ETH zürich
D USYS

Eawag:
Swiss Federal Institute of Aquatic Science and Technology

eawag aquatic research

Modelling Aquatic Ecosystems
Course 701-0426-00

Nele Schuwirth

ETH Zürich, Department of Environmental Systems Sciences
Eawag, Swiss Federal Institute of Aquatic Science and Technology

Lecturer

Nele Schuwirth (nele.Schuwirth@eawag.ch)
PhD in Geology,
Head of Department Systems Analysis and Modelling and
Group leader Integrative Ecological Systems Analysis
at Eawag
Privatdozentin ETHZ

Guest lectures

Andreas Scheidegger (andreas.scheidegger@eawag.ch)
MSc Applied Statistics, University Canberra
Statistician & Scientist at Eawag
Modelling, Systems Analysis, Data Science

Structure of the Course

1. Introduction, principles of modelling environmental systems, mass balance in a mixed reactor, process table notation, simple lake plankton model
   Exercise: R, `ecosim`-package, simple lake plankton model
   Exercise: lake phytoplankton-zooplankton model
2. Process stoichiometry Exercises: analytical solution, calculation with `stoichcalc`
3. Biological processes in lakes
4. Physical processes in lakes, mass balance in multi-box and continuous systems Exercise: structured, biogeochemical-ecological lake model
   Assignments: build your own model by implementing model extensions
5. Physical processes in in rivers, bacterial growth, river model for benthic populations Exercise: river model for benthic populations, nutrients and oxygen
6. Uncertainty, Parameter estimation, Stochasticity
   Exercise: parameter estimation
   Exercise: stochasticity, uncertainty
7. Existing models and applications in research and practice, examples and case studies, preparation of the oral exam, feedback

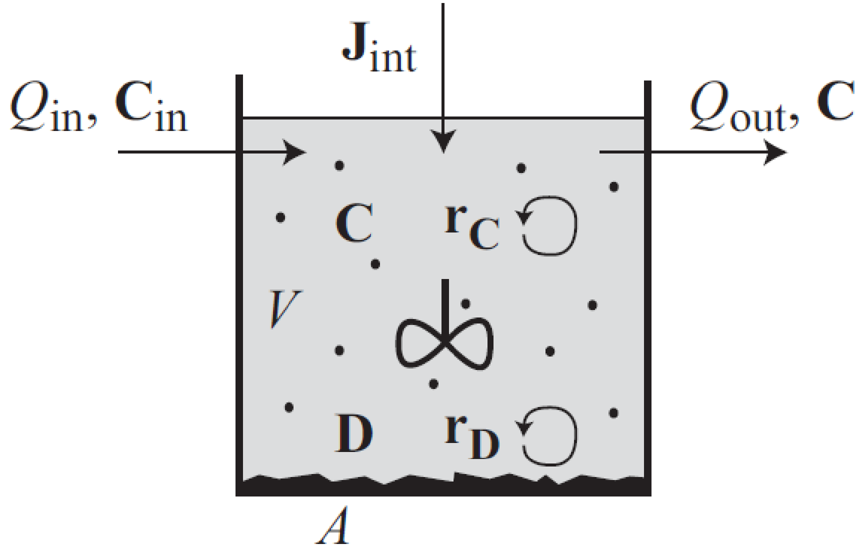
Goals

ETH zürich
eawag aquatic research

- Review exercise 2 and clarify open questions
- Acquire knowledge in process stoichiometry to bridge between ecological and biogeochemical processes.
- Learn to calculate stoichiometric coefficients
  from chemical substance notation (chapter 4.3.1)
  and parameterized elemental mass fractions (chapter 4.3.2).

Mass Balance in a Mixed Reactor

chapter 3.2



$\mathbf{C}$ concentration $[\mathrm{M/L^3}]$
$\mathbf{D}$ surface density $[\mathrm{M/L^2}]$
$Q_{\mathbf{in}}$ inflow, $Q_{\mathbf{out}}$ outflow $[\mathrm{L^3/T}]$
$J_{\mathbf{int}}$ flux across the interface $[\mathrm{M/T}]$

Mass Balance in a Mixed Reactor

$$\frac{\mathrm{d}V}{\mathrm{d}t} = Q_{\mathrm{in}} - Q_{\mathrm{out}}$$

$$\frac{\mathrm{d}\mathbf{C}}{\mathrm{d}t} = \frac{Q_{\mathrm{in}}}{V}\left(\mathbf{C}_{\mathrm{in}} - \mathbf{C}\right) + \frac{\mathbf{J}_{\mathrm{int}}}{V} + \mathbf{r}_{\mathbf{C}}$$

$$\frac{\mathrm{d}\mathbf{D}}{\mathrm{d}t} = \mathbf{r}_{\mathbf{D}}$$

Stoichiometry

ETH zürich
eawag
aquatic research

Process i	Substances j					Rate
	s_1	s_2	s_3	$\cdots$	$\mathsf{s}_{n_\mathrm{s}}$	
p_1	ν_{11}	ν_{12}	ν_{13}	$\cdots$	ν_{1n_s}	ρ_1
p_2	ν_{21}	ν_{22}	ν_{23}	$\cdots$	ν_{2n_s}	ρ_2
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
$\mathsf{p}_{n_\mathrm{p}}$	$\nu_{n_\mathrm{p}1}$	$\nu_{n_\mathrm{p}2}$	$\nu_{n_\mathrm{p}3}$	$\cdots$	$\nu_{n_\mathrm{p}n_\mathrm{s}}$	ρ_{n_p}

$$r_j = \sum_{i=1}^{n_\mathrm{p}} \nu_{ij}\ \rho_i$$

Review Exercise 2: Model description

ETH zürich
eawag aquatic research

chapter 11.2

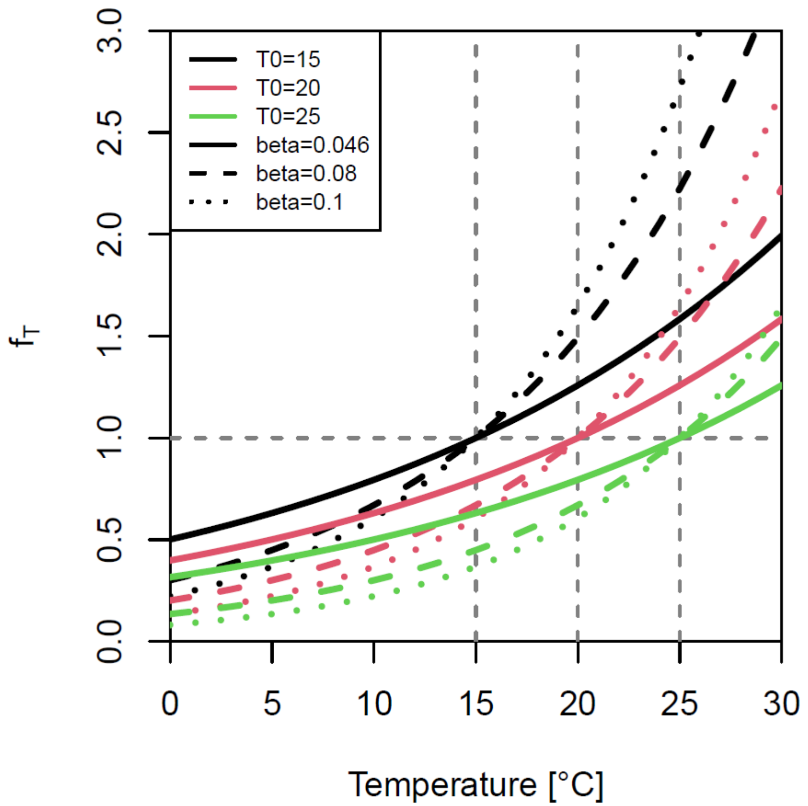
Process	Substances / Organisms HPO4 $[gP/m^3]$	ALG $[gDM/m^3]$	ZOO $[gDM/m^3]$	Rate
Growth of algae	$-\alpha_{P,ALG}$	1		$\rho_{gro,ALG}$
Death of algae		-1		$\rho_{death,ALG}$
Growth of zooplankton		$-\frac{1}{Y_{ZOO}}$	1	$\rho_{gro,ZOO}$
Death of zooplankton			-1	$\rho_{death,ZOO}$

here units of the state variables in the model

Rate	Rate expression
$\rho_{gro,ALG}$	$k_{gro,ALG,T_0} \cdot \exp\left(\beta_{ALG}(T-T_0)\right) \cdot \frac{1}{\lambda h} \log\left(\frac{K_I+I_0}{K_I+I_0\exp(-\lambda h)}\right) \cdot \frac{C_{HPO_4^{2-}}}{K_{HPO_4^{2-},ALG}+C_{HPO_4^{2-}}} \cdot C_{ALG}$
$\rho_{death,ALG}$	$k_{death,ALG}\, C_{ALG}$
$\rho_{gro,ZOO}$	$k_{gro,ZOO,T_0} \cdot \exp\left(\beta_{ZOO}(T-T_0)\right) \cdot C_{ALG}\, C_{ZOO}$
$\rho_{death,ZOO}$	$k_{death,ZOO}\, C_{ZOO}$

Typical Elements of Process Rates

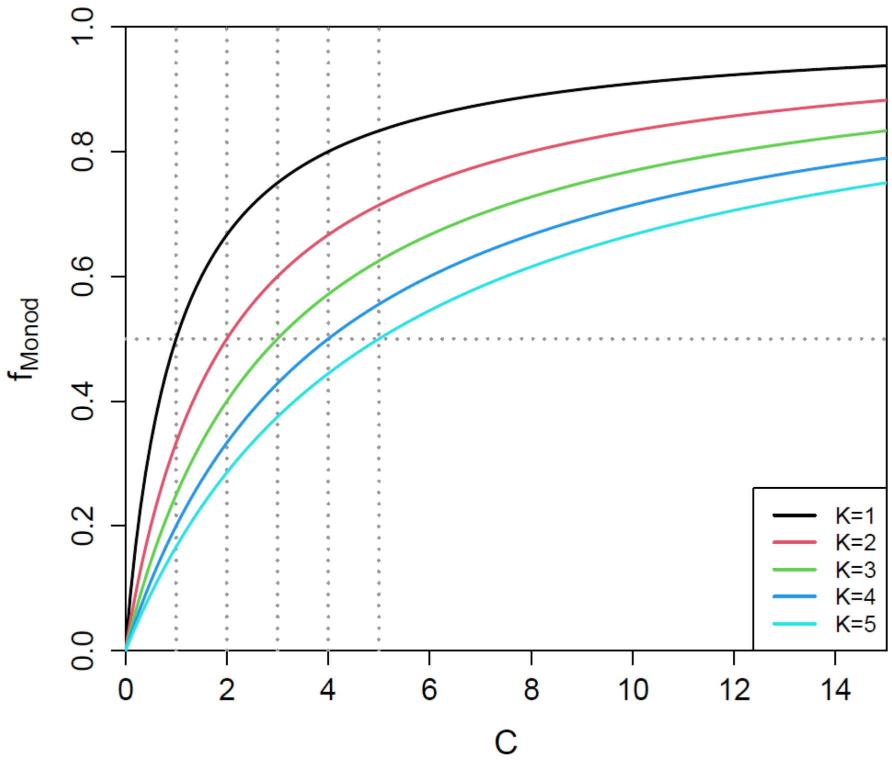
Temperature dependence factor



Exponential:

$$f_{\mathrm{temp}}^{\mathrm{exp}}(T) = \exp\Big(\beta(T - T_0)\Big)$$

Limitation by substance concentrations

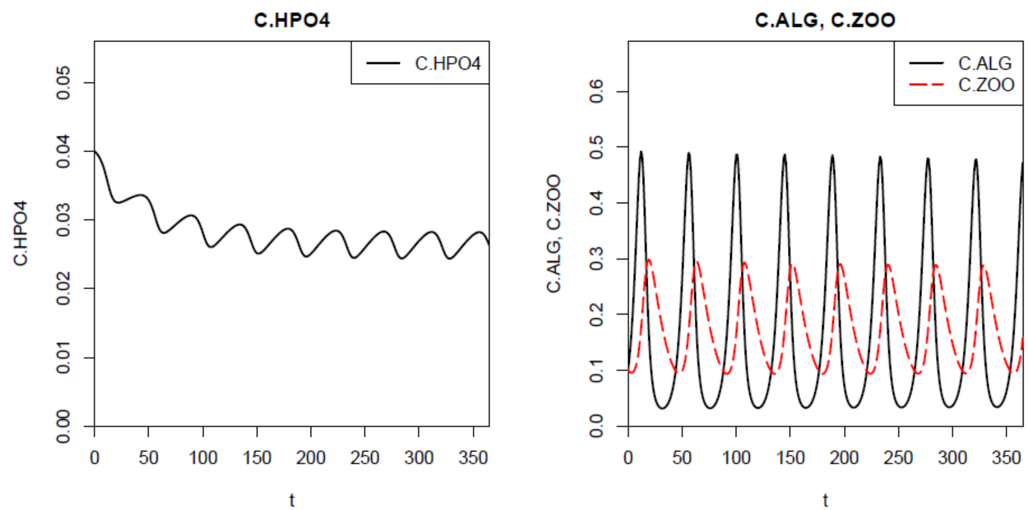


$$f_{\text{lim}}^{\text{Monod}}(C) = \frac{C}{K + C}$$

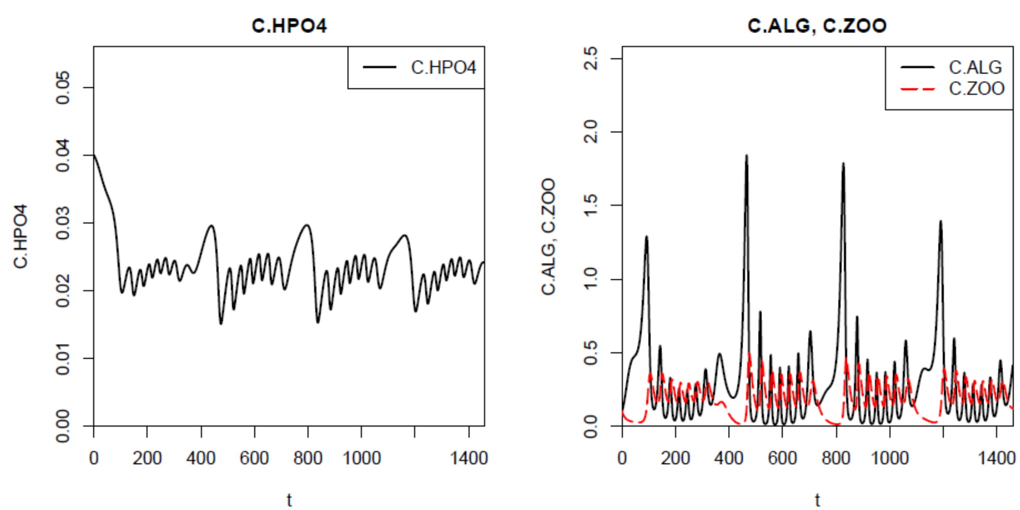
Review Exercise 2: Model results

ETH zürich
eawag
aquatic research

Results for constant environmental conditions



Results for periodic environmental conditions



Review Exercise 2: Questions

Do you have questions?

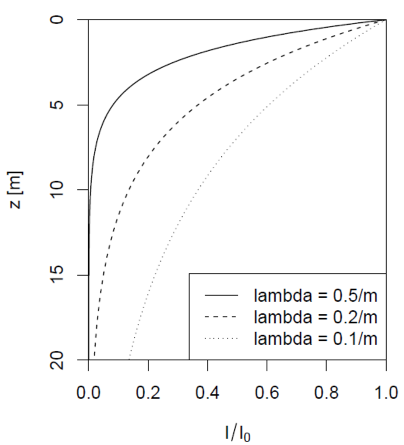
Review Exercise 2: Questions

Rate	Rate expression
$\rho_{\mathrm{gro,ALG}}$	$k_{\mathrm{gro,ALG},T_0} \cdot \exp\Big(\beta_{\mathrm{ALG}}(T - T_0)\Big) \cdot \dfrac{1}{\lambda h} \log\left(\dfrac{K_I + I_0}{K_I + I_0 \exp(-\lambda h)}\right) \cdot \dfrac{C_{\mathrm{HPO_4^{2-}}}}{K_{\mathrm{HPO_4^{2-},ALG}} + C_{\mathrm{HPO_4^{2-}}}} \cdot C_{\mathrm{ALG}}$

Why is the light dependence term so complicated when in other regards the model is such a strong simplification?

$$f_{\mathrm{rad}}^{\mathrm{Monod}}(I) = \frac{I}{K_I + I}$$

$$I(z) = I_0 \exp(-\lambda z);$$



Light attenuation

For a model with a mixed reactor, the light dependence factor (and not the light itself!) has to be averaged across depth.

Average light dependence factor:

$$\bar{f}_{\mathrm{rad}}(I_0, \lambda, h) = \frac{1}{h} \int_0^h f_{\mathrm{rad}}\Big(I_0 \exp(-\lambda z)\Big) \mathrm{d}z$$

$$\bar{f}_{\mathrm{rad}}^{\mathrm{Monod}}(I_0, \lambda, h) = \frac{1}{\lambda h} \log\left(\frac{K_I + I_0}{K_I + I_0 \exp(-\lambda h)}\right)$$

Review Exercise 2: Questions

ETH zürich eawag aquatic research

Rate	Rate expression
$\rho_{\text{gro,ALG}}$	$k_{\text{gro,ALG},T_0} \cdot \exp\left(\beta_{\text{ALG}}(T - T_0)\right) \cdot \frac{1}{\lambda h} \log\left(\frac{K_I + I_0}{K_I + I_0 \exp(-\lambda h)}\right) \cdot \frac{C_{\text{HPO}_4^{2-}}}{K_{\text{HPO}_4^{2-},\text{ALG}} + C_{\text{HPO}_4^{2-}}} \cdot C_{\text{ALG}}$

Ecosim implementation

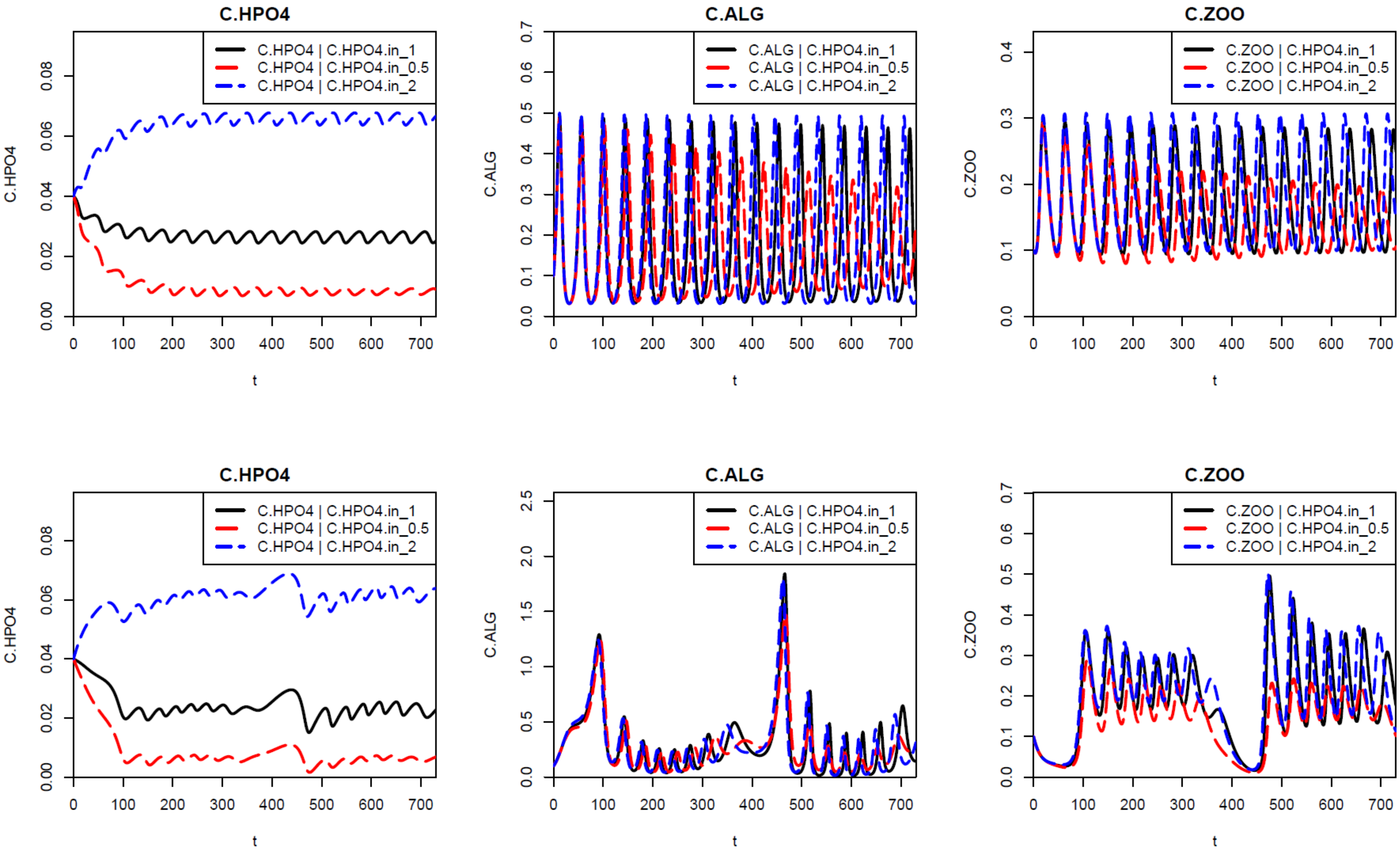
```
gro.ALG.ext <-
   new(Class  = "process",
       name   = "Growth of algae extended",
       rate   = expression(k.gro.ALG*
                            exp(beta.ALG*(T-T0))*
                            C.HPO4/(K.HPO4+C.HPO4)*
                            log((K.I+I0)/
                                (K.I+I0*exp(-(lambda.1+lambda.2*C.ALG)*h.epi)))/
                            ((lambda.1+lambda.2*C.ALG)*h.epi)*
                            C.ALG),
       stoich = list(C.ALG  = 1,                             # gDM/gDM
                     C.HPO4 = expression(-alpha.P.ALG)))     # gP/gDM
```

What does the expression() function do and why do we need it?

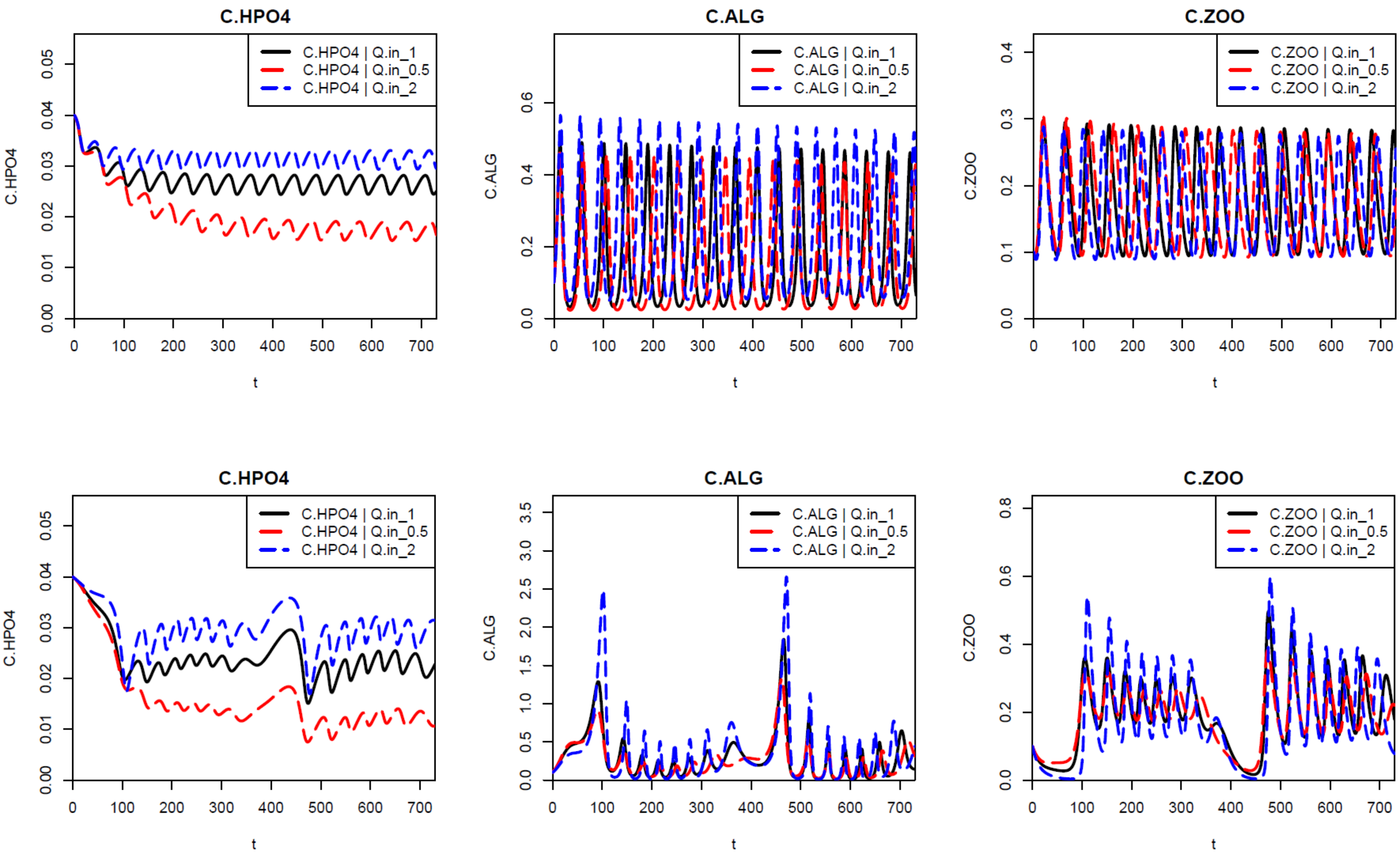
Review Exercise 2: Theory Questions

1. Are the algae concentrations controlled bottom-up (by phosphate limitation) or top-down (by grazing of zooplankton)? How can you find out?
2. What is the reason for oscillating concentrations under constant driving forces?
3. What is the difference in the oscillations between the simulation with constant and periodic driving forces?
4. What are the main deficits of the model compared to a real lake?
5. What is your expectation regarding the response of the model to the change in each parameter, does the result match your expectation and can you explain the observed changes?

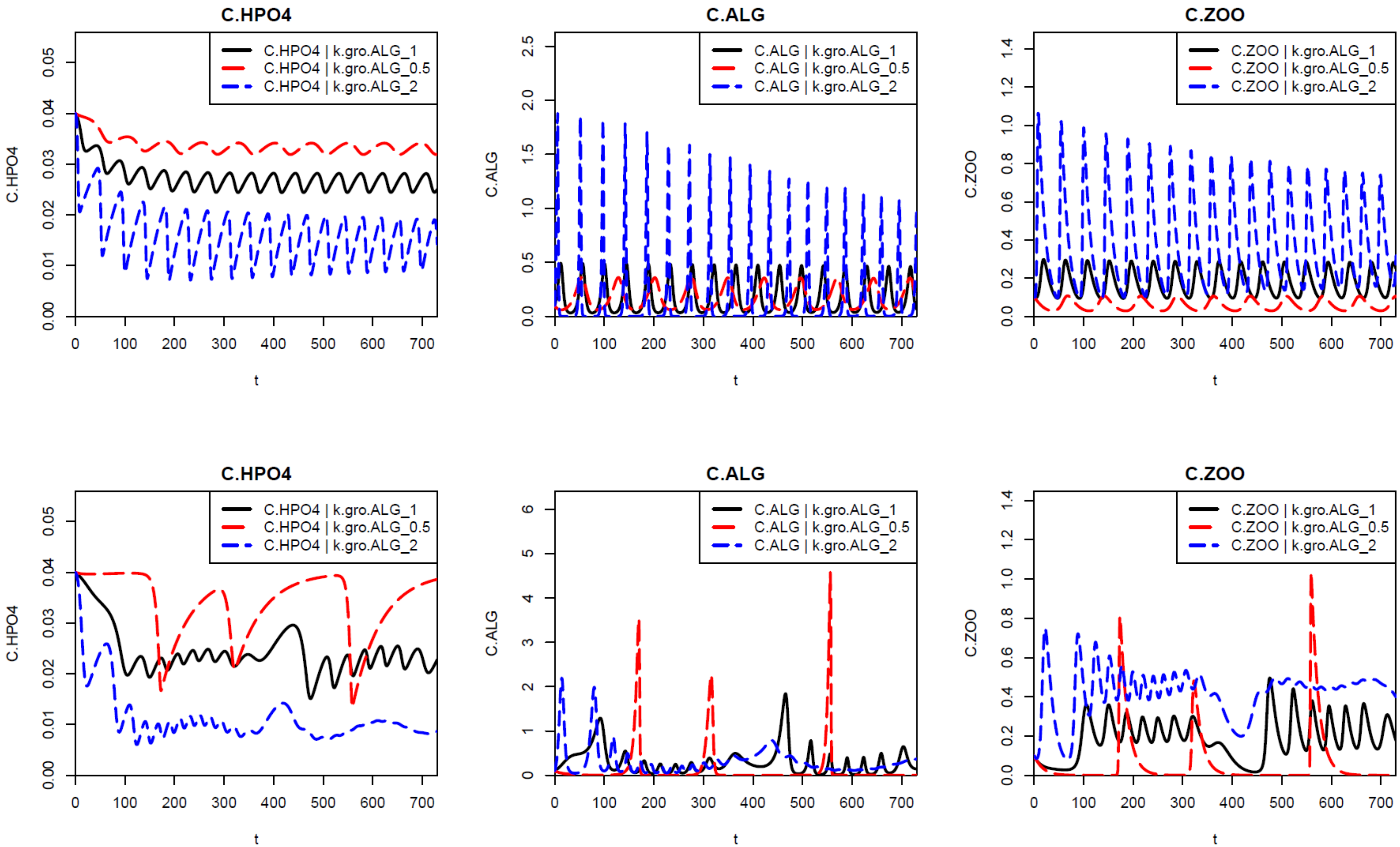
Review Exercise 2: Sensitivity Analysis



Review Exercise 2: Sensitivity Analysis

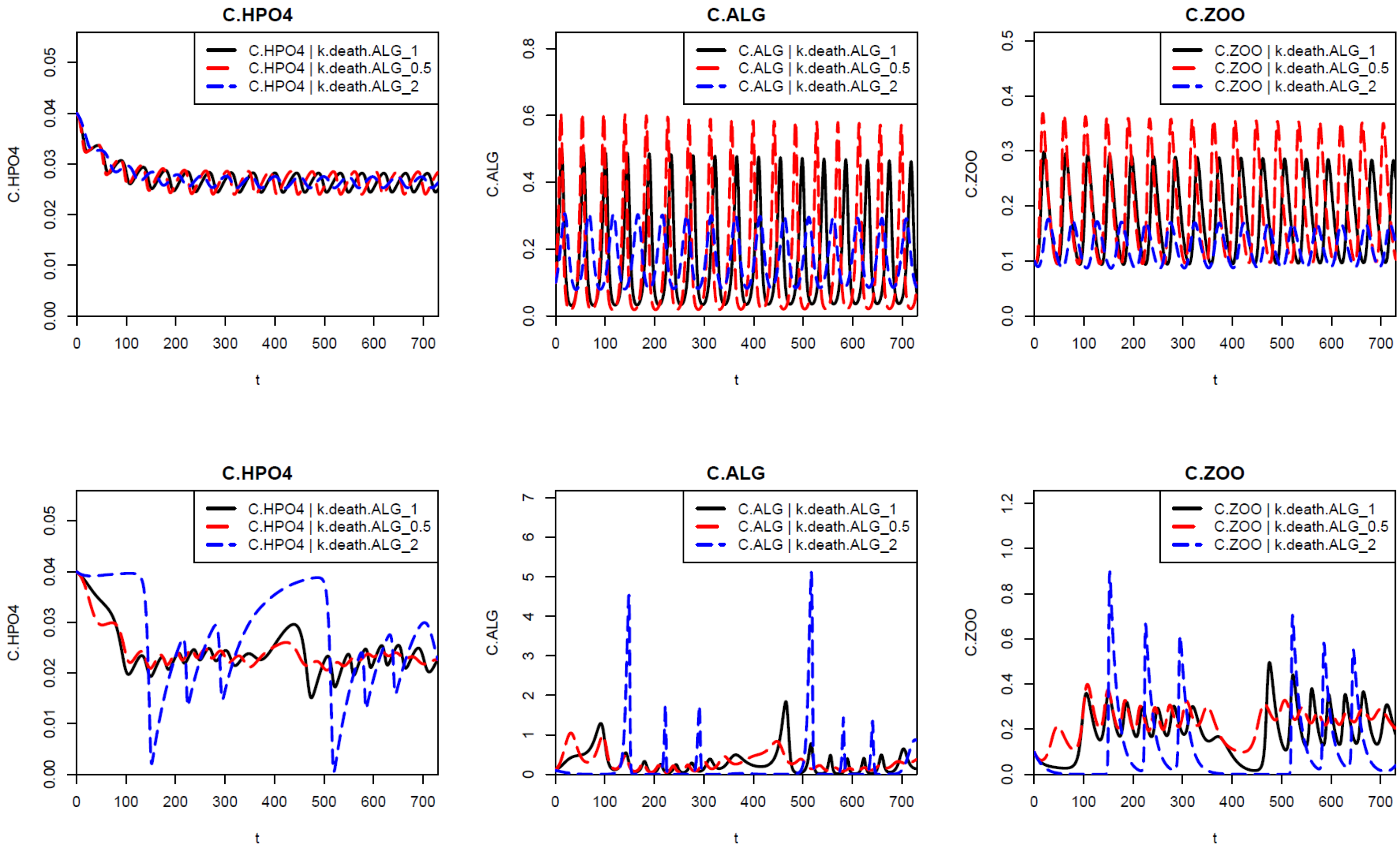


Review Exercise 2: Sensitivity Analysis

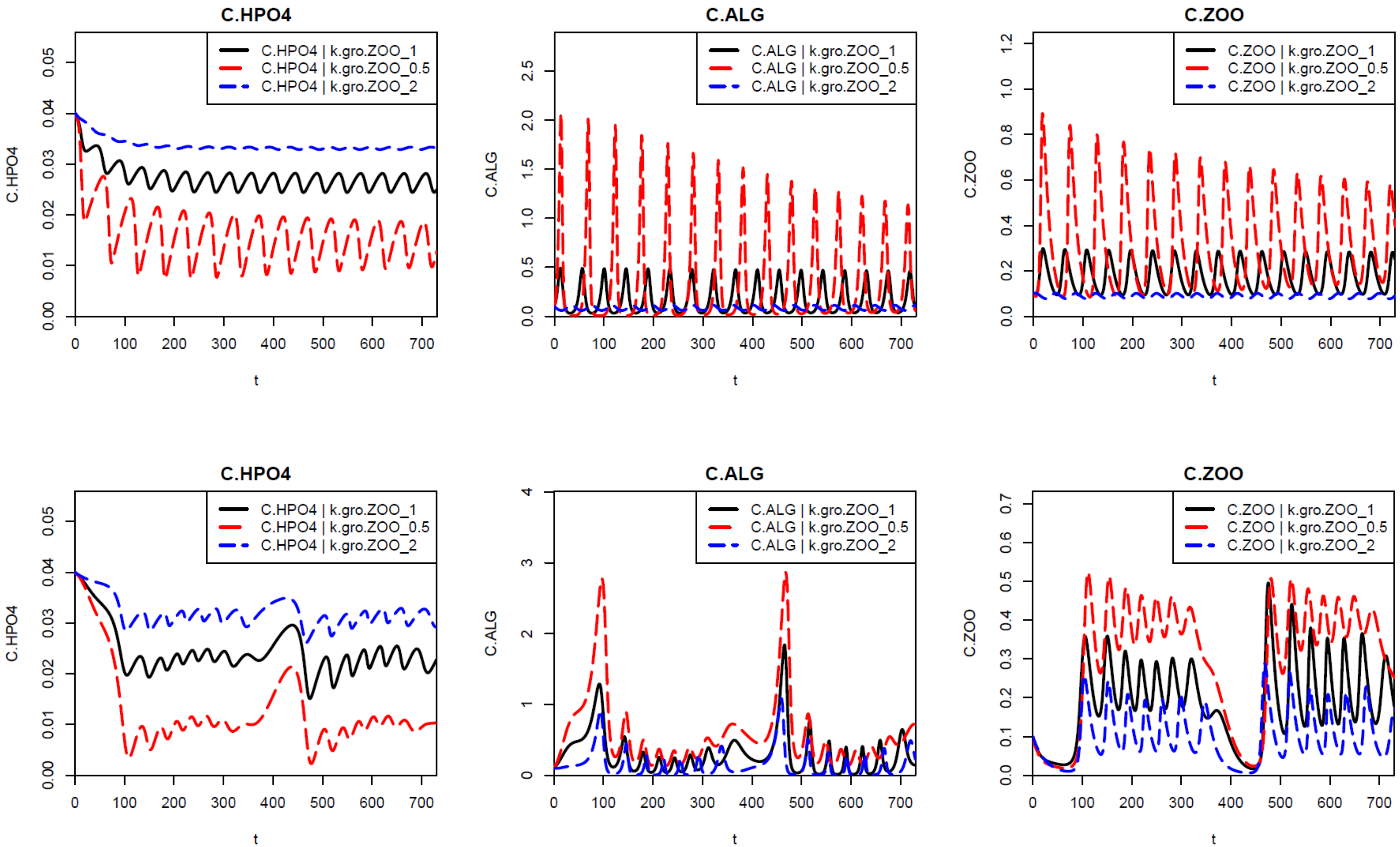


Review Exercise 2: Sensitivity Analysis

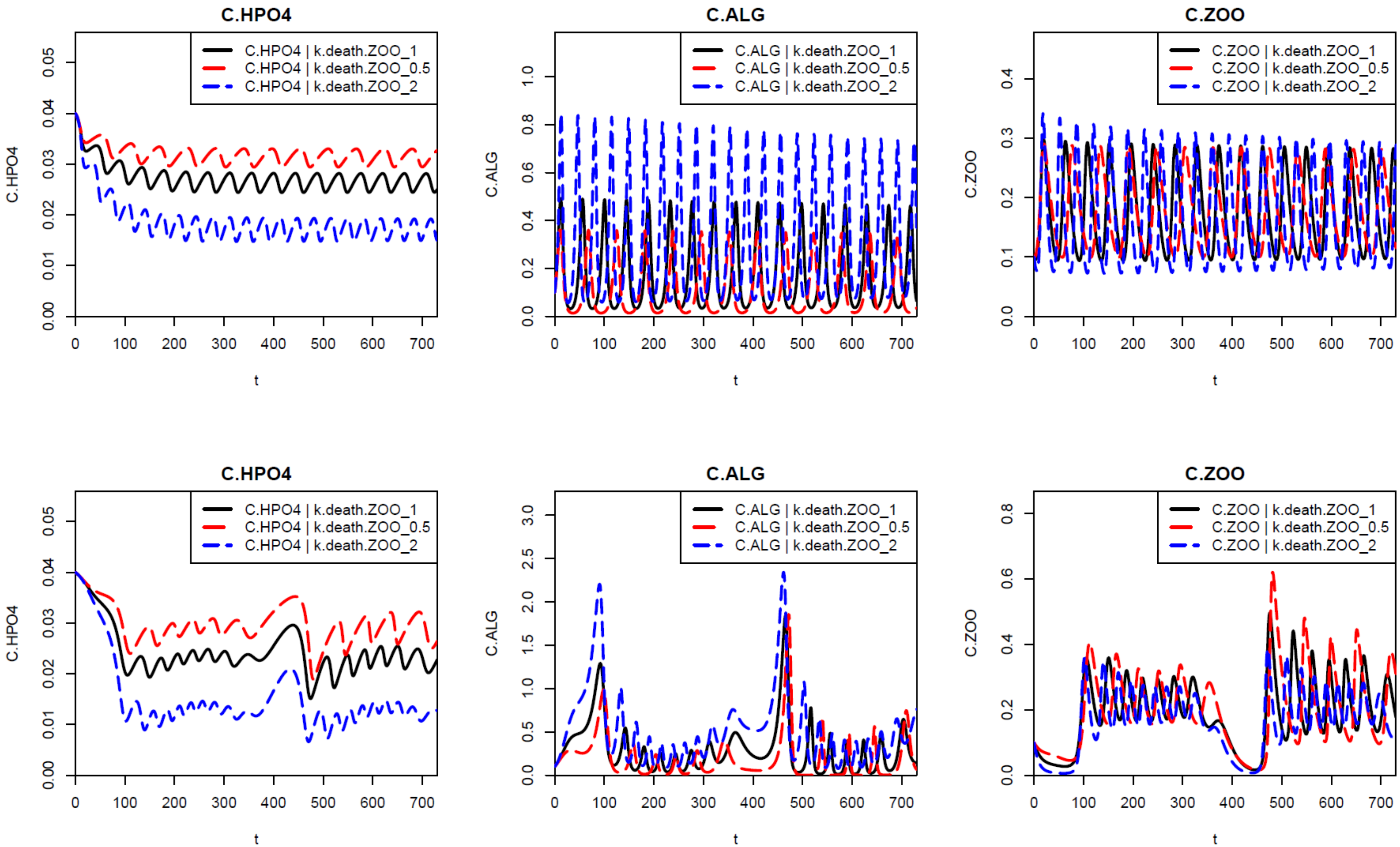
ETH zürich eawag aquatic research



Review Exercise 2: Sensitivity Analysis

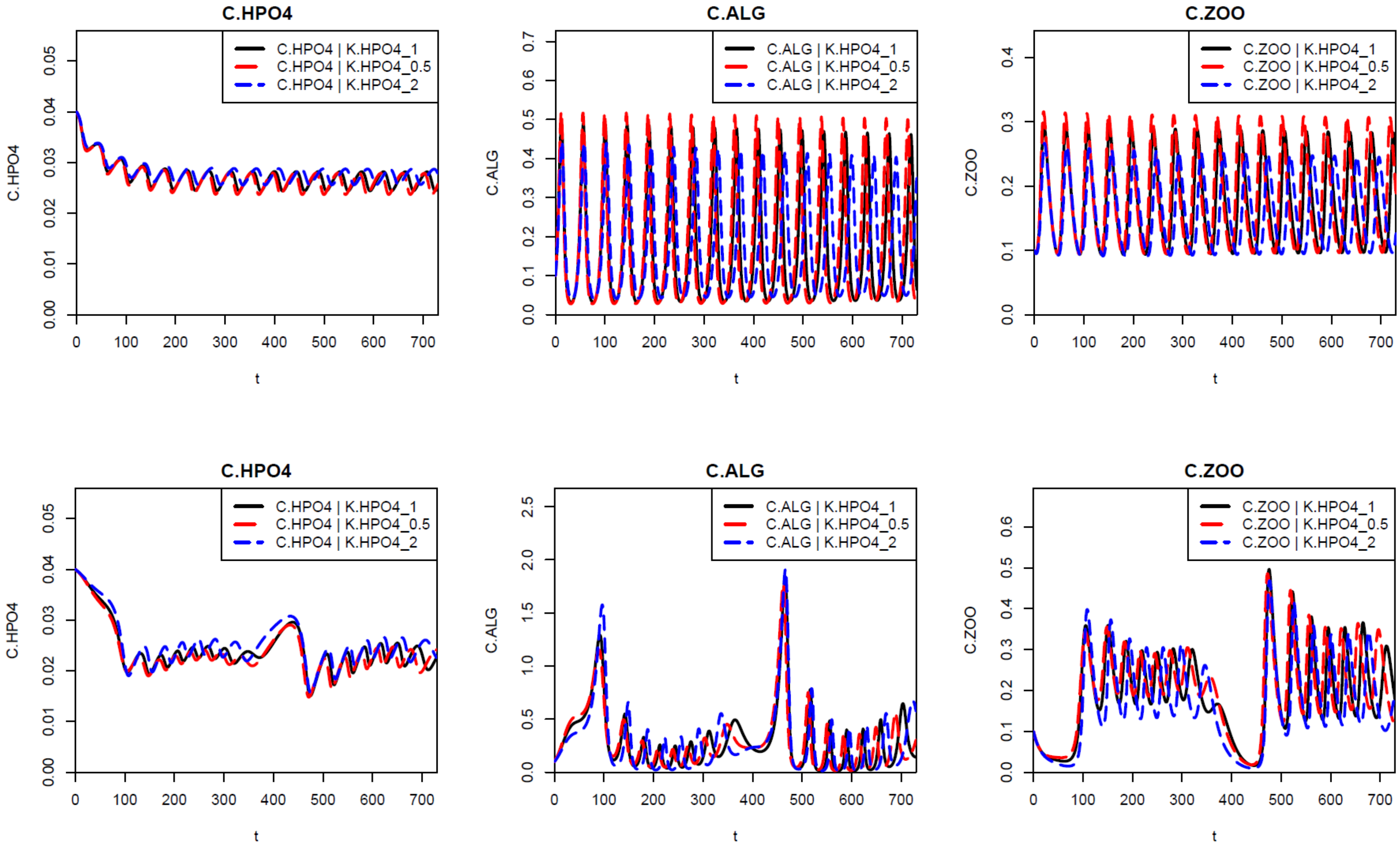


Review Exercise 2: Sensitivity Analysis

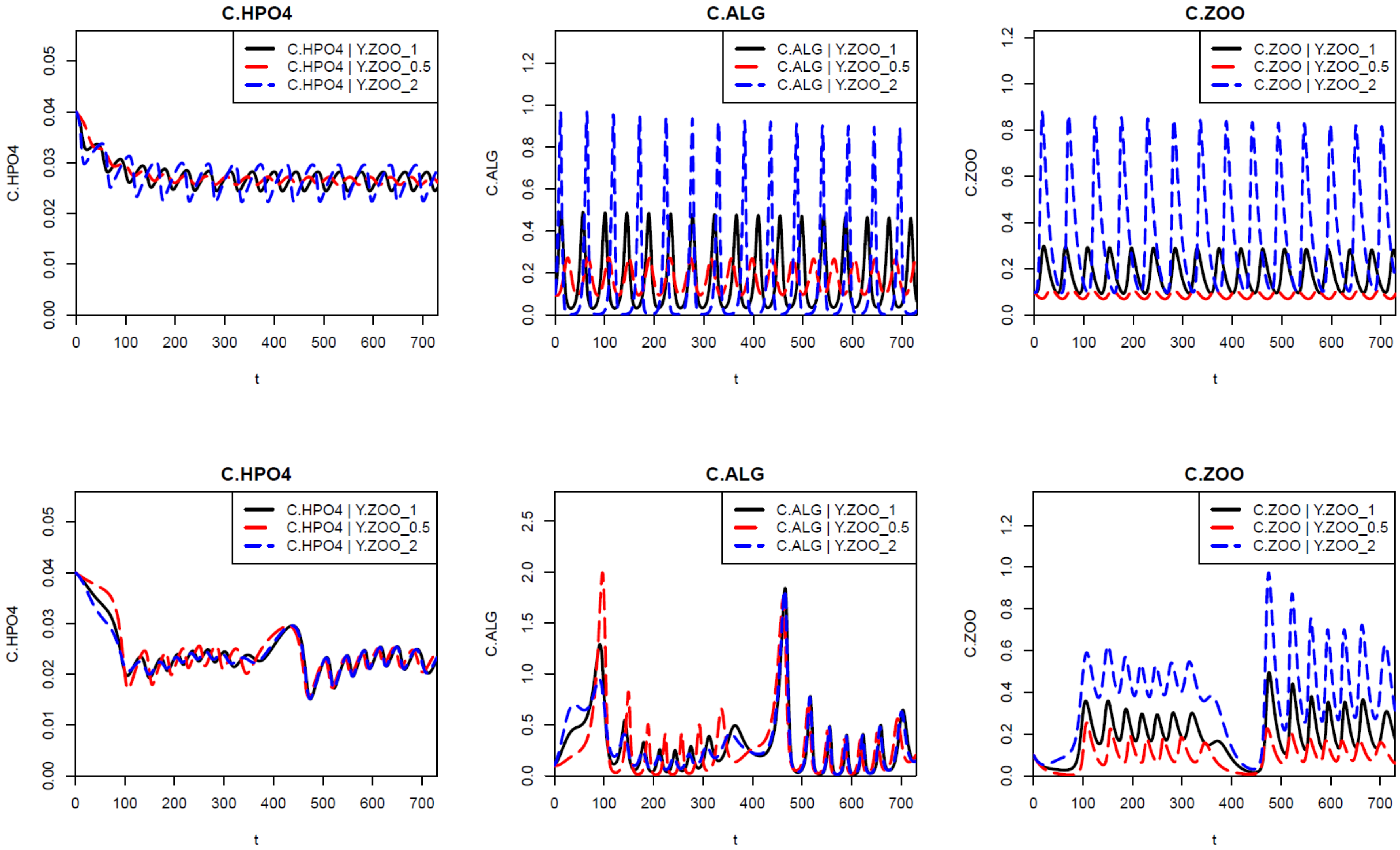


Review Exercise 2: Sensitivity Analysis

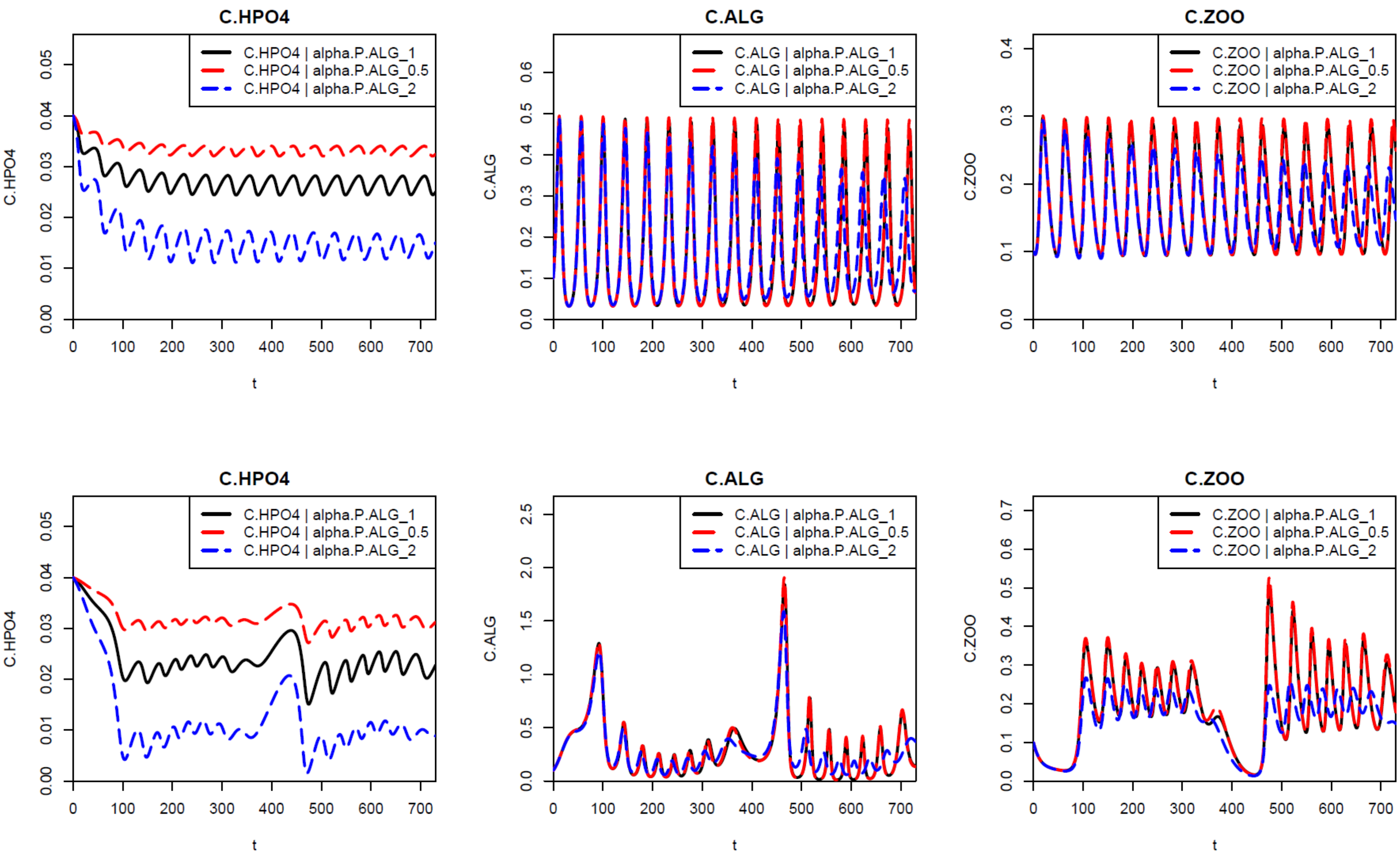
ETH zürich
eawag
aquatic research



Review Exercise 2: Sensitivity Analysis



Review Exercise 2: Sensitivity Analysis



Review Exercise 2: Lessons learned?

Stoichiometry

Process i	Substances j					Rate
	s_1	s_2	s_3	$\cdots$	s_{n_s}	
p_1	ν_{11}	ν_{12}	ν_{13}	$\cdots$	ν_{1n_s}	ρ_1
p_2	ν_{21}	ν_{22}	ν_{23}	$\cdots$	ν_{2n_s}	ρ_2
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
p_{n_p}	ν_{n_p1}	ν_{n_p2}	ν_{n_p3}	$\cdots$	$\nu_{n_pn_s}$	ρ_{n_p}

$$r_j = \sum_{i=1}^{n_p} \nu_{ij}\ \rho_i$$

How to derive the stoichiometric coefficients ν_{ij}?

Stoichiometry: Ingredients for 1 cake?

Best recipe: https://tinyurl.com/Schoggikuchen

Process table for chocolate cake

process	Chocolate [g]	Egg [no.]	Butter [g]	Sugar [g]	Cake [no.]	rate [min^{-1}]
baking a cake	-300	-5	-100	-100	+1	1/25 (at 180 °C)

If you want to try the recipe, consider also the preparation instructions:
https://tinyurl.com/Schoggikuchen

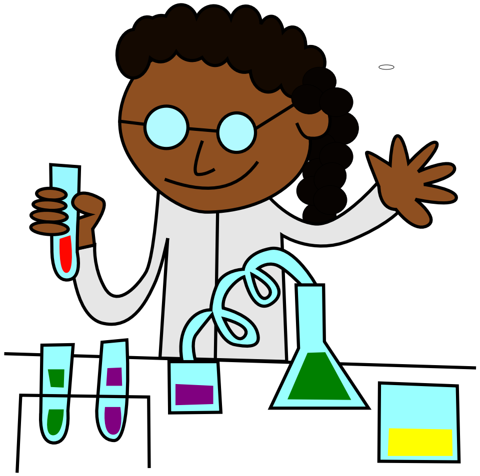
Stoichiometry

ETH zürich
eawag aquatic research

chapter 4.3.1

3 ways to derive stoichiometric coefficients:

- Chemical substance notation
- Parameterized elemental mass fractions
- General solution

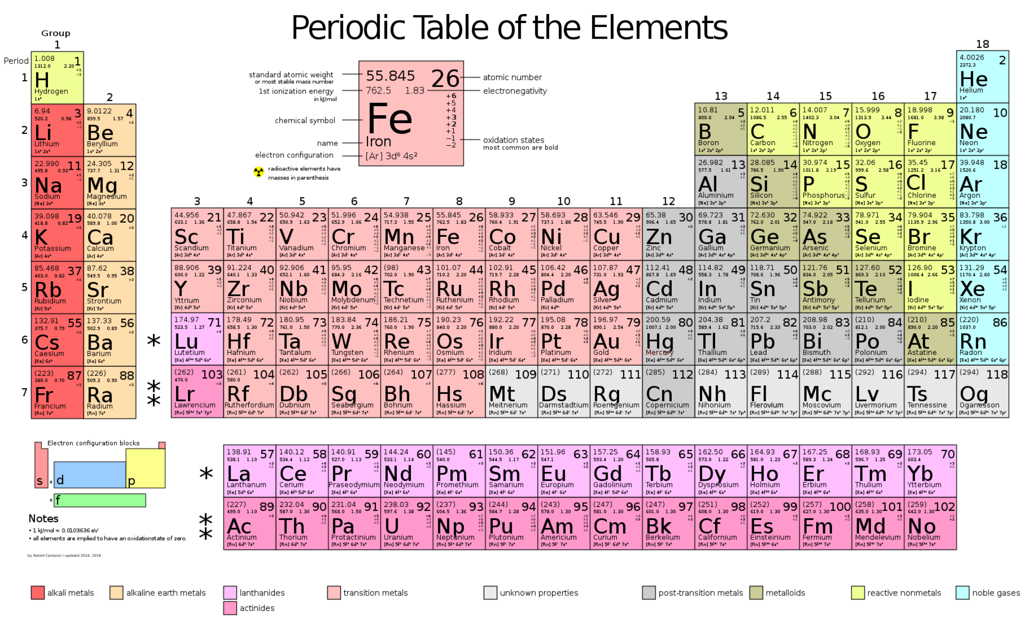


modified openclipart.org

Bevor we start...

Conversion from mole to mass:

$$n[\mathrm{mol}] = \frac{m[\mathrm{g}]}{M[\mathrm{g/mol}]}$$



Molar mass M
(atomic weight)

H: 1 g/mol
C: 12 g/mol
N: 14 g/mol
O: 16 g/mol
P: 31 g/mol

Chemical Substance Notation

Process	Substances / Organisms						
	NH_4^+	NO_3^-	HPO_4^{2-}	O_2	ALG	ZOO	POM
	mol	mol	mol	mol	gDM	gDM	gDM
Growth of ALG,NH4	?		?	?	1		
Growth of ALG,NO3		?	?	?	1		
Respiration of ALG	?		?	?	-1		
Death of ALG					-1		1
Growth of ZOO	?		?	?	?	1	?
Respiration of ZOO	?		?	?		-1	
Death of ZOO						-1	1

here just units of measurement of the different substances

Additional substances for calculation of the stoichiometric coefficients:
HCO_3^-, H^+, H_2O

Chemical Substance Notation

ETH zürich
eawag
aquatic research

1. Example: Growth of algae

Typical composition of marine algae (Redfield, 1958)

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)_1 = C_{106}H_{263}O_{110}N_{16}P$$

Total "molar" mass:

$$\begin{aligned} M &= 106 \cdot 12 \, \frac{\text{gC}}{\text{"mol"}} + 263 \, \frac{\text{gH}}{\text{"mol"}} + 110 \cdot 16 \, \frac{\text{gO}}{\text{"mol"}} \\ &\quad + 16 \cdot 14 \, \frac{\text{gN}}{\text{"mol"}} + 31 \, \frac{\text{gP}}{\text{"mol"}} \\ &= 3550 \, \frac{\text{gDM}}{\text{"mol"}} \end{aligned}$$

Chemical Substance Notation

1. Example: Growth of algae with nitrate:

$$a\,\mathrm{HCO_3^-} + b\,\mathrm{NO_3^-} + c\,\mathrm{HPO_4^{2-}} + d\,\mathrm{H^+} + e\,\mathrm{H_2O} \rightarrow \mathrm{C_{106}H_{263}O_{110}N_{16}P} + f\,\mathrm{O_2}$$

6 unknowns (a, b, c, d, e, f)

equations for the conservation of "mass": ?

Chemical Substance Notation

ETH zürich
eawag aquatic research

1. Example: Growth of algae with nitrate:

$$a\,HCO_3^- + b\,NO_3^- + c\,HPO_4^{2-} + d\,H^+ + e\,H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + f\,O_2$$

6 unknowns (a, b, c, d, e, f)

equations for the conservation of "mass": for C, H, O, N, P and charge

C: $a \cdot 1 = 1 \cdot 106 \rightarrow a = 106$

Chemical Substance Notation

1. Example: Growth of algae with nitrate:

$$a\,HCO_3^- + b\,NO_3^- + c\,HPO_4^{2-} + d\,H^+ + e\,H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + f\,O_2$$

6 unknowns (a, b, c, d, e, f)

equations for the conservation of "mass": for C, H, O, N, P and charge

C: $a \cdot 1 = 1 \cdot 106 \rightarrow a = 106$

N: $b \cdot 1 = 1 \cdot 16 \rightarrow b = 16$

Chemical Substance Notation

1. Example: Growth of algae with nitrate:

$$a\,HCO_3^- + b\,NO_3^- + c\,HPO_4^{2-} + d\,H^+ + e\,H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + f\,O_2$$

6 unknowns (a, b, c, d, e, f)

equations for the conservation of "mass": for C, H, O, N, P and charge

C: $a \cdot 1 = 1 \cdot 106 \rightarrow a = 106$

N: $b \cdot 1 = 1 \cdot 16 \rightarrow b = 16$

P: $c \cdot 1 = 1 \cdot 1 \rightarrow c = 1$

1. Example: Growth of algae with nitrate:

$$a\,HCO_3^- + b\,NO_3^- + c\,HPO_4^{2-} + d\,H^+ + e\,H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + f\,O_2$$

6 unknowns (a, b, c, d, e, f)

equations for the conservation of "mass": for C, H, O, N, P and charge

a = 106, b = 16, c = 1

H: $106 \cdot 1 + 1 \cdot 1 + d \cdot 1 + e \cdot 2 = 1 \cdot 263 \quad ,$

O: $106 \cdot 3 + 16 \cdot 3 + 1 \cdot 4 + e \cdot 1 = 1 \cdot 110 + f \cdot 2 \quad ,$

e⁻: $106 \cdot (-1) + 16 \cdot (-1) + 1 \cdot (-2) + d \cdot (+1) = 0 \quad .$

d =124 e =16 f =138

Chemical Substance Notation

1. Example: Growth of algae with nitrate:

$$a\,HCO_3^- + b\,NO_3^- + c\,HPO_4^{2-} + d\,H^+ + e\,H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + f\,O_2$$

a = 106, b = 16, c = 1, d = 124, e = 16, f = 138

$$106\,HCO_3^- + 16\,NO_3^- + HPO_4^{2-} + 124\,H^+ + 16\,H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138\,O_2$$

$$M_{ALG} = 3550\ \frac{\text{gDM}}{\text{“mol”}}$$

Chemical Substance Notation

ETH zürich eawag aquatic research

Stoichiometric coefficients for growth of algae:

$$\nu_{\mathrm{gro,ALG,NO3\ HCO_3^-}} = -\frac{106}{3550}\ \frac{\mathrm{molHCO_3^-}}{\mathrm{gDM}}$$

$$\nu_{\mathrm{gro,ALG,NO3\ NO_3^-}} = -\frac{16}{3550}\ \frac{\mathrm{molNO_3^-}}{\mathrm{gDM}}$$

$$\nu_{\mathrm{gro,ALG,NO3\ HPO_4^{2-}}} = -\frac{1}{3550}\ \frac{\mathrm{molHPO_4^{2-}}}{\mathrm{gDM}}$$

$$\nu_{\mathrm{gro,ALG,NO3\ H+}} = -\frac{124}{3550}\ \frac{\mathrm{molH^+}}{\mathrm{gDM}}$$

$$\nu_{\mathrm{gro,ALG,NO3\ H_2O}} = -\frac{16}{3550}\ \frac{\mathrm{molH_2O}}{\mathrm{gDM}}$$

$$\nu_{\mathrm{gro,ALG,NO3\ ALG}} = 1\ \frac{\mathrm{gDM}}{\mathrm{gDM}}$$

$$\nu_{\mathrm{gro,ALG,NO3\ O_2}} = \frac{138}{3550}\ \frac{\mathrm{molO_2}}{\mathrm{gDM}}$$

Chemical Substance Notation

Pen and paper exercise task 1

Derive the stoichiometry for the process

“growth of algae with ammonium as nitrogen source”

by calculating the mass balances for the elements and charge.

Assume the Redfield composition for algal biomass (eq. 4.33 and 4.34).

$$a\,\mathrm{HCO_3^-} + b\,\mathrm{NH_4^+} + c\,\mathrm{HPO_4^{2-}} + d\,\mathrm{H^+} + e\,\mathrm{H_2O} \rightarrow \mathrm{C_{106}H_{263}O_{110}N_{16}P} + f\,\mathrm{O_2}$$

Chemical Substance Notation

Process	Substances / Organisms						
	NH_4^+ mol	NO_3^- mol	HPO_4^{2-} mol	O_2 mol	ALG gDM	ZOO gDM	POM gDM
Gro. ALG,NH4	$-\frac{16}{3550}$		$-\frac{1}{3550}$	$\frac{106}{3550}$	1		
Gro. ALG,NO3		$-\frac{16}{3550}$	$-\frac{1}{3550}$	$\frac{138}{3550}$	1		

Chemical Substance Notation

Similarly for algal growth with ammonium:

$$106\,HCO_3^- + 16\,NH_4^+ + HPO_4^{2-} + 92\,H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 106\,O_2$$

Respiration:

$$C_{106}H_{263}O_{110}N_{16}P + 106\,O_2 \rightarrow 106\,HCO_3^- + 16\,NH_4^+ + HPO_4^{2-} + 92\,H^+$$

Death:

$$C_{106}H_{263}O_{110}N_{16}P \rightarrow C_{106}H_{263}O_{110}N_{16}P$$

Chemical Substance Notation

Process	Substances / Organisms						
	NH_4^+	NO_3^-	HPO_4^{2-}	O_2	ALG	ZOO	POM
	mol	mol	mol	mol	gDM	gDM	gDM
Growth of ALG,NH4	?		?	?	1		
Growth of ALG,NO3		?	?	?	1		
Respiration of ALG	?		?	?	-1		
Death of ALG					-1		1
Growth of ZOO	?		?	?	?	1	?
Respiration of ZOO	?		?	?		-1	
Death of ZOO						-1	1

$\rightarrow$ how many unknowns?

Additional substances for calculation of the stoichiometric coefficients:
HCO_3^-, H^+, H_2O

Chemical Substance Notation

ETH zürich
eawag aquatic research

Zooplankton Growth:

8 unknown stoichiometric coefficients

6 mass balance equations

2 additional constraints required:

Fraction of zooplankton biomass produced per algal biomass consumed (yield): Y_{ZOO}

Fraction of dead particles produced (excretion + sloppy feeding) per algal biomass consumed: f_{e}

The fraction of algal biomass respired is then: $f_{\mathrm{r}} = 1 - Y_{\mathrm{ZOO}} - f_{\mathrm{e}}$

Chemical Substance Notation

Process	Substances / Organisms						
	NH_4^+ mol	NO_3^- mol	HPO_4^{2-} mol	O_2 mol	ALG gDM	ZOO gDM	POM gDM
Gro. ALG,NH4	$-\frac{16}{3550}$		$-\frac{1}{3550}$	$\frac{106}{3550}$	1		
Gro. ALG,NO3		$-\frac{16}{3550}$	$-\frac{1}{3550}$	$\frac{138}{3550}$	1		
Resp. ALG	$\frac{16}{3550}$		$\frac{1}{3550}$	$-\frac{106}{3550}$	-1		
Death ALG					-1		1
Growth ZOO	$\frac{f_r}{Y_{ZOO}} \frac{16}{3550}$		$\frac{f_r}{Y_{ZOO}} \frac{1}{3550}$	$-\frac{f_r}{Y_{ZOO}} \frac{106}{3550}$	$-\frac{1}{Y_{ZOO}}$	1	$\frac{f_e}{Y_{ZOO}}$
Resp. ZOO	$\frac{16}{3550}$		$\frac{1}{3550}$	$-\frac{106}{3550}$		-1	
Death ZOO						-1	1

Stoichiometry

Chemical Substance Notation:

Quite some handwork!

If composition changes: redo the calculation!

→ instead of fixed composition use parameters for elemental mass fractions

Stoichiometry

3 ways to derive stoichiometric coefficients:

- Chemical substance notation
- Parameterized elemental mass fractions
- General solution

Extended Process Table Notation

Processes i	Substances j					Rates
	s_1	s_2	s_3	$\cdots$	s_{n_s}	
p_1	ν_{11}	ν_{12}	ν_{13}	$\cdots$	ν_{1n_s}	ρ_1
p_2	ν_{21}	ν_{22}	ν_{23}	$\cdots$	ν_{2n_s}	ρ_2
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
p_{n_p}	ν_{n_p1}	ν_{n_p2}	ν_{n_p3}	$\cdots$	$\nu_{n_pn_s}$	ρ_{n_p}
Elements k						
e_1	α_{11}	α_{12}	α_{13}	$\cdots$	α_{1n_s}	
e_2	α_{21}	α_{22}	α_{23}	$\cdots$	α_{2n_s}	
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	
e_{n_e}	α_{n_e1}	α_{n_e2}	α_{n_e3}	$\cdots$	$\alpha_{n_en_s}$	

ν_{ij}: stoich. coeff. $=$ relative transf. rate of substance j in proc. i

α_{kj}: mass fraction of element k on substance j

$\nu_{ij}\alpha_{kj}$: relative transf. rate of element k contained in subst. j

Extended Process Table Notation

ETH zürich
eawag
aquatic research

Processes i	Substances j					Rates
	s_1	s_2	s_3	$\cdots$	s_{n_s}	
p_1	ν_{11}	ν_{12}	ν_{13}	$\cdots$	ν_{1n_s}	ρ_1
p_2	ν_{21}	ν_{22}	ν_{23}	$\cdots$	ν_{2n_s}	ρ_2
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
p_{n_p}	ν_{n_p1}	ν_{n_p2}	ν_{n_p3}	$\cdots$	$\nu_{n_pn_s}$	ρ_{n_p}
Elements k						
e_1	α_{11}	α_{12}	α_{13}	$\cdots$	α_{1n_s}	
e_2	α_{21}	α_{22}	α_{23}	$\cdots$	α_{2n_s}	
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	
e_{n_e}	α_{n_e1}	α_{n_e2}	α_{n_e3}	$\cdots$	$\alpha_{n_en_s}$	

Mass conservation for element k in process i: $\boxed{\sum_j \nu_{ij}\alpha_{kj} = 0}$

Example

Model 1: Growth and respiration of algae.

			Substances / Organisms j		
			NH_4^+	HPO_4^{2-}	ALG
			gN	gP	gDM
Processes i	Growth of ALG		?	?	1
	Respiration of ALG		?	?	-1
Elements k	N	gN	1	0	α_{NALG}
	P	gP	0	1	α_{PALG}

$$\sum_j \nu_{ij}\alpha_{kj} = 0$$

Parameterized Mass Fractions

Example

Growth of algae:

N conservation:

$$\underbrace{\nu_{\text{groALG NH4}} \cdot 1}_{\text{NH}_4^+} + \underbrace{\nu_{\text{groALG HPO4}} \cdot 0}_{\text{HPO}_4^{2-}} + \underbrace{1 \cdot \alpha_{\text{N,ALG}}}_{\text{ALG}} = 0$$

P conservation:

$$\underbrace{\nu_{\text{groALG NH4}} \cdot 0}_{\text{NH}_4^+} + \underbrace{\nu_{\text{groALG HPO4}} \cdot 1}_{\text{HPO}_4^{2-}} + \underbrace{1 \cdot \alpha_{\text{P,ALG}}}_{\text{ALG}} = 0$$

$$\rightarrow \nu_{\text{groALG NH4}} = -\alpha_{\text{N,ALG}}\,,\quad \nu_{\text{groALG HPO4}} = -\alpha_{\text{P,ALG}}$$

$$\boxed{\sum_j \nu_{ij}\alpha_{kj} = 0}$$

Parameterized Mass Fractions

Example

Model 1: Growth and respiration of algae.

Process		Substances / Organisms		
		NH_4^+	HPO_4^{2-}	ALG
Element		gN	gP	gDM
Growth of ALG		$-\alpha_{\mathrm{N,ALG}}$	$-\alpha_{\mathrm{P,ALG}}$	1
Respiration of ALG		$\alpha_{\mathrm{N,ALG}}$	$\alpha_{\mathrm{P,ALG}}$	-1
N	gN	1	0	α_{NALG}
P	gP	0	1	α_{PALG}

Parameterized Mass Fractions

Process	Substances / Organisms						
	NH_4^+ mol	NO_3^- mol	HPO_4^{2-} mol	O_2 mol	ALG gDM	ZOO gDM	POM gDM
Growth of ALG,NH4	?		?	?	1		
Growth of ALG,NO3		?	?	?	1		
Respiration of ALG	?		?	?	-1		
Death of ALG					-1		1
Growth of ZOO	?		?	?	?	1	?
Respiration of ZOO	?		?	?		-1	
Death of ZOO						-1	1

Additional substances for calculation of the stoichiometric coefficients:
HCO_3^-, H^+, H_2O

Mass balance equations for C,H,O,N,P and charge

Parameterized Mass Fractions

Instead of assuming a fixed chemical composition (e.g. Redfield:)

$$C_{106}H_{263}O_{110}N_{16}P$$

use parameterized mass fractions:

$$C_{\alpha_{C,j}/12}H_{\alpha_{H,j}}O_{\alpha_{O,j}/16}N_{\alpha_{N,j}/14}P_{\alpha_{P,j}/31}$$

with:

$$\alpha_{C,j} + \alpha_{H,j} + \alpha_{O,j} + \alpha_{N,j} + \alpha_{P,j} = 1$$

Parameterized Mass Fractions

ETH zürich
eawag aquatic research

$m[\mathrm{g}] = n[\mathrm{mol}] * M[\mathrm{g/mol}]$

Redfield composition:

$$\alpha_{\mathrm{C,ALG}}^{\mathrm{Redfield}} = \frac{106 \cdot 12}{3550} \frac{\mathrm{gC}}{\mathrm{gDM}} \approx 0.36 \frac{\mathrm{gC}}{\mathrm{gDM}}$$

$$\alpha_{\mathrm{H,ALG}}^{\mathrm{Redfield}} = \frac{263}{3550} \frac{\mathrm{gH}}{\mathrm{gDM}} \approx 0.07 \frac{\mathrm{gH}}{\mathrm{gDM}}$$

$$\alpha_{\mathrm{O,ALG}}^{\mathrm{Redfield}} = \frac{110 \cdot 16}{3550} \frac{\mathrm{gO}}{\mathrm{gDM}} \approx 0.50 \frac{\mathrm{gO}}{\mathrm{gDM}}$$

$$\alpha_{\mathrm{N,ALG}}^{\mathrm{Redfield}} = \frac{16 \cdot 14}{3550} \frac{\mathrm{gN}}{\mathrm{gDM}} \approx 0.06 \frac{\mathrm{gN}}{\mathrm{gDM}}$$

$$\alpha_{\mathrm{P,ALG}}^{\mathrm{Redfield}} = \frac{1 \cdot 31}{3550} \frac{\mathrm{gP}}{\mathrm{gDM}} \approx 0.01 \frac{\mathrm{gP}}{\mathrm{gDM}}$$

Parameterized Mass Fractions

$$a\,\mathrm{HCO_3^-} + b\,\mathrm{NO_3^-} + c\,\mathrm{HPO_4^{2-}} + d\,\mathrm{H^+} + e\,\mathrm{H_2O}$$
$$\rightarrow \mathrm{C_{106}H_{263}O_{110}N_{16}P} + f\,\mathrm{O_2}$$

Setting up equation for algal growth with unknown coefficients:

$$a\,\mathrm{HCO_3^-} + b\,\mathrm{NO_3^-} + c\,\mathrm{HPO_4^{2-}} + d\,\mathrm{H^+} + e\,\mathrm{H_2O}$$
$$\rightarrow \mathrm{C}_{\alpha_{\mathrm{C,ALG}}/12}\mathrm{H}_{\alpha_{\mathrm{H,ALG}}}\mathrm{O}_{\alpha_{\mathrm{O,ALG}}/16}\mathrm{N}_{\alpha_{\mathrm{N,ALG}}/14}\mathrm{P}_{\alpha_{\mathrm{P,ALG}}/31} + f\,\mathrm{O_2}$$

Conservation of C: $a = \frac{\alpha_{\mathrm{C,ALG}}}{12}$

Conservation of N: $b = \frac{\alpha_{\mathrm{N,ALG}}}{14}$

Conservation of P: $c = \frac{\alpha_{\mathrm{P,ALG}}}{31}$

Parameterized Mass Fractions

$$\frac{\alpha_{C,ALG}}{12} HCO_3^- + \frac{\alpha_{N,ALG}}{14} NO_3^- + \frac{\alpha_{P,ALG}}{31} HPO_4^{2-} + d\,H^+ + e\,H_2O$$

$$\rightarrow C_{\alpha_{C,ALG}/12} H_{\alpha_{H,ALG}} O_{\alpha_{O,ALG}/16} N_{\alpha_{N,ALG}/14} P_{\alpha_{P,ALG}/31} + f\,O_2$$

Conservation of H, O and charge:

H: $\frac{\alpha_{C,ALG}}{12} \cdot 1 + \frac{\alpha_{P,ALG}}{31} \cdot 1 + d \cdot 1 + e \cdot 2 = 1 \cdot \alpha_{H,ALG}$

O: $\frac{\alpha_{C,ALG}}{12} \cdot 3 + \frac{\alpha_{N,ALG}}{14} \cdot 3 + \frac{\alpha_{P,ALG}}{31} \cdot 4 + e \cdot 1 = 1 \cdot \frac{\alpha_{O,ALG}}{16} + f \cdot 2$

charge: $\frac{\alpha_{C,ALG}}{12} \cdot (-1) + \frac{\alpha_{N,ALG}}{14} \cdot (-1) + \frac{\alpha_{P,ALG}}{31} \cdot (-2) + d \cdot (+1) = 0$

Parameterized Mass Fractions

$$d = \frac{\alpha_{\mathrm{C,ALG}}}{12} + \frac{\alpha_{\mathrm{N,ALG}}}{14} + \frac{2\;\alpha_{\mathrm{P,ALG}}}{31}$$

$$e = \frac{\alpha_{\mathrm{H,ALG}}}{2} - \frac{\alpha_{\mathrm{C,ALG}}}{12} - \frac{\alpha_{\mathrm{N,ALG}}}{28} - \frac{3\;\alpha_{\mathrm{P,ALG}}}{62}$$

$$f = \frac{\alpha_{\mathrm{C,ALG}}}{12} + \frac{\alpha_{\mathrm{H,ALG}}}{4} - \frac{\alpha_{\mathrm{O,ALG}}}{32} + \frac{5\;\alpha_{\mathrm{N,ALG}}}{56} + \frac{5\;\alpha_{\mathrm{P,ALG}}}{124}$$

Parameterized Mass Fractions

ETH zürich
eawag aquatic research

Growth of algae:

$$\frac{\alpha_{C,ALG}}{12}\,HCO_3^- + \frac{\alpha_{N,ALG}}{14}\,NO_3^- + \frac{\alpha_{P,ALG}}{31}\,HPO_4^{2-}$$

$$+\left(\frac{\alpha_{C,ALG}}{12} + \frac{\alpha_{N,ALG}}{14} + \frac{2\,\alpha_{P,ALG}}{31}\right) H^+$$

$$+\left(\frac{\alpha_{H,ALG}}{2} - \frac{\alpha_{C,ALG}}{12} - \frac{\alpha_{N,ALG}}{28} - \frac{3\,\alpha_{P,ALG}}{62}\right) H_2O$$

$$\rightarrow C_{\alpha_{C,ALG}/12} H_{\alpha_{H,ALG}} O_{\alpha_{O,ALG}/16} N_{\alpha_{N,ALG}/14} P_{\alpha_{P,ALG}/31}$$

$$+\left(\frac{\alpha_{C,ALG}}{12} + \frac{\alpha_{H,ALG}}{4} - \frac{\alpha_{O,ALG}}{32} + \frac{5\,\alpha_{N,ALG}}{56} + \frac{5\,\alpha_{P,ALG}}{124}\right) O_2$$

Parameterized Mass Fractions

Pen and paper exercise task 2

Derive the stoichiometry of the process
“growth of algae with ammonium as the nitrogen source”
assuming an arbitrary composition of algal biomass considering the mass fractions α_C, α_H, α_O, α_N, and α_P of the elements C, H, O, N and P.

$$a\,HCO_3^- + b\,NH_4^+ + c\,HPO_4^{2-} + d\,H^+ + e\,H_2O \rightarrow C_{\alpha_{C,ALG}/12}H_{\alpha_{H,ALG}}O_{\alpha_{O,ALG}/16}N_{\alpha_{N,ALG}/14}P_{\alpha_{P,ALG}/31} + f\,O_2$$

Parameterized Mass Fractions:

Changes in composition are now easy to handle,
just change the numerical values of the parameters.

What about adding additional elements?

The equations must be revised.

This is a laborious process.

Is there a general solution to this process?

Structure of the Course

1. Introduction, principles of modelling environmental systems, mass balance in a mixed reactor, process table notation, simple lake plankton model
   Exercise: R, `ecosim`-package, simple lake plankton model
   Exercise: lake phytoplankton-zooplankton model
2. Process stoichiometry Exercises: analytical solution, calculation with `stoichcalc`
3. Biological processes in lakes
4. Physical processes in lakes, mass balance in multi-box and continuous systems Exercise: structured, biogeochemical-ecological lake model
   Assignments: build your own model by implementing model extensions
5. Physical processes in in rivers, bacterial growth, river model for benthic populations Exercise: river model for benthic populations, nutrients and oxygen
6. Uncertainty, Parameter estimation, Stochasticity
   Exercise: parameter estimation
   Exercise: stochasticity, uncertainty
7. Existing models and applications in research and practice, examples and case studies, preparation of the oral exam, feedback

→ Swiss Army Knife of Linear Algebra

Preparation for next week

ETH zürich eawag aquatic research

1. Find out what the Swiss Army Knife of Linear Algebra is and how it roughly works

2. Read chapter 4.3.3 (general solution)

3. Read chapter 15 (`Stoichcalc` package)

4. Think about your open questions

5. Bonus: Try out the chocolate cake recipe or

bring your own favorite cake recipe in the form of a process table.