Appendix 1

MECHANISTIC MODEL TO SIMULATE MICROALGAE GROWTH

This ordinary differential equation (ODE)-based model for microalgae growth was adopted from the work of Solimeno, Samsó [1]: Solimeno, A., et al., *New mechanistic model to simulate microalgae growth.* Algal Research, 2015. **12**: p. 350-358. This model follows the same structure as the ADM1 and ASM3 formulated by the International Water Association.

The reaction rate for each component of the model r_i is formulated using the following expression: $r_i = \sum_j (\upsilon_{j,i} \times \rho_i)$, where i is the chemical component, j is the process, ρ_i is the rate expression for i, and $\upsilon_{j,i}$ is the stoichiometric coefficient.

The ODEs for each model variable is consequently formulated as:

$$\frac{dS_i}{dt} = \frac{q_{in}}{V_{liq}}(S_{i,in} - S_i) + \sum_j (\upsilon_{j,i} \times \rho_i)$$

$$\frac{dX_i}{dt} = \frac{q_{in}}{V_{liq}}(X_{i,in} - X_i) + \sum_j (\upsilon_{j,i} \times \rho_i)$$

Key definitions for algae model:

Photosynthetic factor: $\eta_{PS}(I, S_{O2}) = f_L(I) \cdot f_{PR}(S_{O2})$

where f_L is the light factor and f_{PR} the photorespiration factor.

$f_L(I) = \frac{\alpha\delta I}{\alpha\beta I^2 + (\alpha+\beta)\delta I + \gamma\delta}$, α is rate of activation, γ is rate of constant production, β is rate of inhibition, δ is rate of recovery

$$f_{PR}(S_{O2}) = \begin{cases} 1 - \tanh\left(\dfrac{K_{PR} \cdot \left(\dfrac{SO_2}{\tau \cdot S_{O2}^{SAT}}\right)}{1 - \dfrac{SO_2}{\tau \cdot S_{O2}^{SAT}}}\right), & SO_2 \leq \tau \cdot S_{O2}^{SAT} \\ 0, & SO_2 > \tau \cdot S_{O2}^{SAT} \end{cases}$$

where τ is the coefficient of excess dissolved oxygen.

Thermic photosynthetic factor: $f_{T,FS}(T) = e^{-(\frac{T - T_{opt}}{s})^2}$

where T_{opt} is assumed 25^{o}C and s is a parameter value for empirical fitting

Table 1. Process rate expressions.

Processes:	Process rate expression
Microalgae growth on ammonia	$\rho_{1a} = \mu_{ALG} * f_{T,FS}(T) * \eta_{PS}(I, S_{O2}) * \frac{S_{CO2} + S_{HCO3}}{K_{C,ALG} + S_{CO2} + S_{HCO3} + \left(\frac{S_{CO2}^2}{I_{CO2,ALG}}\right)} * \frac{S_{NH3} + S_{NH4}}{K_{N,ALG} + S_{NH3} + S_{NH4}} * X_{ALG}$
Microalgae growth on nitrate	$\rho_{1b} = \mu_{ALG} * f_{T,FS}(T) * \eta_{PS}(I, S_{O2}) * \frac{S_{CO2} + S_{HCO3}}{K_{C,ALG} + S_{CO2} + S_{HCO3} + \left(\frac{S_{CO2}^2}{I_{CO2,ALG}}\right)} * \frac{S_{NO3}}{K_{N,ALG} + S_{NO3}} * \frac{K_{N,ALG}}{K_{N,ALG} + S_{NH3} + S_{NH4}} * X_{ALG}$
Microalgae endogenous respiration	$\rho_2 = k_{resp,ALG} * f_{T,FS}(T) * \frac{S_{O2}}{K_{O2,ALG} + S_{O2}} * X_{ALG}$
Microalgae inactivation	$\rho_3 = k_{death,ALG} * f_{T,FS}(T) * X_{ALG}$
Chemical equilibrium $CO_2 \leftrightarrow HCO_3^-$	$\rho_4 = k_{eq,1} * (S_{CO2} - \frac{S_H S_{HCO3}}{K_{eq,1}})$
Chemical equilibrium $HCO_3^- \leftrightarrow CO_3^{2-}$	$\rho_5 = k_{eq,2} * (S_{HCO3} - \frac{S_H S_{CO3}}{K_{eq,2}})$
Chemical equilibrium $NH_4^+ \leftrightarrow NH_3$	$\rho_6 = k_{eq,3} * (S_{NH4} - \frac{S_H S_{NH3}}{K_{eq,3}})$
Chemical equilibrium $H^+ \leftrightarrow OH^-$	$\rho_7 = k_{eq,w} * (1 - \frac{S_H S_{OH}}{K_{eq,w}})$
Oxygen transfer to the atmosphere	$\rho_{O2} = Ka, O_2 * (S_{O2}^{WAT} - S_{O2})$
Carbon dioxide transfer to the atmosphere	$\rho_{CO2} = Ka, CO_2 * (S_{CO2}^{WAT} - S_{CO2})$
Ammonia transfer to the atmosphere	$\rho_{NH3} = Ka, NH_3 * (S_{NH3}^{WAT} - S_{NH3})$

Table 2. Matrix of stoichiometric parameters that relates processes through stoichiometric coefficients

State variables→i		S_{NH4}	S_{NH3}	S_{NO3}	S_{O2}	S_{CO2}	S_{HCO3}	S_{CO3}	S_H	S_{OH}	X_{ALG}
Processes↓j		gNm⁻³	gNm⁻³	gNm⁻³	gO₂m⁻³	gCm⁻³	gCm⁻³	gCm⁻³	gHm⁻³	gHm⁻³	gCODm⁻³
Microalgae growth on ammonia	ρ_{1a}	$v_{1,1a}$			$v_{4,1a}$	$v_{5,1a}$			$v_{8,1a}$		$v_{10,1a}$
Microalgae growth on nitrate	ρ_{1b}			$v_{3,1b}$	$v_{4,1b}$	$v_{5,1b}$			$v_{8,1b}$		$v_{10,1b}$
Microalgae endogenous respiration	ρ_2	$v_{1,2}$			$v_{4,2}$	$v_{5,2}$			$v_{8,2}$		$v_{10,2}$
Microalgae inactivation	ρ_3	$v_{1,3}$			$v_{4,3}$	$v_{5,3}$			$v_{8,3}$		$v_{10,3}$
Chemical equilibrium $CO_2 \leftrightarrow HCO_3^-$	ρ_4					$v_{5,4}$	$v_{6,4}$		$v_{8,4}$		
Chemical equilibrium $HCO_3^- \leftrightarrow CO_3^{2-}$	ρ_5						$v_{6,5}$	$v_{7,5}$	$v_{8,5}$		
Chemical equilibrium $NH_4^+ \leftrightarrow NH_3$	ρ_6	$v_{1,6}$	$v_{2,6}$						$v_{8,6}$		
Chemical equilibrium $H^+ \leftrightarrow OH^-$	ρ_7								$v_{8,7}$	$v_{9,7}$	
Oxygen transfer to the atmosphere	ρ_{O2}				$v_{4,O2}$						
Carbon dioxide transfer to the atmosphere	ρ_{CO2}					$v_{5,CO2}$					
Ammonia transfer to the atmosphere	ρ_{NH3}		$v_{2,NH3}$								

Table 3. Values of biokinetic and physic parameters.

Parameters	Description	Value	Unit	Source
Microalgae processes				
μ_{ALG}	Maximum growth rate of microalgae	1.6	d^{-1}	Calibrated
$k_{resp,ALG}$	Endogenous respiration constant	0.1	d^{-1}	[49]
$k_{death,ALG}$	Inactivation constant	0.1	d^{-1}	[49]
$K_{C,ALG}$	Affinity constant of microalgae on carbon species	0.00432	$gC\ m^{-3}$	[43]
$I_{CO2,ALG}$	CO_2 inhibition constant of microalgae	120	$gC\ m^{-3}$	[53]
$K_{N,ALG}$	Affinity constant of microalgae on nitrogen species	0.1	$gN\ m^{-3}$	[49]
$K_{O2,ALG}$	Affinity constant of microalgae on dissolved oxygen	0.2	$gO_2\ m^{-3}$	[49]
Photorespiration factor				
K_{PR}	Inhibition constant of photorespiration	0.01	–	Assumption
τ	Coefficient of excess dissolved oxygen	4	–	[15]
S_{O2}^{SAT}	Saturation concentration of oxygen in the air	7.1904	$gO_2\ m^{-3}$	[14]
Photosynthetic thermal factor				
T_{OPT}	Optimum temperature for microalgae growth	25	°C	[19]
s	Normalized parameter	13	–	[19]
Light factor				
α	Parameter activation	0.001935	$(\mu E\ m^{-2})^{-1}$	[58]
β	Parameter inhibition	$5.7848E^{-7}$	$(\mu E\ m^{-2})^{-1}$	[58]
γ	Parameter production	0.1460	s^{-1}	[58]
δ	Parameter recovery	0.0004796	s^{-1}	[58]
Irradiance solar incident				
E_f	Photosynthetic efficiency of solar radiation	1.74	$\mu E\ J^{-1}$	[38]
$\aleph$	Index atmospheric clarity	0.74	–	[38]
ζ	Universal solar constant	1353	$W\ m^{-2}$	[38]
ω	Hour angle	Calculated	º	[36]
ω_s	Sunset hour angle	Calculated	º	[36]
ϕ	Latitude	Observed	º	-
δ	Sun declination	Calculated	º	[36]
Transfer of gases to the atmosphere				
$K_{a,O2}$	Mass transfer coefficient for oxygen	4	d^{-1}	Calibrated
$K_{a,CO2}$	Mass transfer coefficient for dioxide carbon	0.7	d^{-1}	Calibrated
$K_{a,NH3}$	Mass transfer coefficient for ammonia	0.7	d^{-1}	Calibrated

Table 4. Values of chemical parameters.

Parameters	Equations
Chemical equilibrium $CO_2 \leftrightarrow HCO_3^-$.	$K_{eq,1} = 10^{17.843-\frac{3404.71}{273.15+T}-0.032786(273.15+T)}$
Chemical equilibrium $HCO_3^- \leftrightarrow CO_3^{2-}$	$K_{eq,2} = 10^{9.494-\frac{2902.39}{273.15+T}-0.02379(273.15+T)}$
Chemical equilibrium $NH_4^+ \leftrightarrow NH_3$	$K_{eq,3} = 10^{2.891-\frac{2727}{(273.15+T)}}$
Chemical equilibrium $H^+ \leftrightarrow OH^-$	$K_{eq,w} = 10^{-\frac{4470.99}{273.15+T}+12.0875-0.01706(273.15+T)}$

Kinetics parameters				
$k_{eq,1}$	Dissociation constant of $CO_2 \leftrightarrow HCO_3^-$.	10000	d^{-1}	[49]
$k_{eq,2}$	Dissociation constant of $HCO_3^- \leftrightarrow CO_3^{2-}$	1000	d^{-1}	[49]
$k_{eq,3}$	Dissociation constant of $NH_4^+ \leftrightarrow NH_3$	1000	d^{-1}	[49]
$k_{eq,w}$	Dissociation constant of $H^+ \leftrightarrow OH^-$	1000	$g\ m^{-1}\ d^{-1}$	[49]

Table 5. Mathematical expressions of the stoichiometric coefficients of each process.

Stoichiometric coefficient	Unit
Microalgae growth on ammonia	
$v_{1,1a} = -i_{N,ALG}$	$gN\ gCOD^{-1}$
$v_{4,1a} = \frac{8i_{C,ALG}}{3} + 8i_{H,ALG} - i_{O,ALG} - \frac{12i_{N,ALG}}{7}$	$gO_2\ gCOD^{-1}$
$v_{5,1a} = -i_{C,ALG}$	$gC\ gCOD^{-1}$
$v_{8,1a} = \frac{i_{N,ALG}}{14}$	$gH\ gCOD^{-1}$
$v_{10,1a} = 1$	$gCOD\ gCOD^{-1}$
Microalgae growth on nitrate	
$v_{3,1b} = -i_{N,ALG}$	$gN\ gCOD^{-1}$
$v_{4,1b} = \frac{8i_{C,ALG}}{3} + 8i_{H,ALG} - i_{O,ALG} - \frac{20i_{N,ALG}}{7}$	$gO_2\ gCOD^{-1}$
$v_{5,1b} = -i_{C,ALG}$	$gC\ gCOD^{-1}$
$v_{8,1b} = -\frac{i_{N,ALG}}{14}$	$gH\ gCOD^{-1}$
$v_{10,1b} = 1$	$gCOD\ gCOD^{-1}$
Microalgae endogenous respiration	
$v_{1,2} = i_{N,ALG}$	$gN\ gCOD^{-1}$
$v_{4,2} = (i_{O,ALG}) - 8(i_{H,ALG}) - \frac{8}{3}(i_{C,ALG}) + \frac{12}{7}(i_{N,ALG})$	$gO_2\ gCOD^{-1}$
$v_{5,2} = i_{C,ALG}$	$gC\ gCOD^{-1}$
$v_{8,2} = -\frac{1}{14}(i_{N,ALG})$	$gH\ gCOD^{-1}$
$v_{10,2} = -1$	$gCOD\ gCOD^{-1}$
Microalgae inactivation	
$v_{1,3} = i_{N,ALG}$	$gN\ gCOD^{-1}$
$v_{4,3} = (i_{O,ALG}) - 8(i_{H,ALG}) - \frac{8}{3}(i_{C,ALG}) + \frac{12}{7}(i_{N,ALG})$	$gO_2\ gCOD^{-1}$
$v_{5,3} = i_{C,ALG}$	$gC\ gCOD^{-1}$
$v_{8,3} = -\frac{1}{14}(i_{N,ALG})$	$gH\ gCOD^{-1}$
$v_{10,3} = -1$	$gCOD\ gCOD^{-1}$
Chemical equilibria $CO_2 \leftrightarrow HCO_3^-$	
$v_{5,4} = -1$	$gC\ gC^{-1}$
$v_{6,4} = 1$	$gC\ gC^{-1}$
$v_{8,4} = 1/12$	$gH\ gC^{-1}$
Chemical equilibria $HCO_3^- \leftrightarrow CO_3^{2-}$	
$v_{6,5} = -1$	$gC\ gC^{-1}$
$v_{7,5} = 1$	$gC\ gC^{-1}$
$v_{8,5} = 1/12$	$gH\ gC^{-1}$
Chemical equilibria $NH_4^+ \leftrightarrow NH_3$	
$v_{1,6} = -1$	$gN\ gN^{-1}$
$v_{2,6} = 1$	$gN\ gN^{-1}$
$v_{8,6} = 1/14$	$gH\ gN^{-1}$
Chemical equilibria $H^+ \leftrightarrow OH^-$	

$v_{8,7} = 1$	gH gH^{-1}
$v_{9,7} = 1$	gH gH^{-1}
Oxygen transfer to the atmosphere	
$v_{4,O2} = 1$	–
Carbon dioxide transfer to the atmosphere	
$v_{5,CO2} = 1$	–
Ammonia transfer to the atmosphere	
$v_{2,NH3} = 1$	–

Table 6. Values of fraction of carbon, hydrogen, oxygen and nitrogen in microalgae biomass.

Parameter	Description	Value	Unit	Source
Fractions of microalgal biomass				
$i_{C,ALG}$	Fraction of carbon in microalgae	0.387	gC $gCOD^{-1}$	[49]
$i_{H,ALG}$	Fraction of hydrogen in microalgae	0.075	gH $gCOD^{-1}$	[49]
$i_{O,ALG}$	Fraction of oxygen in microalgae	0.538	gO_2 $gCOD^{-1}$	[49]
$i_{N,ALG}$	Fraction of nitrogen in microalgae	0.065	gN $gCOD^{-1}$	[49]

Table 7. Values of calibrated parameters.

Parameter	Description	Value
μ_{ALG}	Maximum specific growth rate of algae	1.5 d^{-1}
Ka, O_2	Mass transfer coefficient for oxygen	4 d^{-1}
Ka, CO_2	Mass transfer coefficient for carbon dioxide	0.6 d^{-1}
Ka, NH_3	Mass transfer coefficient for ammonia	0.6 d^{-1}

References

[36] B. Liu, R. Jordan, The interrelationship and characteristic distribution of direct, diffuse and total solar radiation, Sol. Energy 4 (3) (July 1960) 1–19.
[38] E. Molina Grima, G. Acién Fernández, Y. Chisti, Photobioreactors: light regime, mass transfer, and scaleup, J. Biotechnol. 70 (1999) 231–247.
[43] J.T. Novak, D.E. Brune, Inorganic carbon limited growth kinetics of some freshwater algae, Water Res. 19 (1985) 215–225.

1. Solimeno, A., et al., *New mechanistic model to simulate microalgae growth.* Algal Research, 2015. **12**: p. 350-358.