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Modeling green microalgal growth, nutrient uptake and storage in the ASM framework

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Modeling green microalgal growth, nutrient uptake and storage in the ASM framework

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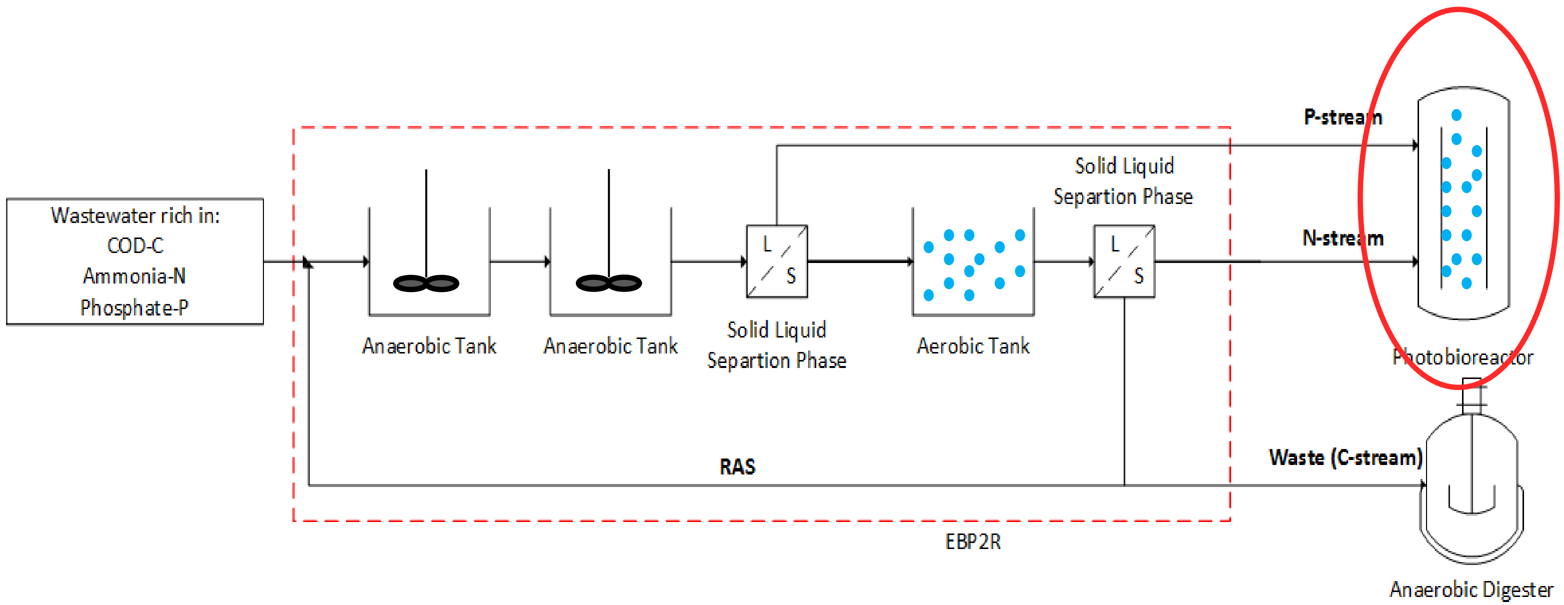
Motivation

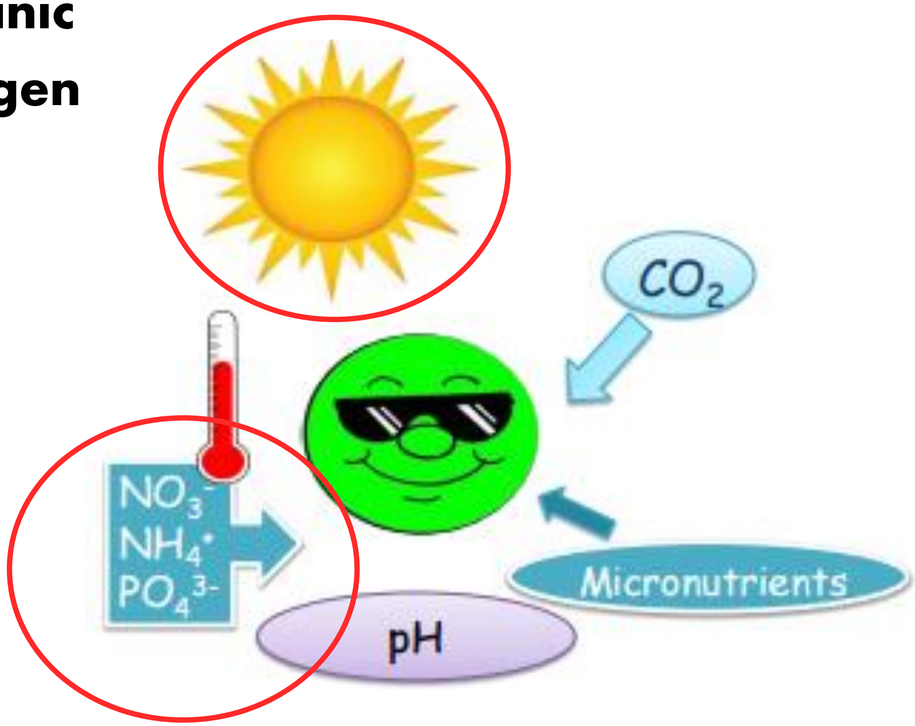
- **Microalgae photobioreactors can be used for wastewater treatment as:**
  - **Tertiary treatment step for nutrient removal**
  - **Nutrient recovery technology due to the phosphorus and nitrogen internal storage**



Valverde-Pérez et al. (2015)

Motivation

- Available models are good, however the applicability may be limited:
  - By the number of considered variables
  - By the model structure
- Factors affecting microalgal growth:
  - Carbon, both organic and inorganic
  - Nutrients: phosphorus and nitrogen
  - pH
  - Light
  - Micronutrients (e.g. iron)



Agenda

- Model development
- Targeted experiments for parameter estimation:
  - Green microalgae identification and equipment
  - Microbatch and 1-L batch experiments
  - Open pond experiments
- Model evaluation

Model development (ASM-A)

- **Mechanistic** description of **biokinetic** processes: multiple-substrate kinetic process rate equations based on literature

Model	Autotrophic algal growth										Heterotrophic algal growth
	Nutrients		*DIC*	*Light*							
	N	*P*		*Monod*	*Haldane*	*Steele*	*P&E*	*P&J*	*Smith*	*Poisson*	
Moya et al.[46]											H
Bouterfas et al. [48]											
Ambrose et al.[31]	D	D									
Wolf et al.[32]	M										
Bougaran et al.[42]	D	D									
Quinn et al. [33]	D										
Broekhuizen et al.[34]	M										
Skjelbred et al.[49]											
Guest et al.[35]	D										
Decostere et al. [36]											
Coppens et al. [38]	M										
Van Wagenen et al.[52]											
ASM-A (This study)	D										M

D: Droop

M: Monod

H: Haldane

Model development (ASM-A)

- Developed as an **extension of ASM-2d**, so compatible with activated sludge models
- Units and nomenclature expressed according to the **ASM** (activated sludge modelling) **framework**

Component	NH_4	NO_3	Internal quota N	PO_4	Internal quota P	Inorg. carbon	Acetate	O_2	Algal Biomass	Inert Particulates
Symbol Unit	S_{NH4} gN/m^3	S_{NO} gN/m^3	$X_{Alg,N}$ gN/m^3	S_{PO4} gP/m^3	$X_{Alg,PP}$ gP/m^3	S_{Alk} gC/m^3	S_A $gCOD/m^3$	S_{O2} $gCOD/m^3$	X_{Alg} $gCOD/m^3$	X_I $gCOD/m^3$
Process	**Stoichiometric Matrix**									
Uptake and storage of nitrogen from NH4	-1		1							
Uptake and storage of nitrogen from NO3		-1	1							
Uptake and Storage of PO4				-1	1					
Autotrophic growth			$-i\_NX_{alg}$		$-i\_PX_{alg}$	$-1/Y_{Xalg,SAlk}$		$1/(2.67*Y_{Xalg},S_{Alk})$	1	
Heterotrophic growth			$-i\_NX_{alg}$		$-i\_PX_{alg}$	$1/(0.4*Y_{Xalg},S_A)$	$-1/(1.067*Y_{Xalg},S_A)$	$-1/(1.067*Y_{Xalg},S_A)$	1	
Decay	$i\_NX_{alg}-f_{Xi}*i\_N_{XAlg,D}$			$i\_PX_{alg}-f_{Xi}*i\_P_{XAlg,D}$				$-(1-f_{Xi})$	-1	f_{Xi}

Microalgal nutrient uptake and storage

- **Processes 1&2: uptake and storage of nitrogen using ammonia and nitrate as nitrogen source**

$$k_{NH4} \cdot \frac{S_{NH4}}{S_{NH4} + K_{NH4,Alg}} \cdot \frac{X_{Alg,Nmax} \cdot X_{Alg} - X_{Alg,N}}{X_{Alg,Nmax} \cdot X_{Alg}} \cdot X_{Alg}$$

$$k_{NO} \cdot \frac{S_{NO}}{S_{NO} + K_{NO,Alg}} \cdot \frac{K_{NH4,Alg}}{K_{NH4,Alg} + S_{NH4}} \cdot \frac{X_{Alg,Nmax} \cdot X_{Alg} - X_{Alg,N}}{X_{Alg,Nmax} \cdot X_{Alg}} \cdot X_{Alg}$$

- **Process 3: uptake and storage of phosphate**

$$k_{PO4} \cdot \frac{S_{PO4}}{S_{PO4} + K_{PO4,Alg}} \cdot \frac{X_{Alg,PPmax} \cdot X_{Alg} - X_{Alg,PP}}{X_{Alg,PPmax} \cdot X_{Alg}} \cdot X_{Alg}$$

Rieger et al. (2001)
Rhee (1973)
Ambrose et al. (2006)

Microalgal growth and decay

- **Processes 4: autotrophic growth rate**

$$\mu_{A,max} \cdot \left(1 - \frac{X_{Alg,Nmin} X_{Alg}}{X_{Alg,N}}\right) \cdot \left(1 - \frac{X_{Alg,PPmin} X_{Alg}}{X_{Alg,PP}}\right) \cdot \frac{S_{Alk}}{S_{Alk} + K_{Alk}} \cdot \frac{I_{Av}}{I_S} \cdot e^{1-\frac{I_{Av}}{I_S}} \cdot X_{Alg}$$

- **Process 5: heterotrophic growth rate**

$$\mu_{H,max} \cdot \left(1 - \frac{X_{Alg,Nmin} X_{Alg}}{X_{Alg,N}}\right) \cdot \left(1 - \frac{X_{Alg,PPmin} X_{Alg}}{X_{Alg,PP}}\right) \cdot \frac{S_A}{S_A + K_A} \cdot \frac{S_{O2}}{S_{O2} + K_{O2}} \cdot \frac{K_I}{K_I + I_{Av}} \cdot X_{Alg}$$

- **Process 6: decay**

$$b_{Xalg} \cdot X_{Alg}$$

Droop (1974)
Broekhuizen et al. (2012)
Rieger et al. (2001)
Ambrose et al. (2006)
Chen and Johns (1994)

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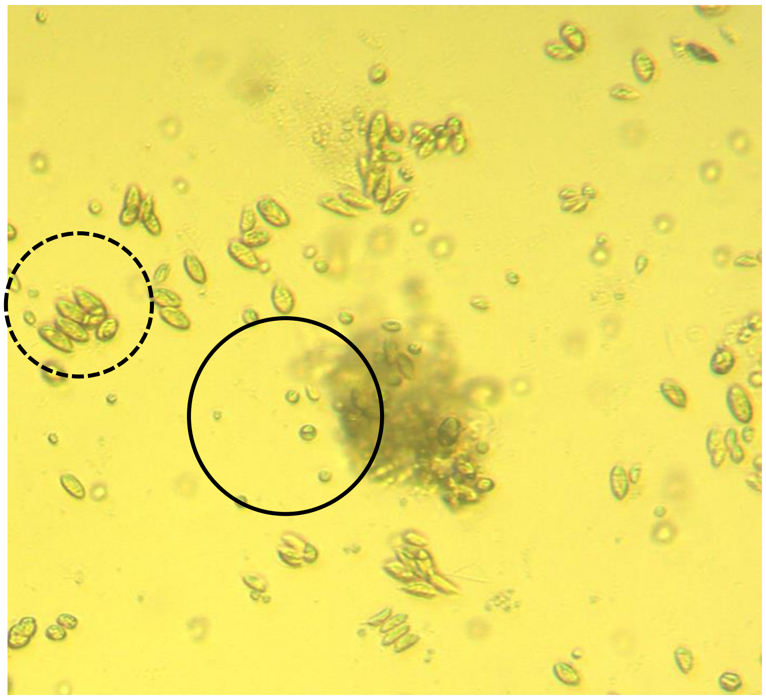
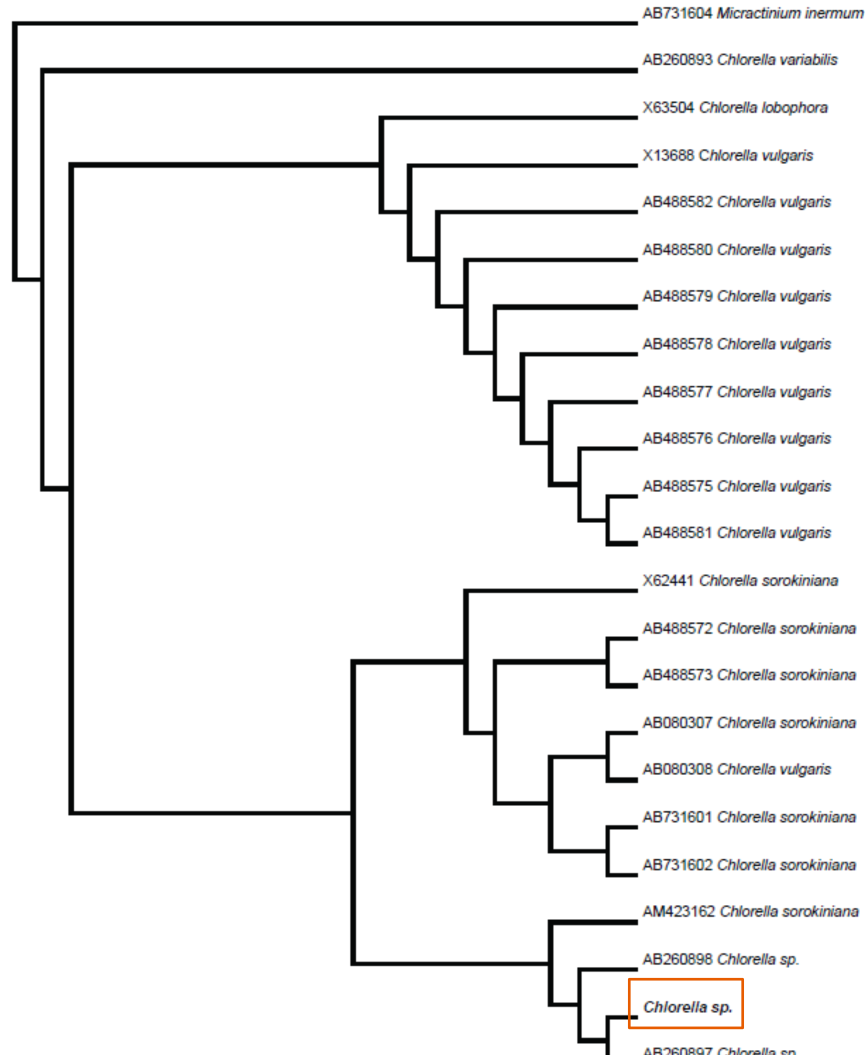
Microalgal culture

- Mixed green microalgal culture consists mainly of ***Chlorella sp.*** (*C. sorokiniana*) and ***Scenedesmus sp.***

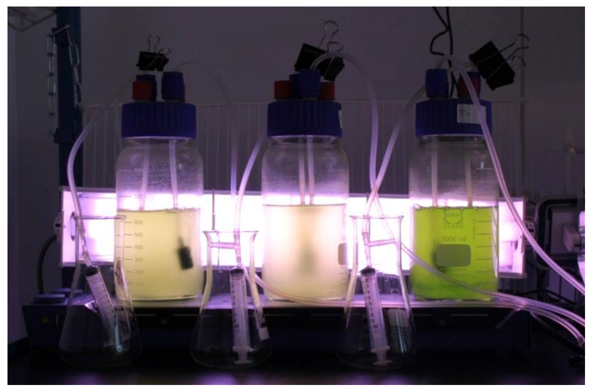


Microscope image of the mixed green microalgae culture in the batch experiment.



Reactors

2 mL microbatches

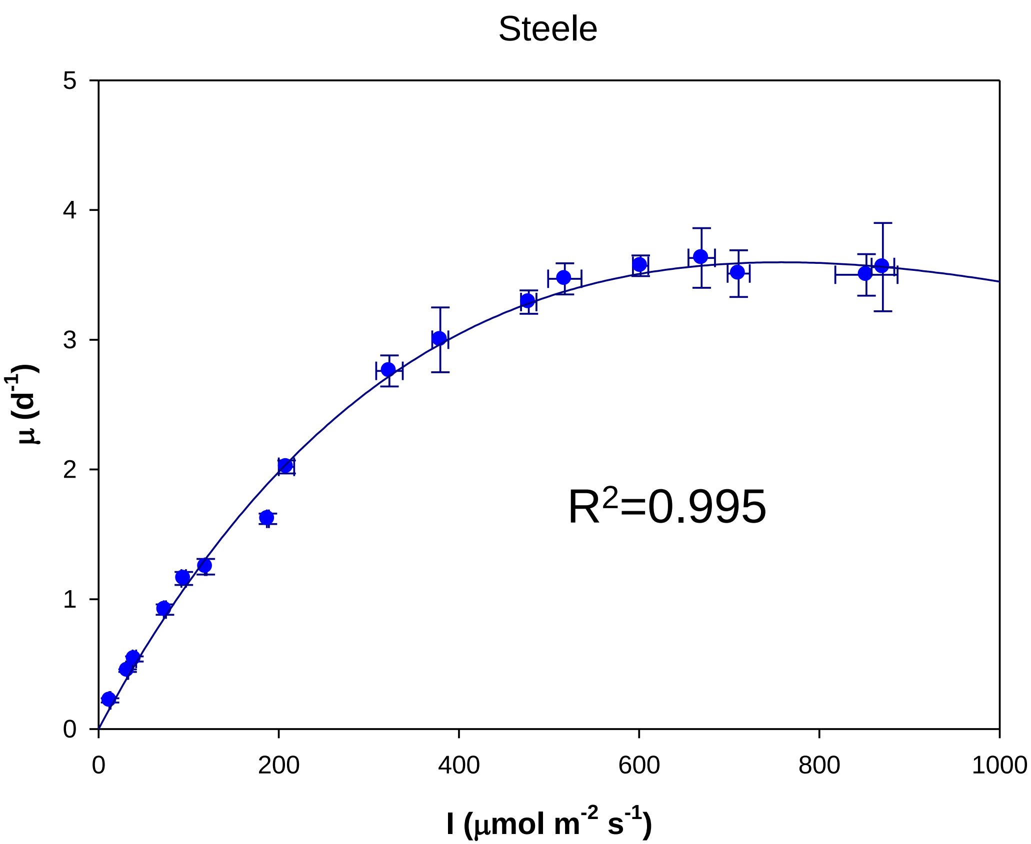


1-L batches

24 L open airlift PhBR

Microbath experiments: light intensity effect

- **Assessing the specific growth rate under different light intensities**

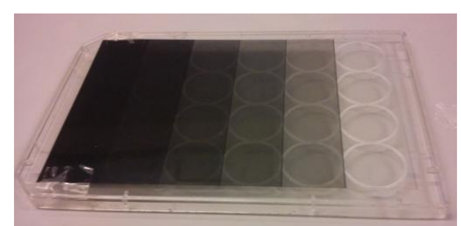


Steele equation:

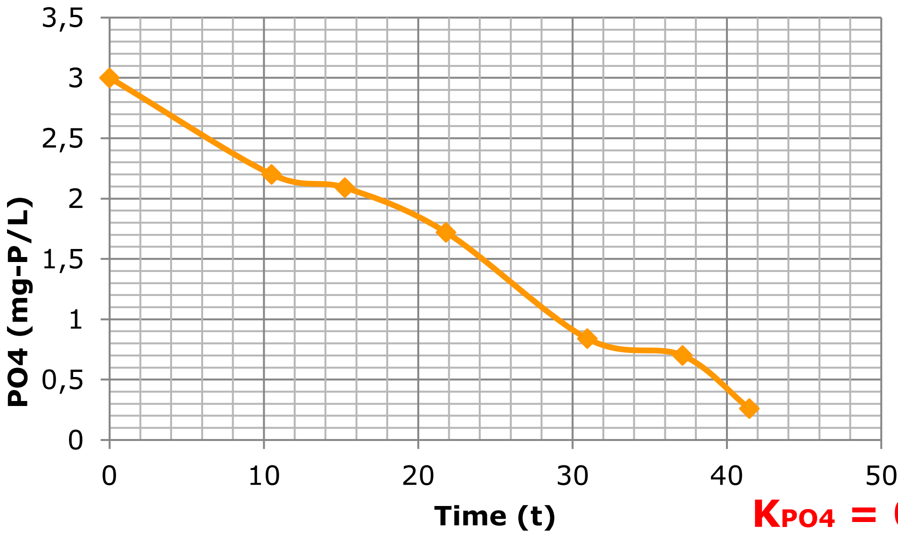
$$\mu = \frac{\mu_{max} * I}{I_s} exp^{1-I/I_s}$$

μ_{max} = 3.6 d^{-1}

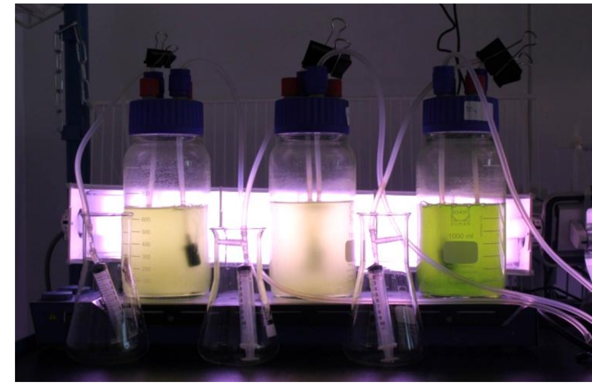
I_s = 758 μmol m^{-2} s^{-1}



Nutrient uptake and storage: P-uptake and storage



Parameter estimation using Simplex

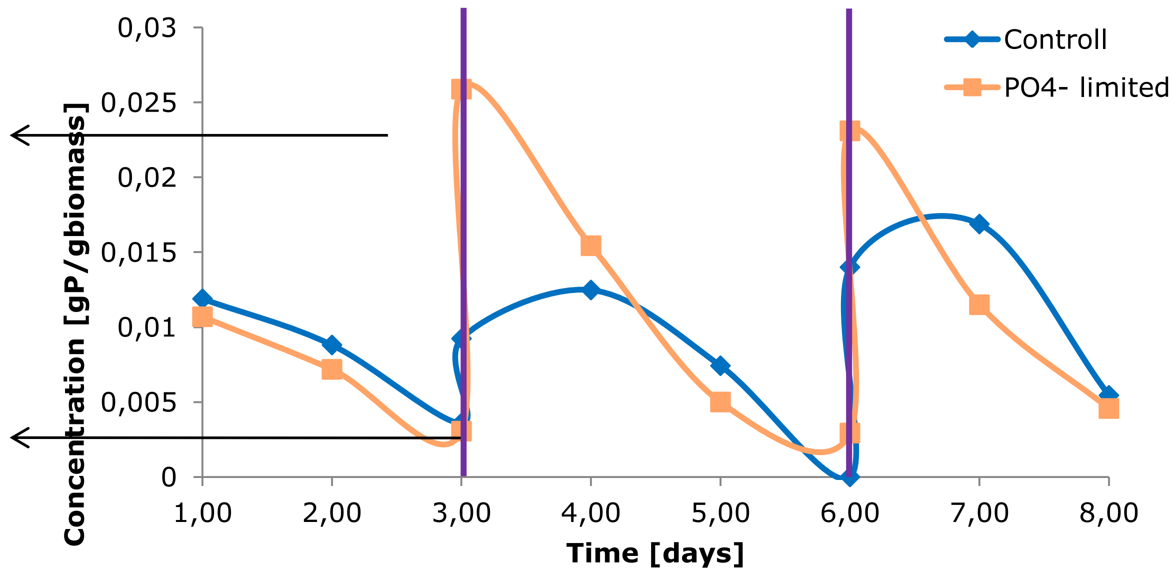


I_{av}=100 µmol $m^{-2}s^{-1}$

K_{PO4} = 0.71 mgPO$_4$-P/L

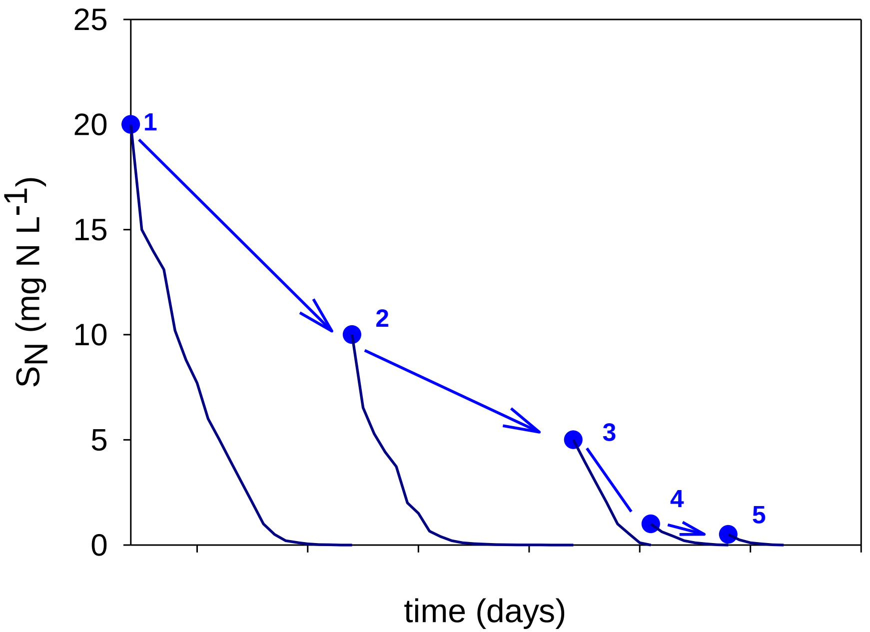
X $_{Alg,PPmax}$ = 0.025 gP/gBiomass

X $_{Alg,PPmin}$ = 0.002 gP/gBiomass



N-uptake and storage

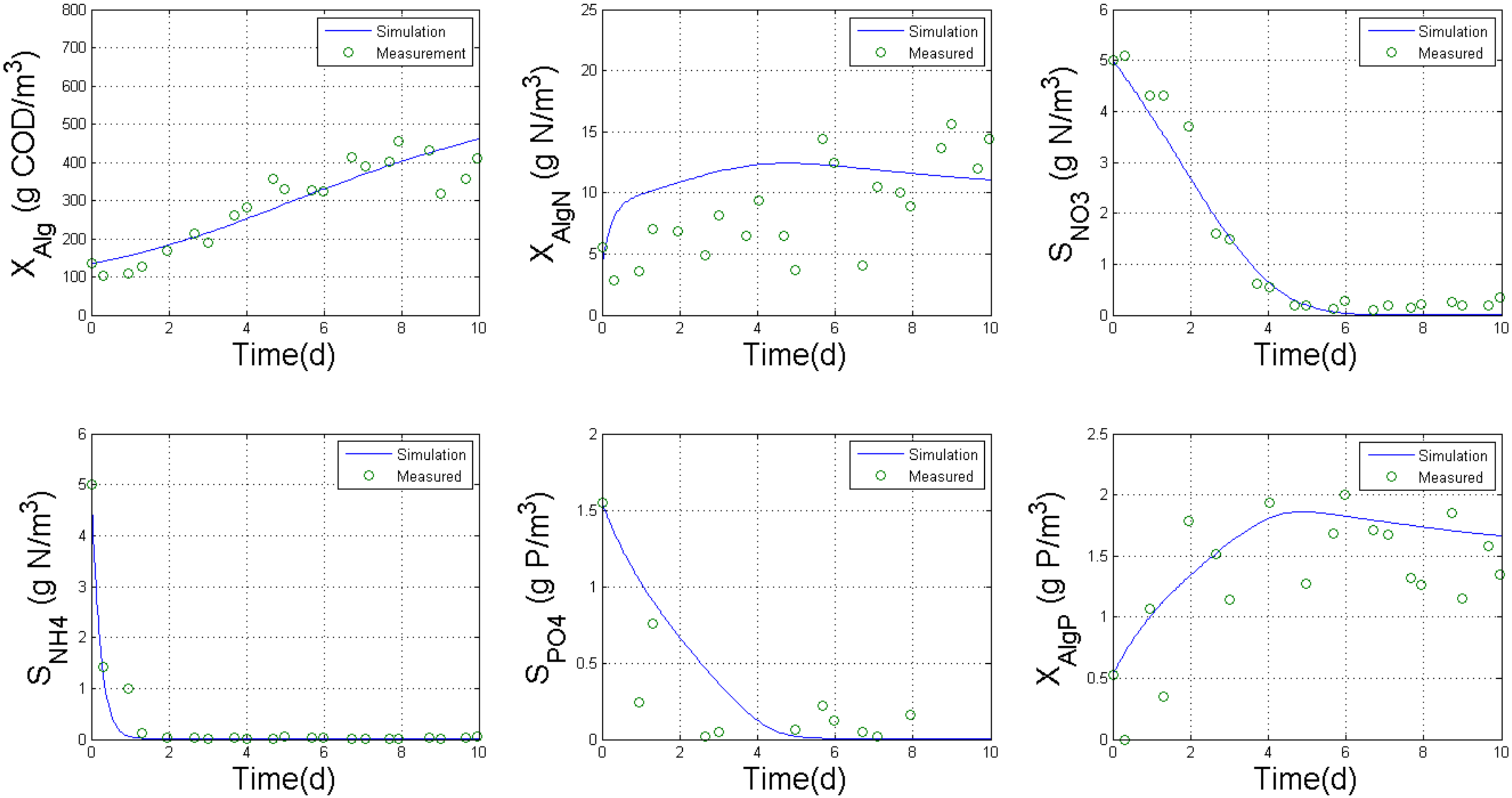
Cycle	Initial N conc. (g N/m³)
1	20
2	10
3	5
4	1
5	0.5



Parameter estimation using Simplex

ASM-A calibration

Model calibration using data from cycle 2



Parameter Values

Parameter	Microplate	1-L batch	24-L batch	Literature Value	Unit
$\mu_{A,max}$	3.6 ± 0.04[a]	3.3 ± 0.55[e]	**4.19±1.19**[g]	4.7 [30]; 0.1-11 [36]; 1.4 [70]; 0.15 [71]; 2.64 [67]; 1.47 [67]; 3.26 [72]	d^{-1}
$\mu_{H,max}$	0.75 ± 0.1[b]	**3.23 ± 1.1**[f]	-	14 [37]; 3.48 [73]; 2.35-2.64 [67]; 0.96-1 [67]	d^{-1}
I_s	**758.2 ± 22.9**[a]	-	-	-	µmol m^{-2} s^{-1}
$X_{Alg,PPmin}$	-	**0.002±0.0008**[e]	-	-	g P·g^{-1}COD
$X_{Alg,Nmin}$	-	**0.014±0.0015**[e]	-	0.023 [37]; 0.02 [72]	g N· g^{-1}COD
$X_{Alg,PPmax}$	-	**0.02±0.008**[e]	-	-	g P· g^{-1}COD
$X_{Alg,Nmax}$	-	**0.9±0.5**[e]	-	0.0683 [37]; 0.067 [72]	g N· g^{-1}COD
$K_{NO,Alg}$	-	3.39 ± 1.89[e]	**8.22±0.97**[g]	0.0602 [37]; 0.3 [71]	g N·m^{-3}
$K_{NH4,Alg}$	-	2.4 ± 0.42[e]	**3.91±0.88**[g]	5 [34]; 0.1-31.5 [71]	g N·m^{-3}
$K_{PO4,Alg}$	-	0.25 ± 0.18[e]	**0.36±0.046**[g]	0.046-10.5 [71]	g P·m^{-3}
$k_{NH4,Alg}$	-	2.97 ± 2.42	**0.22±0.01**[g]	-	g N·g^{-1}COD·d^{-1}
$k_{NO,Alg}$	-	2.97 ± 2.42	**0.018±0.012**[g]	0.49 [37]; 0.43 [72]	g N·g^{-1}COD·d^{-1}
$k_{PO4,Alg}$	-	0.066 ± 0.042	**0.028±0.021**[g]	-	g P·g^{-1}COD·d^{-1}
K_{Alk}	-	-	-	**3** [34]; 0.035-0.29 [71]	g C·m^{-3}
K_A	11.87 ± 5.2[b]	**89 ± 28**[f]	-	-	gCOD·m^{-3}
$K_{i,A}$	550.58 ± 232.1[b]	-	-	-	gCOD·m^{-3}
K_I	**878.6±75**[d]	-	-	-	µmol $m^{-2}s^{-1}$
K_O				2 (20% of DO_{sat}) [56]	gCOD m^{-3}
b_{Xalg}	-	-	**0.091±0.0**[g]	0.072 (2%*$\mu_{A,max}$) [33]; 3.7% $\mu_{A,max}$ [30]; 0.003-0.1 [71]	d^{-1}
Y_{Alk}	-	-	-	**2.33;** 1.06 [71]	g COD·g^{-1}C
Y_{Ac}	-	**0.39**[f]	-	0.34 [45]	g COD·g^{-1}COD
iP_{Xalg}	-	-		**0.00067**[31, 34]	g P ·g^{-1}COD
iN_{Xalg}	-	-		**0.0049** [31]; 0.0534 [34]	g N· g^{-1}COD
fX_I	-	-		**0.1**	g COD·g^{-1}COD
N_{XAlgD}				**0.00441**	g N·g^{-1}COD
P_{XAlgD}				**0.000603**	g P·g^{-1}COD

Agenda

- Model development
- Targeted experiments for parameter estimation:
  - Green microalgae identification and equipment
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- Model evaluation

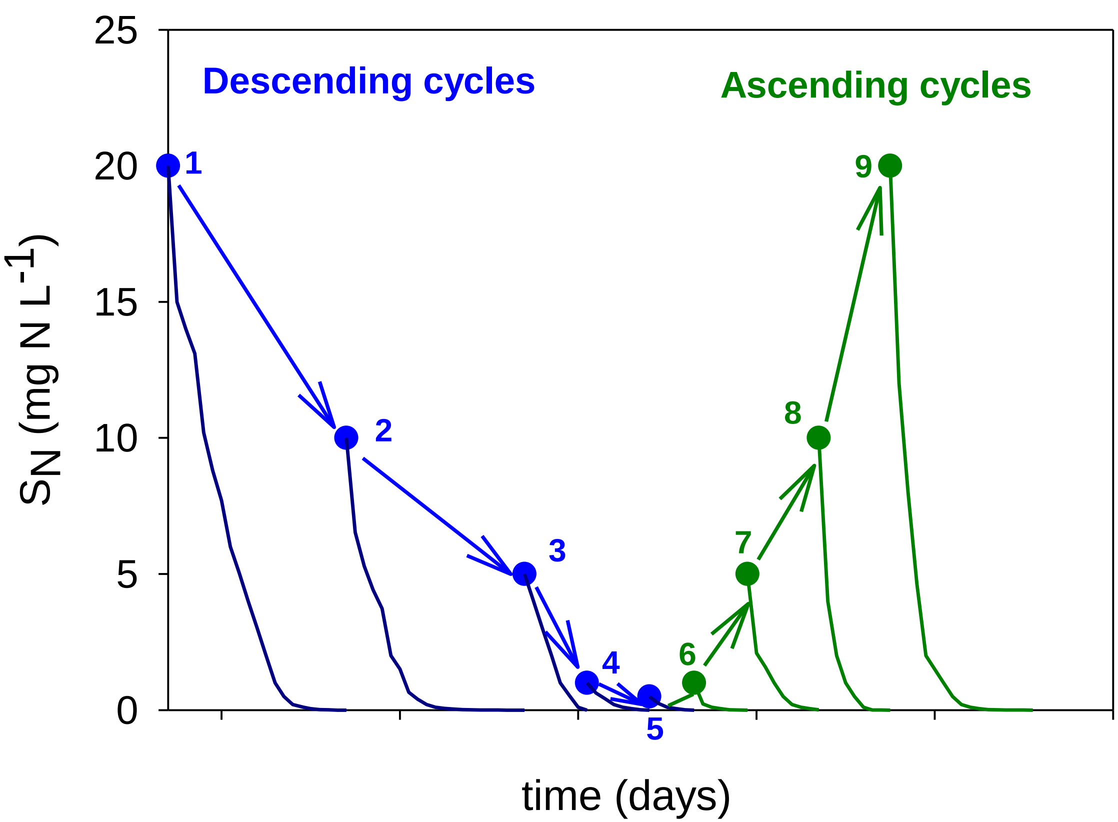
Model evaluation: assessment of parameter variability impact

Research questions:

- What is the influence of culture history and/or substrate availability on parameter estimates?
- Can we use a default parameter set?
- Can we explain the discrepancy as a result of parameter variability?

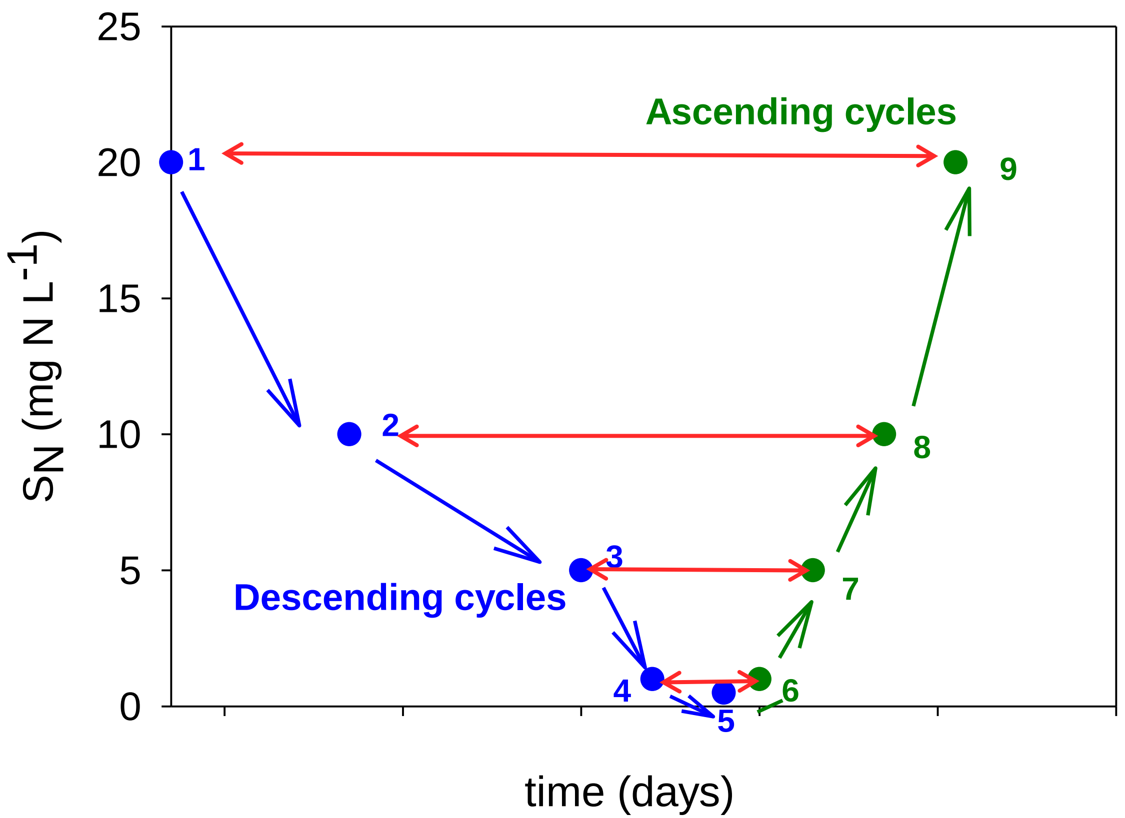
Model evaluation: experimental design

Cycle	Initial N conc. (g N/m³)
1 and 9	20
2 and 8	10
3 and 7	5
4 and 6	1
5	0.5



Model evaluation: two evaluation steps

- Does culture history affect parameter values?
  - Parameter sets obtained through the descending cycles confronted with data from ascending cycles
  - Janus coefficient



Model evaluation: two evaluation steps

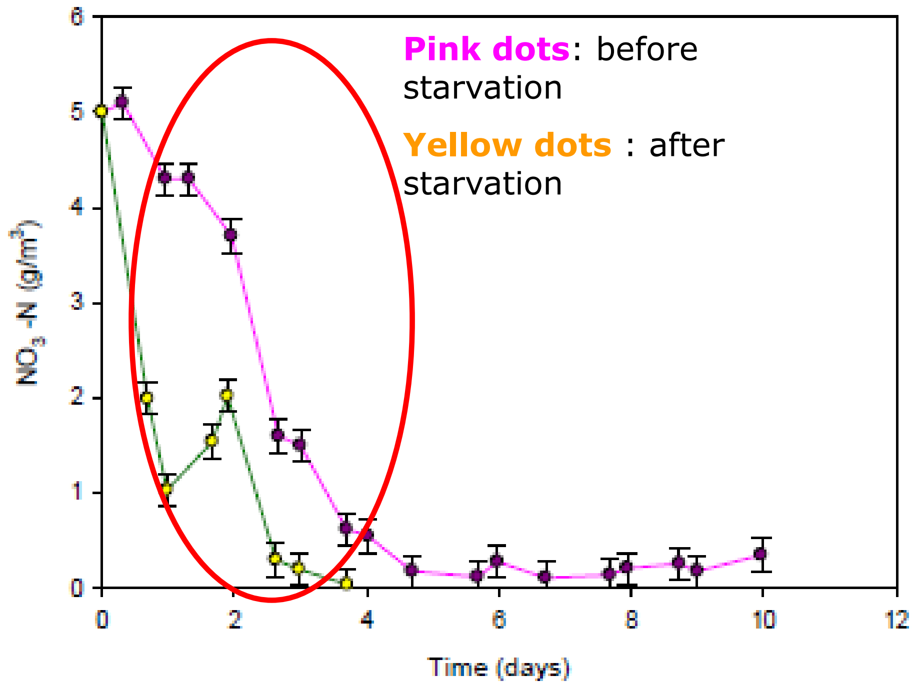
Cycle 2-8	RMSE calibration	RMSE evaluation	Janus coefficient
Ammonium in bulk liquid (S_{NH4})	0.72	0.44	0.61
Nitrate in bulk liquid (S_{NO3})	0.71	14.00	19.72
Phosphate in bulk liquid (S_{PO4})	0.91	0.51	0.56
Algal biomass (X_{Alg})	0.19	0.1	0.53
Nitrogen quota (X_{AlgN})	1.27	0.70	0.55
Phosphorous quota (X_{AlgP})	0.91	0.14	0.15
Total	4.71	15.9	3.38

Nitrate prediction in the other cycles:

Cycle	RMSE calibration	RMSE evaluation	Janus coefficient
1-9	0.24	23.9	99.58
3-7	0.26	3.85	14.81
4-6	0.23	9.35	40.65

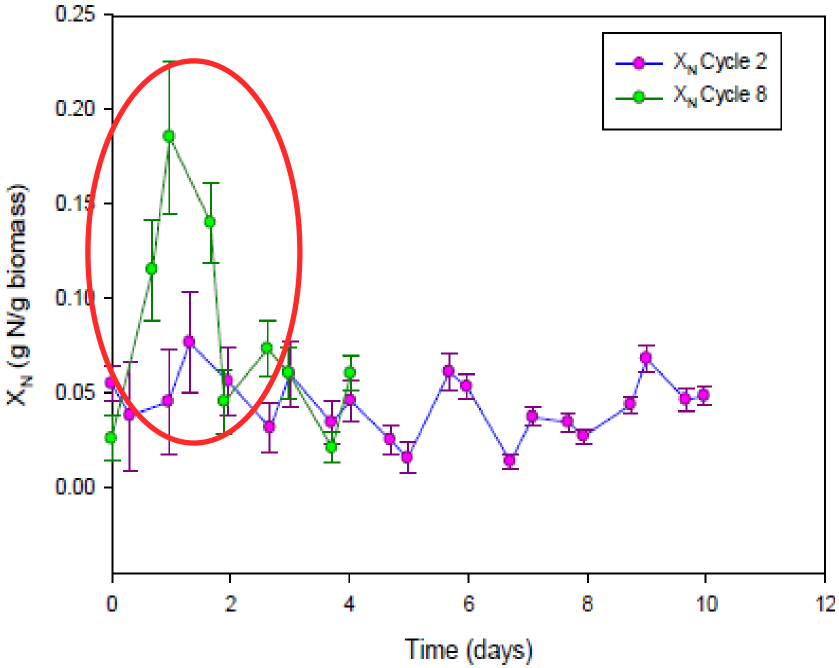
- J~1 calibrated model prediction is good
- J>> calibrated model prediction fails

Model evaluation: experimental results



- The **nitrate uptake** after starvation conditions is **enhanced**

Model evaluation: experimental results

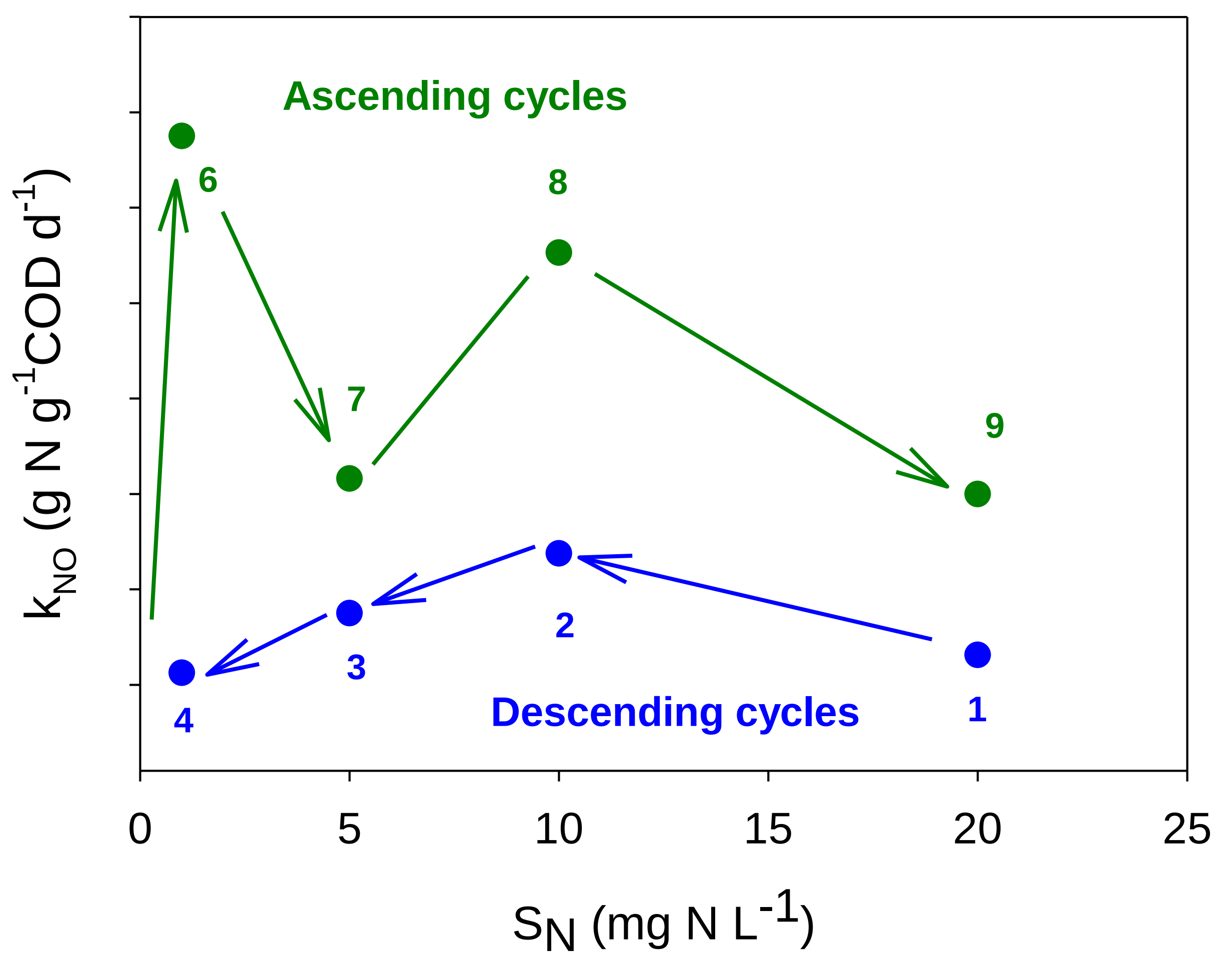


Pink dots: before starvation

Green dots: after starvation

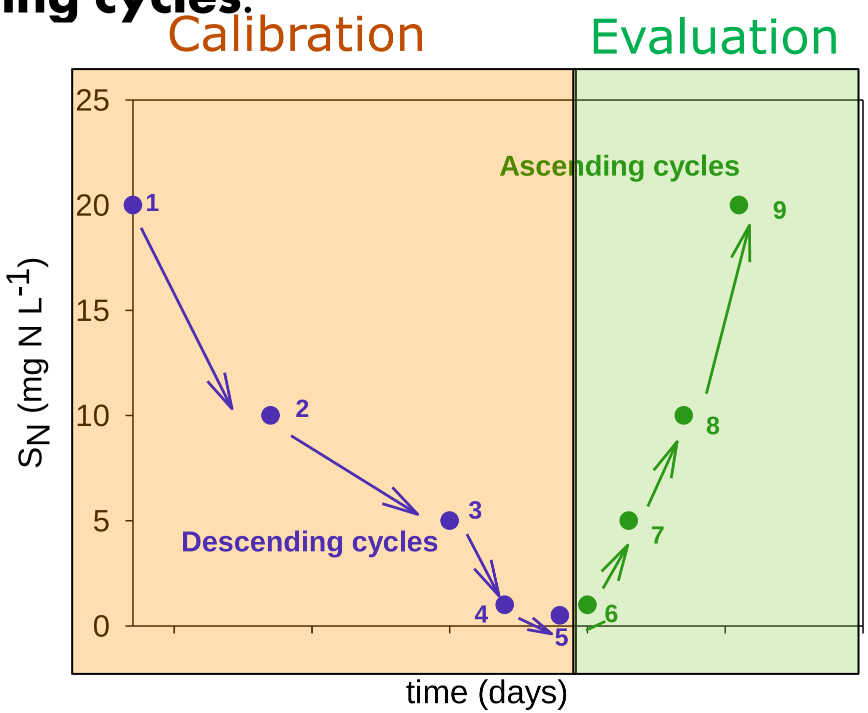
- After the **N quota** is replenished there is a **temporary enhanced** N storage

Model evaluation: parameter variability



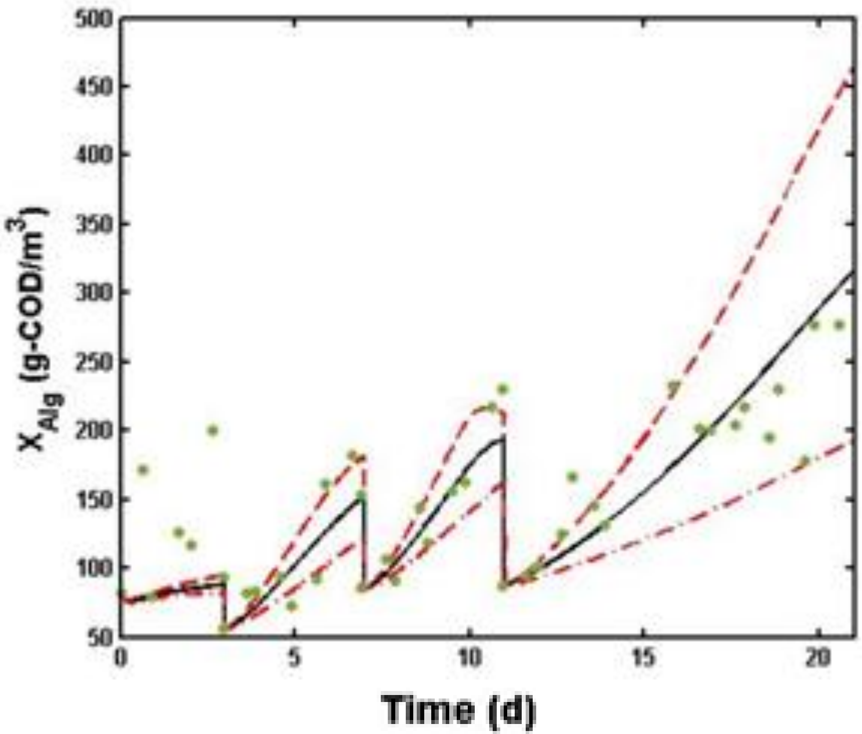
Model evaluation: two evaluation steps

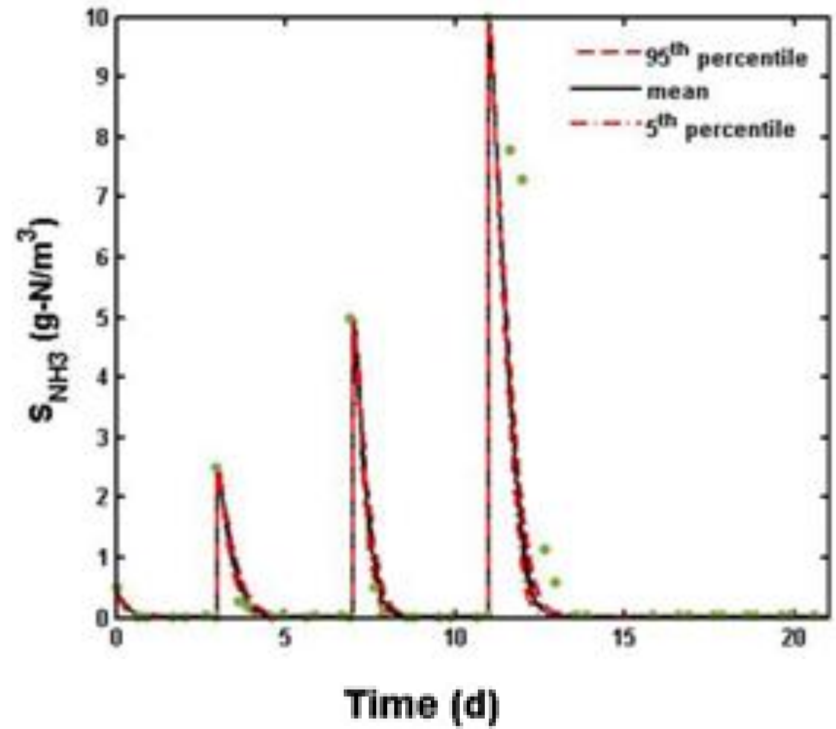
- **Can we use an average parameter set? Can we explain the discrepancy as a result of parameter variability?**
  - **Monte Carlo simulations run on the 4 ascending cycles**
  - **Parameter values: mean values of the estimated parameters through descending cycles.**
  - **Probability range: standard deviation of the mean values through descending cycles.**



Model evaluation: second steps

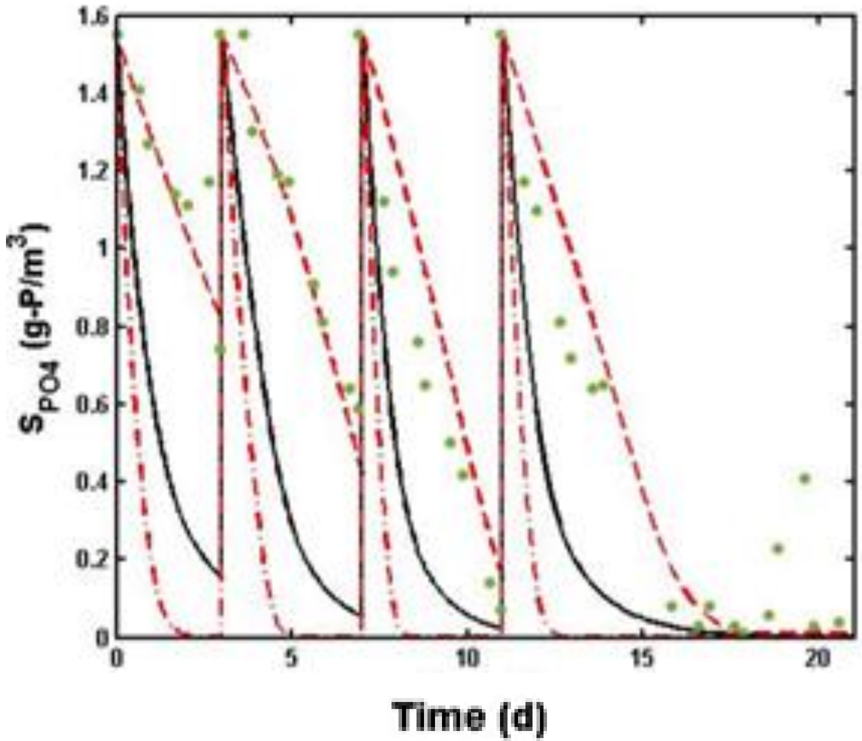
- Algal biomass & ammonia: discrepancies can be explained by parameter variability

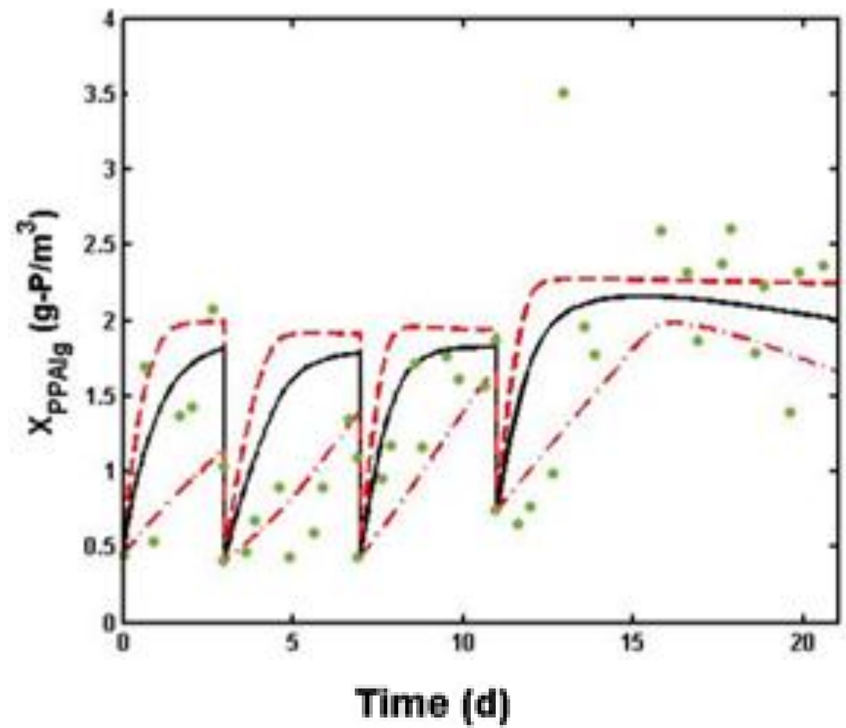




Model evaluation: two evaluation steps

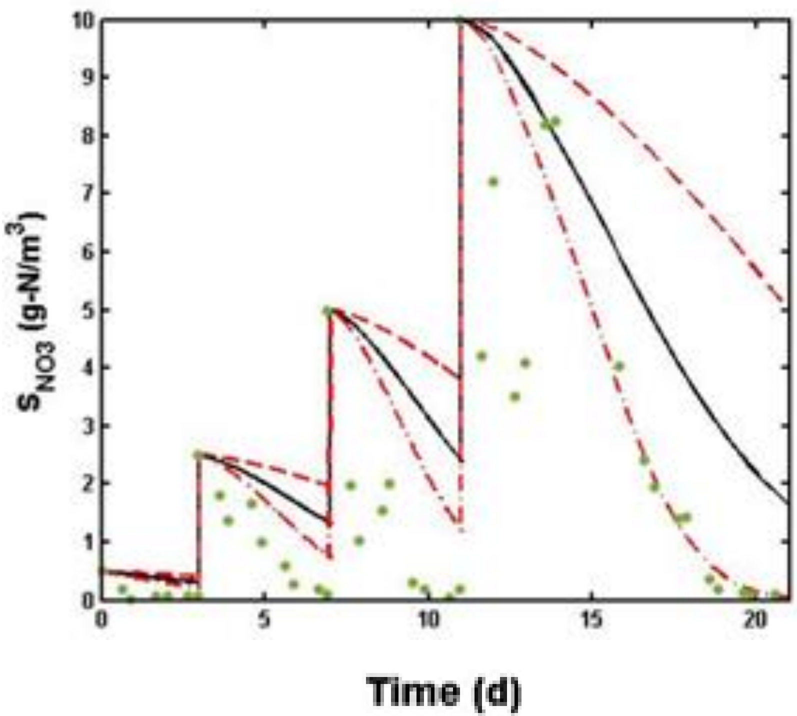
- **Soluble and stored phosphate: discrepancies can be explained by parameter variability**

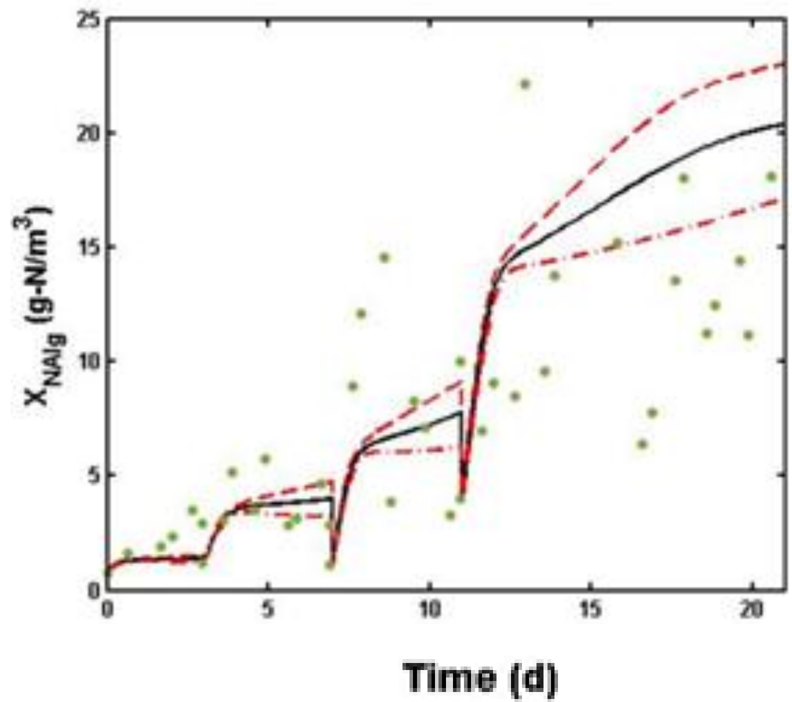




Model evaluation: two evaluation steps

- Soluble nitrate & stored nitrogen: the model prediction is compromised by
  - Culture history for nitrate
  - Substrate availability for nitrogen storage





Concluding remarks

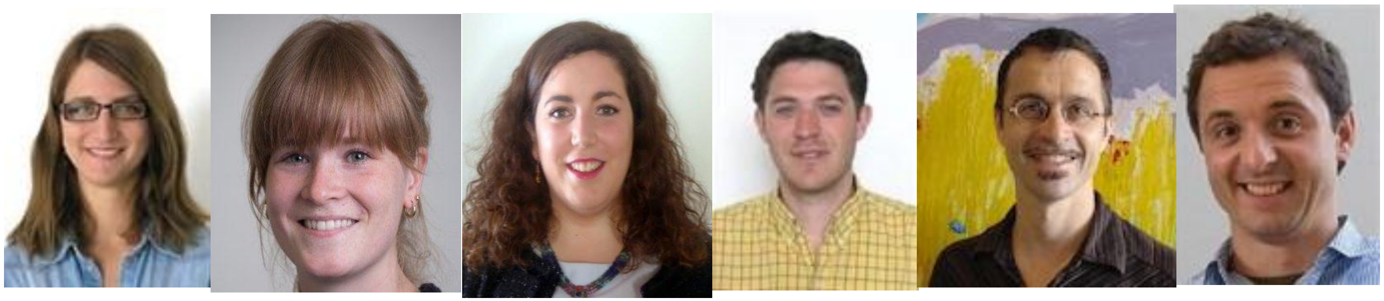
- A novel process model in the ASM framework for predicting algal behavior in PBR has been identified, calibrated and critically evaluated
- Different scale lab experiments have been used to estimate different parameter sets.
- The model can predict algal biomass, ammonia, phosphate and internal PP quota using a mean parameter set
- Maximum nitrate uptake rate depends on the history of the culture

Future perspectives

- Model extensions including physic-chemical processes:
  - Mass transfer
  - pH
  - Light attenuation
  - Hydrodynamics
- Model extensions relevant to other end-uses: lipid accumulation for biodiesel
- Model calibration and evaluation using other microalgae species

Aknowlegement

Dorottya S. Wágner, Mariann Sæbø,Marta Bregua de la Sotilla, Jonathan van Wagenen, Barth F. Smets, Benedek Gy. Plósz



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