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### Out of balance: implications of climate change for the ecological stoichiometry of harmful cyanobacteria

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# Appendix 1

## Lake data

We measured *Microcystis* biomass, microcystin composition and seston N:C ratios in 12 *Microcystis*-dominated lakes in The Netherlands. Samples were taken from the open water (at 1 m depth) and, if present, from surface blooms (at 5 cm depth), resulting in a total of 19 lake samples. The data are presented in Table A1 below. In addition to the relationships reported in Fig. 3 of the main text, we note here that the biomass, microcystin concentration and seston N:C ratio were higher in surface blooms than in the open water.

Table A1. *Microcystis* biomass, microcystin composition and seston N:C ratios measured in the lake samples.

Lake sample	Lake	Sample position*	<i>Microcystis</i> biomass (mm <sup>3</sup> L <sup>-1</sup> )	Total MC (µg L <sup>-1</sup> )	MC-LR (µg L <sup>-1</sup> )	MC-RR (µg L <sup>-1</sup> )	MC-YR (µg L <sup>-1</sup> )	Seston N:C ratio (molar)
1	Braassemermeer	W	2.88	1.49	1.0	0.49	0	0.103
2	Braassemermeer	S	566	36.3	17.2	7.2	11.9	0.143
3	Eemmeer	W	59.8	3.38	1.4	0.58	1.4	0.131
4	Eemmeer	S	15202	3310	1737	1247	326	0.174
5	Gooimeer-Almere 1	W	7.8	2.26	0.92	0.62	0.72	0.094
6	Gooimeer Almere 1	S	4356	346	179	167	0	0.192
7	Gooimeer-Almere 2	W	3.0	0.68	0.68	0	0	0.078
8	Gooimeer-Almere 2	S	11039	1940	1073	867	0	0.164
9	Gooimeer-Huizen	W	380	8.6	5.9	2.7	0	0.126
10	Nijkerkernauw	S	1063	429	276	153	0	0.178
11	Noord Aa	W	14.6	13.7	7.0	5.4	1.3	0.128
12	Noord Aa	S	155	171.3	91.4	79.9	0	0.157
13	't Joppe	W	4.2	4.34	2.6	1.5	0.24	0.097
14	't Joppe	S	1800	858.4	415	349	94.4	0.173
15	Vlietlanden	W	2.5	2.3	1.6	0.70	0	0.072
16	Vlietlanden	S	224	320.7	210	86.3	24.4	0.162
17	Westeinderplassen	W	5.4	0.73	0.73	0	0	0.078
18	Wijde Aa	W	11.4	1.79	0.85	0	0.94	0.111
19	Zegerplas	W	1.6	1.65	0.79	0.65	0.21	0.082

\*W = sample from open water; S = sample from surface bloom.

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# Appendix 2

## Full description of the model

We develop a model that considers several phytoplankton species competing for inorganic carbon in a well-mixed water column. The population dynamics of the phytoplankton species depend on the assimilation of carbon dioxide and bicarbonate. Uptake of carbon dioxide induces dynamic changes in pH. These changes in pH, in turn, affect the availability of the different carbon species, which feeds back on phytoplankton growth. In addition, the growing phytoplankton populations cast more shade and thereby reduce light availability for photosynthesis. Here, we describe the full structure of the model.

*Population dynamics* - We assume that the specific growth rates of the competing species depend on their intracellular carbon content, also known as carbon quota (Droop 1973; Grover 1991). Let  $n$  denote the number of phytoplankton species, let  $X_i$  denote the population density of phytoplankton species  $i$ , and let  $Q_i$  denote its carbon quota. The population dynamics of the competing species, and the dynamic changes of their carbon quota, can be summarized by two sets of differential equations:

$$\frac{dX_i}{dt} = \mu_i X_i - DX_i \quad (\text{A1})$$

$$\frac{dQ_i}{dt} = u_{\text{CO}_2,i} + u_{\text{HCO}_3,i} - r_i - \mu_i Q_i \quad (\text{A2})$$

where  $i=1,\dots,n$ . The first set of equations describes the population densities of the competing species, where  $\mu_i$  is the specific growth rate of species  $i$  and  $D$  is the dilution rate (i.e., the turnover rate) of the system. The second set of equations describes the carbon quota of the species, which increase through uptake of carbon dioxide ( $u_{\text{CO}_2,i}$ ) and bicarbonate ( $u_{\text{HCO}_3,i}$ ), and decrease through respiration ( $r_i$ ) and through dilution of the carbon quota by growth.

The model assumes that the cellular carbon assimilated by phytoplankton consists of structural biomass and a transient carbon pool. The relative size of the transient carbon pool,  $S_i$ , is defined as:

$$S_i = \frac{Q_i - Q_{\text{MIN},i}}{Q_{\text{MAX},i} - Q_{\text{MIN},i}} \quad (\text{A3})$$

where  $Q_{\text{MIN},i}$  is the minimum amount of cellular carbon incorporated into the structural biomass of species  $i$ , and  $Q_{\text{MAX},i}$  is its maximum amount of cellular carbon. The transient carbon pool can be invested to make new structural biomass, which contributes to further

phytoplankton growth. More precisely, we assume that the specific growth rate of a species is determined by its transient carbon pool:

$$\mu_i = \mu_{MAX,i} S_i = \mu_{MAX,i} \left( \frac{Q_i - Q_{MIN,i}}{Q_{MAX,i} - Q_{MIN,i}} \right) \quad (A4)$$

where  $\mu_{MAX,i}$  is the maximum specific growth rate of species  $i$ . Our model formulation resembles Droop's (1973) classic growth model. However, we assume that the cellular carbon quota are constrained between  $Q_{MIN,i}$  and  $Q_{MAX,i}$ , as there are physical limits to the amount of carbon that can be stored inside a cell. Hence, the specific growth rate equals zero if the transient carbon pool is exhausted (i.e.,  $\mu_i = 0$  if  $Q_i = Q_{MIN,i}$ ), and reaches its maximum if cells are satiated with carbon (i.e.,  $\mu_i = \mu_{MAX,i}$  if  $Q_i = Q_{MAX,i}$ ).

*Dissolved inorganic carbon* - Carbon dioxide readily dissolves in water, but only a small fraction of the dissolved carbon dioxide reacts with water forming carbonic acid ( $H_2CO_3$ ). Carbonic acid may subsequently dissociate into bicarbonate and a proton. The reaction from dissolved carbon dioxide to bicarbonate, and vice versa, depends on pH and is relatively slow (Stumm and Morgan 1996). Bicarbonate can dissociate further into carbonate and a proton. This is a much faster process, such that the dissociation of bicarbonate into carbonate and its reverse reaction are essentially in equilibrium with alkalinity and pH (Stumm and Morgan 1996). The chemical reactions of inorganic carbon are summarized in Table A2. In addition to these chemical processes, carbon dioxide and bicarbonate are consumed for phytoplankton photosynthesis, and carbon dioxide is released by respiration.

Dissolved carbon dioxide and carbonic acid cannot be distinguished experimentally. Therefore, let  $[CO_2]$  denote the total concentration of dissolved carbon dioxide and carbonic acid. In addition, let  $[CARB]$  denote the total concentration of bicarbonate and carbonate. Changes in dissolved inorganic carbon can then be described by (Portielje and Lijklema 1995; Stumm and Morgan 1996):

$$\frac{d[CO_2]}{dt} = D([CO_2]_{IN} - [CO_2]) + g_{CO_2} + c_{CO_2} + \sum_{i=1}^n r_i X_i - \sum_{i=1}^n u_{CO_2,i} X_i \quad (A5)$$

$$\frac{d[CARB]}{dt} = D([CARB]_{IN} - [CARB]) - c_{CO_2} - \sum_{i=1}^n u_{HCO_3,i} X_i \quad (A6)$$

The first equation describes changes in the concentration of dissolved carbon dioxide through the influx ( $[CO_2]_{IN}$ ) and efflux of water containing dissolved  $CO_2$ , through gas exchange with atmospheric  $CO_2$  ( $g_{CO_2}$ ), and through the chemical reactions from dissolved  $CO_2$  to bicarbonate and vice versa ( $c_{CO_2}$ ). In addition, the concentration of dissolved carbon dioxide increases through respiration ( $r_i$ ) and decreases through uptake of  $CO_2$  ( $u_{CO_2,i}$ ) by the phytoplankton species. The second equation describes changes in the summed concentration of bicarbonate and carbonate through in- and efflux of water containing these

inorganic carbon species, through the chemical reactions from bicarbonate to dissolved CO<sub>2</sub> and vice versa ( $c_{\text{CO}_2}$ ), and through uptake of bicarbonate ( $u_{\text{HCO}_3, i}$ ) by the phytoplankton species. The concentrations of bicarbonate and carbonate are calculated from [CARB] assuming equilibrium with alkalinity and pH (Portielje and Lijklema 1995; Stumm and Morgan 1996).

The chemostat is continuously aerated with a defined concentration of CO<sub>2</sub>. The CO<sub>2</sub> from this gas mixture dissolves in water. We assume that the CO<sub>2</sub> gas influx ( $g_{\text{CO}_2}$ ) is proportional to the aeration rate ( $a$ ), and to the concentration difference between dissolved CO<sub>2</sub> in equilibrium with the gas pressure ( $[\text{CO}_2^*]$ ) and the actual dissolved CO<sub>2</sub> (Siegenthaler and Sarmiento 1993):

$$g_{\text{CO}_2} = \gamma a ([\text{CO}_2^*] - [\text{CO}_2]) \quad (\text{A7})$$

where  $\gamma$  is a constant of proportionality. The value of  $[\text{CO}_2^*]$  is calculated from the partial pressure of CO<sub>2</sub> in the gas inflow ( $p_{\text{CO}_2}$ ) and the solubility of CO<sub>2</sub> gas in water (Table A2).

Dissolved CO<sub>2</sub> reacts with water and subsequently dissociates into HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup>. This process occurs at a rate  $k_{\text{CO}_2}$  (Table A2). Dissolved CO<sub>2</sub> can also react with OH<sup>-</sup> forming HCO<sub>3</sub><sup>-</sup>, which occurs at a rate  $k_{\text{OH}}$ . Conversely, HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup> associate to dissolved CO<sub>2</sub> and water at a rate  $k_{\text{H}}$ , while HCO<sub>3</sub><sup>-</sup> can also react to dissolved CO<sub>2</sub> and OH<sup>-</sup> at a rate  $k_{\text{HCO}_3}$ . The overall change in dissolved CO<sub>2</sub> through these chemical reactions ( $c_{\text{CO}_2}$ ) can then be described as follows (Johnson 1982):

$$c_{\text{CO}_2} = -(k_{\text{CO}_2} + k_{\text{OH}}[\text{OH}^-])[\text{CO}_2] + (k_{\text{H}}[\text{H}^+] + k_{\text{HCO}_3})[\text{HCO}_3^-] \quad (\text{A8})$$

*Alkalinity and pH* - Concentrations of bicarbonate and carbonate depend on pH and alkalinity, where alkalinity is defined as the acid-neutralizing capacity of the water. In our experiments, alkalinity is largely determined by dissolved inorganic carbon and inorganic phosphates. Contributions of nitrate and sulfate are negligible as they do not function as proton donor or acceptor in the pH range observed in our experiments (pH = 7-11). Hence, the alkalinity in our experimental system can be defined as (Wolf-Gladrow *et al.* 2007):

$$\text{ALK} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{OH}^-] - [\text{H}_3\text{PO}_4] - [\text{H}^+] \quad (\text{A9})$$

We note from this equation that biological uptake or release of carbon dioxide does not change alkalinity. Furthermore, uptake of bicarbonate for phytoplankton photosynthesis is accompanied by the release of a hydroxide ion or uptake of a proton to maintain charge balance, and therefore does not change alkalinity either. Hence, carbon assimilation by phytoplankton does not affect alkalinity. Nitrate, phosphate and sulfate assimilation, however, are accompanied by proton consumption in order to maintain charge balance. Therefore, assimilation of these nutrients increases alkalinity (Brewer and Goldman 1976; Wolf-Gladrow *et al.* 2007). More specifically, both nitrate and phosphate uptake increase alkalinity by 1 mole equivalent, whereas sulfate uptake increases alkalinity by 2 mole

equivalents (Wolf-Gladrow *et al.* 2007). Accordingly, changes in alkalinity can be described as:

$$\frac{dALK}{dt} = D(ALK_{IN} - ALK) + \sum_{i=1}^n (u_{N,i} + u_{P,i} + 2u_{S,i})X_i \quad (A10)$$

This equation states that changes in alkalinity depend on in- and efflux of water with a given alkalinity, and on the uptake rates of nitrate ( $u_{N,i}$ ), phosphate ( $u_{P,i}$ ), and sulfate ( $u_{S,i}$ ) by the phytoplankton species.

The pH is calculated iteratively at each time step from alkalinity using the summed concentrations of bicarbonate and carbonate (CARB) and the summed concentrations of dissolved inorganic phosphates ( $R_p$ ) (Portielje and Lijklema 1995; Stumm and Morgan 1996). Initial values of bicarbonate, carbonate, phosphoric acid ( $H_3PO_4$ ), dihydrogen phosphate ( $H_2PO_4^-$ ), hydrogen phosphate ( $HPO_4^{2-}$ ), and phosphate ( $PO_4^{3-}$ ) are estimated using the proton concentration ( $H^+$ ) calculated from the pH at the previous time step ( $pH_{t-1}$ ):

$$[HCO_3^-] = \frac{[H^+]}{K_2 + [H^+]} [CARB] \quad (A11)$$

$$[CO_3^{2-}] = \frac{K_2}{K_2 + [H^+]} [CARB] \quad (A12)$$

$$[H_3PO_4] = \frac{[H^+]^3}{\alpha_p} R_p \quad (A13)$$

$$[H_2PO_4^-] = \frac{K_{p1}[H^+]^2}{\alpha_p} R_p \quad (A14)$$

$$[HPO_4^{2-}] = \frac{K_{p1}K_{p2}[H^+]}{\alpha_p} R_p \quad (A15)$$

$$[PO_4^{3-}] = \frac{K_{p1}K_{p2}K_{p3}}{\alpha_p} R_p \quad (A16)$$

where  $K_2$  is the equilibrium constant of bicarbonate and carbonate,  $K_{p1}$ ,  $K_{p2}$  and  $K_{p3}$  are the equilibrium constants of the inorganic phosphates, and  $\alpha_p$  is calculated as:

$$\alpha_p = [H^+]^3 + K_{p1}[H^+]^2 + K_{p1}K_{p2}[H^+] + K_{p1}K_{p2}K_{p3} \quad (A17)$$

Alkalinity can be calculated from these initial estimates using equation A9. From the discrepancy,  $dALK$ , between this newly calculated alkalinity and the actual alkalinity predicted by equation A10, a new pH estimate is made:

$$pH_t = pH_{t-1} + dpH \quad (A18)$$

Where  $dpH$  is calculated according to (Stumm and Morgan 1996):

$$dpH = \frac{dALK}{2.3 \left( [H^+] + [OH^-] + \alpha_{HCO_3} \alpha_{CO_3} [CARB] + \alpha_{01} \alpha_{10} [P_{01}] \right.} \quad (A19)$$

$$\left. + \alpha_{12} \alpha_{21} [P_{12}] + \alpha_{23} \alpha_{32} [P_{23}] \right)$$

where  $\alpha_{\text{HCO}_3} = [\text{H}^+]/([\text{H}^+] + K_2)$ ,  $\alpha_{\text{CO}_3} = K_2/([\text{H}^+] + K_2)$ ,  $\alpha_{01} = [\text{H}^+]/([\text{H}^+] + K_{\text{P}1})$ ,  $\alpha_{10} = K_{\text{P}1}/([\text{H}^+] + K_{\text{P}1})$ ,  $\alpha_{12} = [\text{H}^+]/([\text{H}^+] + K_{\text{P}2})$ ,  $\alpha_{21} = K_{\text{P}2}/([\text{H}^+] + K_{\text{P}2})$ ,  $\alpha_{23} = [\text{H}^+]/([\text{H}^+] + K_{\text{P}3})$ ,  $\alpha_{32} = K_{\text{P}3}/([\text{H}^+] + K_{\text{P}3})$ ,  $[\text{P}_{01}] = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-]$ ,  $[\text{P}_{12}] = [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$ , and  $[\text{P}_{23}] = [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$ . This new pH is then used to calculate new values for bicarbonate, carbonate, the inorganic phosphates and alkalinity using equations A11-A17, and so on. This iterative procedure is continued until pH and alkalinity have both reached a stable value.

*Carbon assimilation* - We assume that uptake rates of carbon dioxide and bicarbonate are increasing but saturating functions  $f_{\text{CO}_2,i}$  and  $f_{\text{HCO}_3,i}$  of the availability of carbon dioxide and bicarbonate, respectively, as in Michaelis-Menten kinetics:

$$f_{\text{CO}_2,i} = u_{\text{MAX,CO}_2,i} \left( \frac{[\text{CO}_2]}{H_{\text{CO}_2,i} + [\text{CO}_2]} \right) \quad (\text{A20})$$

$$f_{\text{HCO}_3,i} = u_{\text{MAX,HCO}_3,i} \left( \frac{[\text{HCO}_3^-]}{H_{\text{HCO}_3,i} + [\text{HCO}_3^-]} \right) \quad (\text{A21})$$

where  $u_{\text{MAX,CO}_2,i}$  and  $u_{\text{MAX,HCO}_3,i}$  are the maximum uptake rates of carbon dioxide and bicarbonate, respectively,  $H_{\text{CO}_2,i}$  and  $H_{\text{HCO}_3,i}$  are the half-saturation constants. In addition, we assume that carbon uptake rates are suppressed when cells become satiated with carbon (Morel 1987; Ducobu *et al.* 1998), and depend on the photosynthetic activities of the species. The uptake rates of carbon dioxide and bicarbonate by a phytoplankton species can then be described by:

$$u_{\text{CO}_2,i} = f_{\text{CO}_2,i} (1 - S_i) P_i \quad (\text{A22})$$

$$u_{\text{HCO}_3,i} = f_{\text{HCO}_3,i} (1 - S_i) P_i \quad (\text{A23})$$

where  $S_i$  is the relative size of the transient carbon pool as defined by equation A3, and  $P_i$  is a measure of photosynthetic activity (with  $0 < P_i < 1$ ).

We assume that the respiration rate is proportional to the size of the transient carbon pool:

$$r_i = r_{\text{MAX},i} S_i \quad (\text{A24})$$

where  $r_{\text{MAX},i}$  is the maximum respiration rate when cells are fully satiated with carbon.

*Nutrient assimilation* - In our experiments, uptake of nitrate, phosphate and sulfate by phytoplankton species affects alkalinity. The model therefore keeps track of dynamic changes in the concentrations of nitrate ( $R_N$ ), phosphate ( $R_P$ ), and sulfate ( $R_S$ ):

$$\frac{dR_j}{dt} = D(R_{\text{IN},j} - R_j) - \sum_{i=1}^n u_{j,i} X_i \quad j = N, P, S \quad (\text{A25})$$

This equation states that changes in these nutrient concentrations depend on the in- and efflux of water containing these nutrients, and on the nutrient uptake rates ( $u_{j,i}$ ) of the

phytoplankton species. For simplicity, we assume that phytoplankton species have a constant C:N:P:S stoichiometry. That is, uptake rates of nitrate, phosphate and sulfate are proportional to the net uptake rate of carbon:

$$u_{j,i} = y_{j,i} (u_{CO_2,i} + u_{HCO_3^-,i} - r_i) \quad j = N, P, S \quad (A26)$$

where  $y_{N,i}$ ,  $y_{P,i}$  and  $y_{S,i}$  are the cellular N:C, P:C and S:C ratios of phytoplankton species  $i$ .

*Light-dependence of carbon assimilation* - Light availability determines the photosynthetic rate, and thereby the amount of energy available for carbon assimilation. According to Lambert-Beer's law, the underwater light intensity varies with depth (Huisman and Weissing 1994; Huisman *et al.* 1999):

$$I(z) = I_{in} \exp\left(-K_{bg}z - \sum_{i=1}^n k_i X_i z\right) \quad (A27)$$

This equation states that the light intensity transmitted through the water column increases with the incident light intensity ( $I_{in}$ ), but decreases with the depth of the water column ( $z$ ), the background turbidity of the water itself ( $K_{bg}$ ), the specific light attenuation coefficients of the phytoplankton species ( $k_i$ ), and the population densities of the phytoplankton species ( $X_i$ ).

The photosynthetic activity of the phytoplankton species can be calculated as the integral of their photosynthetic rate over the depth of the water column:

$$P_i = \frac{1}{z_M} \int_0^{z_M} p_i(I(z)) dz \quad (A28)$$

where  $z_M$  is the total depth of the water column, and the notation  $p_i(I(z))$  indicates that the photosynthetic rate of species  $i$  is a function  $p_i$  of light intensity  $I$ , which in turn is a function of depth  $z$ . Our model assumes that the light dependence of the photosynthetic rate of phytoplankton species can be described by a Monod function:

$$p_i(I) = \frac{p_{max,i} I}{H_{l,i} + I} \quad (A29)$$

where  $p_{max,i}$  is the maximum photosynthetic rate of species  $i$ , and  $H_{l,i}$  is its half-saturation constant for light. The maximum carbon uptake rate is already specified in equations A20 and A21. Therefore, we set  $p_{max,i} = 1$ , which constrains  $P_i$  to  $0 < P_i < 1$  (as required in equations A22 and A23). The depth integral in equation A28 can now be solved (Huisman and Weissing 1994), which yields:

$$P_i = \left( \frac{1}{\ln(I_{in}/I_{out})} \right) \ln \left( \frac{H_{l,i} + I_{in}}{H_{l,i} + I_{out}} \right) \quad (A30)$$

where  $I_{out}$  is the light intensity at the bottom of the water column (i.e.,  $I_{out} = I(z_M)$ ).

Table A2. Reactions and equilibrium constants of dissolved inorganic carbon and dissolved inorganic phosphates in water. Equilibrium constants and rates values assume a temperature of 21.5 °C and a pressure of 1 atm.

Reactions	Equilibrium constants	Description	Value <sup>(1)</sup>	Units
$[\text{H}_2\text{O}] \leftrightarrow [\text{H}^+] + [\text{OH}^-]$	$[\text{H}^+][\text{OH}^-] = K_W$	Equilibrium constant of water	$7.71 \times 10^{-15}$	$\text{mol L}^{-1} \text{atm}^{-1}$
$\text{pCO}_2 + [\text{H}_2\text{O}] \leftrightarrow [\text{CO}_2]$	$\frac{[\text{CO}_2^*]}{\text{pCO}_2} = K_0$	Solubility of $\text{CO}_2$ gas in water	$3.73 \times 10^{-2}$	-
$[\text{CO}_2] \leftrightarrow [\text{H}^+] + [\text{HCO}_3^-]$	$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = K_1$	Dissociation constant of $\text{CO}_2$	$4.25 \times 10^{-7}$	-
$[\text{HCO}_3^-] \leftrightarrow [\text{H}^+] + [\text{CO}_3^{2-}]$	$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2$	Dissociation constant of $\text{HCO}_3^-$	$4.34 \times 10^{-11}$	-
$[\text{H}_2\text{O}] + [\text{CO}_2] \rightarrow [\text{HCO}_3^-] + [\text{H}^+]$	$k_{\text{CO}_2}$	Reaction rate of $\text{H}_2\text{O}$ and $\text{CO}_2$	$2.68 \times 10^{-2}$	$\text{s}^{-1}$
$[\text{OH}^-] + [\text{CO}_2] \rightarrow [\text{HCO}_3^-]$	$k_{\text{OH}}$	Reaction rate of $\text{OH}^-$ and $\text{CO}_2$	$6.32 \times 10^4$	$\text{s}^{-1}$
$[\text{HCO}_3^-] + [\text{H}^+] \rightarrow [\text{H}_2\text{O}] + [\text{CO}_2]$	$k_{\text{HCO}_3}$	Reaction rate of $\text{HCO}_3^-$ and $\text{H}^+$	$1.36 \times 10^{-4}$	$\text{s}^{-1}$
$[\text{HCO}_3^-] \rightarrow [\text{OH}^-] + [\text{CO}_2]$	$k_{\text{H}}$	Reaction rate of the dissociation of $\text{HCO}_3^-$	$7.47 \times 10^3$	$\text{s}^{-1}$
$[\text{H}_3\text{PO}_4] \leftrightarrow [\text{H}^+] + [\text{H}_2\text{PO}_4^-]$	$\frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = K_{\text{P1}}$	Dissociation constant of $\text{H}_3\text{PO}_4$	$7.11 \times 10^{-3}$	-
$[\text{H}_2\text{PO}_4^-] \leftrightarrow [\text{H}^+] + [\text{HPO}_4^{2-}]$	$\frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = K_{\text{P2}}$	Dissociation constant of $\text{H}_2\text{PO}_4^-$	$6.32 \times 10^{-8}$	-
$[\text{HPO}_4^{2-}] \leftrightarrow [\text{H}^+] + [\text{PO}_4^{3-}]$	$\frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = K_{\text{P3}}$	Dissociation constant of $\text{HPO}_4^{2-}$	$4.47 \times 10^{-13}$	-

<sup>(1)</sup> The solubility of  $\text{CO}_2$  in water and the dissociation constants are based on Stumm and Morgan (1996); the reaction rates are based on Welch *et al.* (1969).

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# Appendix 3

## Parameter values

This Appendix provides the parameter values used in the model simulations. The species parameters are provided in Table A3, and the system parameters in Table A4.

Table A3. Parameter values estimated for the toxic strain *Microcystis* CYA140 and the nontoxic strain *Microcystis* CYA43.

Parameter	Description	CYA43	CYA140	Units
$\mu_{MAX}$	Maximum growth rate	1.04	1.04	d <sup>-1</sup>
$k$	Specific light attenuation coefficient	$5.0 \times 10^{-5}$	$6.9 \times 10^{-5}$	m <sup>2</sup> mm <sup>-3</sup>
$H_I$	Half-saturation constant for light	11	14	μmol photons m <sup>-2</sup> s <sup>-1</sup>
$u_{MAX,CO_2}$	Maximum uptake rate of CO <sub>2</sub>	10	7.8	μmol mm <sup>-3</sup> d <sup>-1</sup>
$H_{CO_2}$	Half-saturation constant for CO <sub>2</sub>	2.5	0.5	μmol L <sup>-1</sup>
$r_{MAX}$	Maximum respiration rate	1.3	1.3	μmol mm <sup>-3</sup> d <sup>-1</sup>
$u_{MAX,HCO_3}$	Maximum uptake rate of HCO <sub>3</sub> <sup>-</sup>	9.5	7.3	μmol mm <sup>-3</sup> d <sup>-1</sup>
$H_{HCO_3}$	Half-saturation constant for HCO <sub>3</sub> <sup>-</sup>	500	100	μmol L <sup>-1</sup>
$Q_{MIN}$	Minimum carbon content	14	10	μmol mm <sup>-3</sup>
$Q_{MAX}$	Maximum carbon content	19	17	μmol mm <sup>-3</sup>
$y_N$	Cellular N:C ratio	0.14	0.18	molar
$y_P$	Cellular P:C ratio	$7.0 \times 10^{-3}$	$4.0 \times 10^{-3}$	molar
$y_S$	Cellular S:C ratio	$8.3 \times 10^{-3}$	$6.1 \times 10^{-3}$	molar
$V$	Cell volume	$87 \times 10^{-9}$	$35 \times 10^{-9}$	mm <sup>3</sup> cell <sup>-1</sup>

Table A4. System parameters used in the chemostat experiments.

Parameter	Description	Carbon-limited chemostat	Light-limited chemostat	Units
$D$	Dilution rate	0.011	0.011	$\text{h}^{-1}$
$I_{IN}$	Incident irradiance	50	25	$\mu\text{mol photons m}^{-2} \text{s}^{-1}$
$z_M$	Mixing depth	0.05	0.05	m
$K_{bg}$	Background turbidity*	5–12.5	5–12.5	$\text{m}^{-1}$
$T$	Temperature	21.5	21.5	$^{\circ}\text{C}$
$a$	Gas flow rate	25	25	$\text{L h}^{-1}$
$\gamma$	Constant of proportionality for gas influx*	$1.4 \times 10^{-4}$ – $2.0 \times 10^{-4}$	$1.4 \times 10^{-4}$ – $2.0 \times 10^{-4}$	$\text{L}^{-1}$
$\text{pCO}_2$	Partial pressure of $\text{CO}_2$ in gas inflow	200	1,200	ppm
$[\text{CO}_2]_{IN}$	Concentration of dissolved $\text{CO}_2$ at inflow	8	29	$\mu\text{mol L}^{-1}$
$[\text{CARB}]_{IN}$	Summed concentration of bicarbonate and carbonate at inflow	500	2,000	$\mu\text{mol L}^{-1}$
$ALK_{IN}$	Alkalinity at inflow	0.80	2.1	$\text{mEq L}^{-1}$
$R_{IN,N}$	Concentration of nitrate at inflow	12,000	6,000	$\mu\text{mol L}^{-1}$
$R_{IN,P}$	Concentration of phosphate at inflow	300	300	$\mu\text{mol L}^{-1}$
$R_{IN,S}$	Concentration of sulfate at inflow	400	400	$\mu\text{mol L}^{-1}$

\*The background turbidity and constant of proportionality for the gas influx had different values for different chemostat vessels.

# Appendix 4

## Drawing the zero isoclines

Resource competition theory has developed a graphical approach using zero isoclines to assess the competitive abilities of species competing for two resources (Tilman 1982). The zero isoclines are plotted in a resource plane, with CO<sub>2</sub> concentrations on the x-axis and bicarbonate concentrations on the y-axis (Fig. 6.2). From our model, we can derive an explicit expression to calculate the zero isoclines.

At steady state, the cellular carbon quota will not change (i.e.,  $dQ_i/dt = 0$ ). Applying this to equation 6.2, with equation 6.4 and equations A22-A24, we obtain:

$$(f_{CO_2,i} + f_{HCO_3,i})(1 - S_i)P_i = \mu_{MAX,i}^* S_i Q_i^* + r_{MAX,i} S_i \quad (A31)$$

where the superscript \* indicates that the cellular carbon quota are evaluated at steady state,  $S_i$  is defined by equation 6.3, and  $P_i$  is defined by equation A30. This can be written as:

$$f_{CO_2,i} + f_{HCO_3,i} = (\mu_{MAX,i}^* Q_i^* + r_{MAX,i}) \left( \frac{S_i}{1 - S_i} \right) \frac{1}{P_i} \quad (A32)$$

Furthermore, at steady state, net population growth is zero (i.e.,  $dX_i/dt = 0$ ). This implies that the specific growth rate equals the dilution rate (i.e.,  $\mu_{MAX,i} S_i = D$ ). According to equation 6.4, the cellular carbon quota will then be:

$$Q_i^* = Q_{MIN,i} + (Q_{MAX,i} - Q_{MIN,i}) \frac{D}{\mu_{MAX,i}} \quad (A33)$$

Inserting this equation into equation A32, we obtain:

$$f_{CO_2,i} + f_{HCO_3,i} = A_i \quad (A34)$$

where we defined:

$$A_i = \frac{1}{P_i} \left( \frac{D}{\mu_{MAX,i} - D} \right) (Q_{MIN,i} (\mu_{MAX,i} - D) + Q_{MAX,i} D + r_{MAX,i}) \quad (A35)$$

The zero isocline is implicitly given by equation A34. Inserting equation A21 into A34, the bicarbonate concentration can be written as a function of the CO<sub>2</sub> concentration:

$$[HCO_3^-] = \frac{H_{HCO_3,i} (A_i - f_{CO_2,i})}{u_{MAX,HCO_3,i} - A_i + f_{CO_2,i}} \quad (A36)$$

where  $f_{CO_2,i}$  depends on the CO<sub>2</sub> concentration according to equation A20. The zero isoclines can now be plotted from equation A36, using the definitions of  $A_i$  and  $f_{CO_2,i}$  in equations A35 and A20.