reality correctly
2. For some parameters/processes we need more data:
   - Ammonium oxidation
   - Mass transfer limitation
   - Kla, Cix, inhibitions

What we do we want?

More experimental data to minimize gap semi-fundamental parameter values and optimized parameter values

Outlook

Experiments

Establish semi-empirical mass transfer relation

LAB +

Test several treatments:

1. Irrigation/Recirculation
2. Aeration
3. 1 & 2 intermittent
4. 1 & 2 continuous
5. Nothing

Measure complete dataset
…Main ions, Carbonate system, VFA, CO_2, CH_4, H_2S, NH_3, NO_2, O_2, pH, EC, …

Establish semi-empirical settlement relation

Outlook

Calibrated model

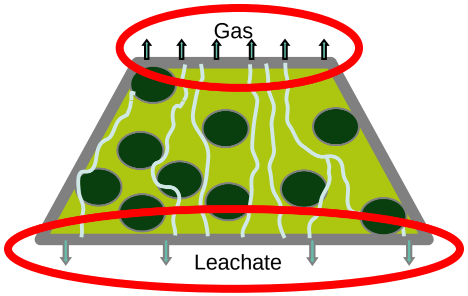
IC (Stochastic distribution)

Gray model

IC (Measured)

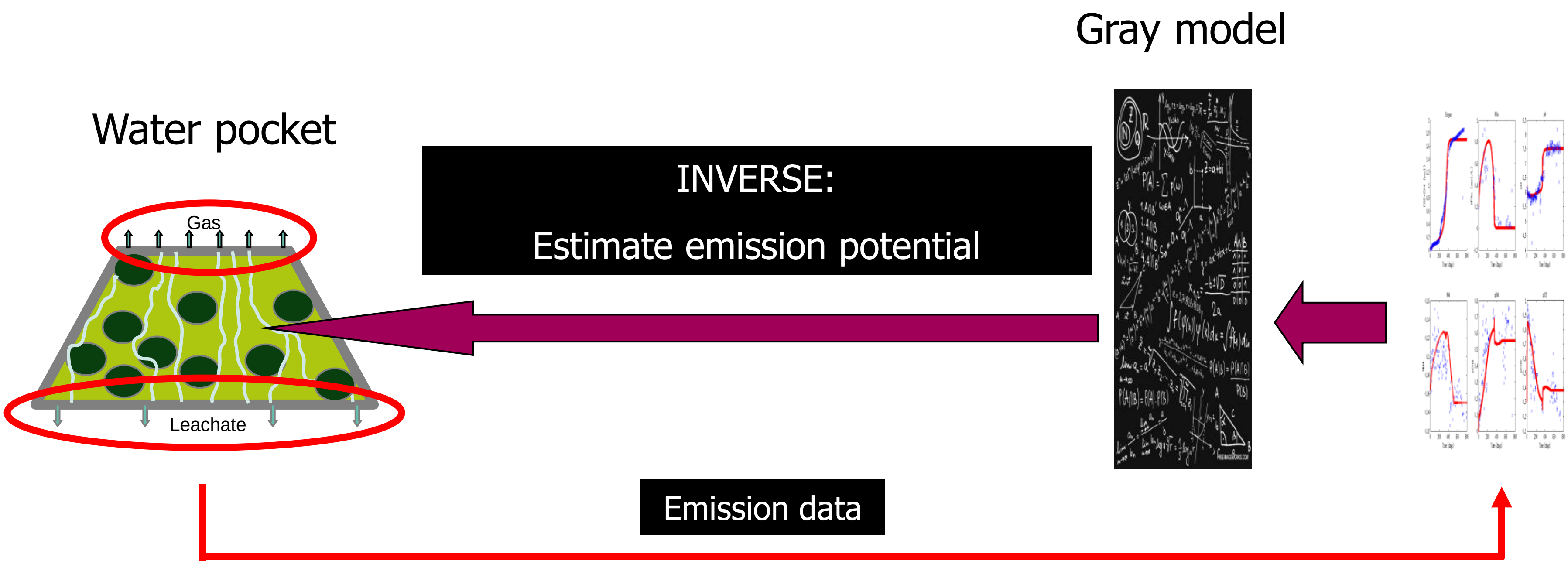
IC (Coupled model)

Water pocket



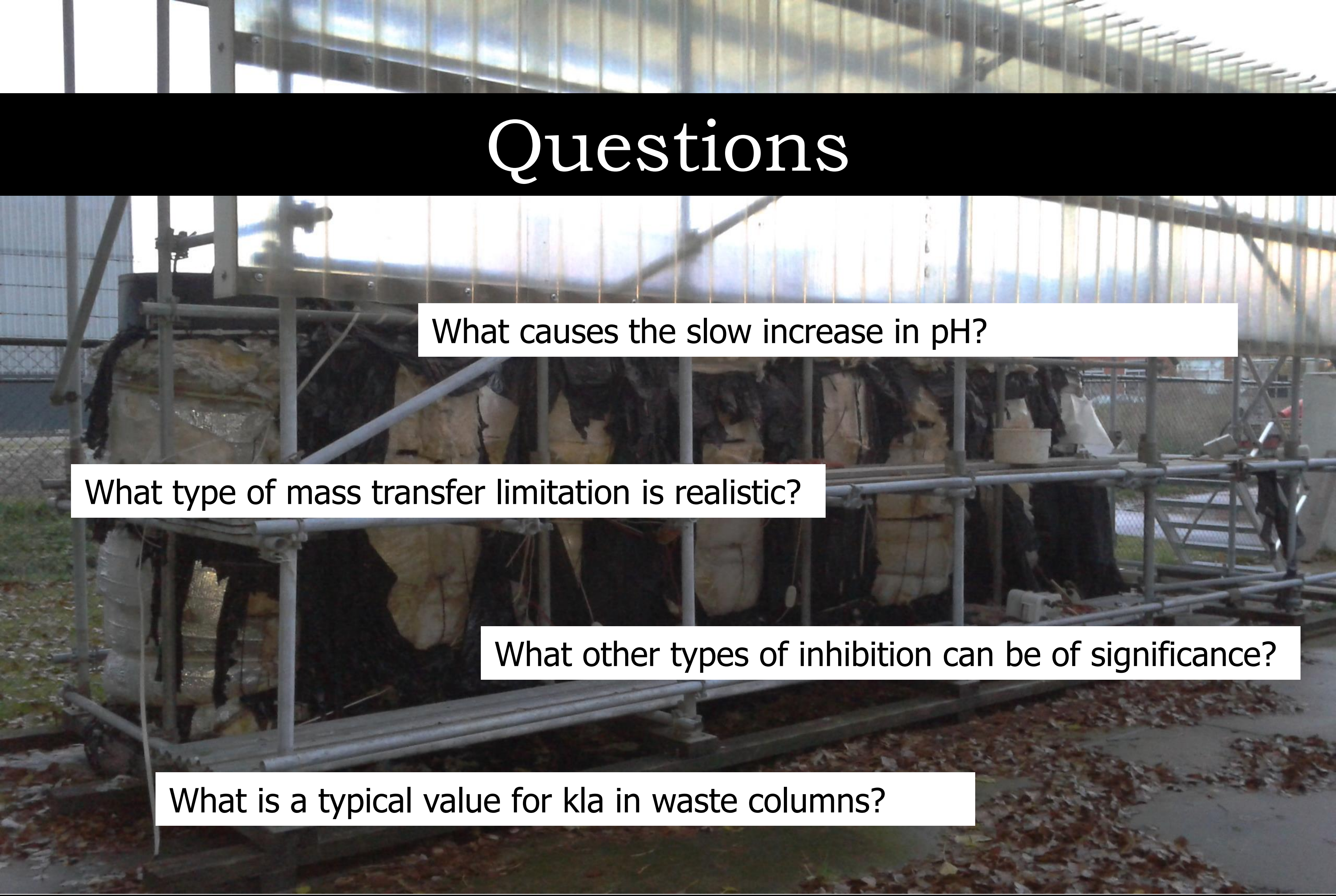
Outlook

Calibrated model



Questions

Questions



What causes the slow increase in pH?

What type of mass transfer limitation is realistic?

What other types of inhibition can be of significance?

What is a typical value for kla in waste columns?