

Contents

4 A data assimilating state-space model for algal growth under controlled conditions within a photobioreactor	2
4.1 Introduction	2
4.2 Methods	2
4.2.1 Data Model: Data description and collection methods	2
4.2.2 Process model: Carbon chemistry	2
4.2.3 Process model: Gas transfer equilibrium concentrations for O ₂ and CO ₂	3
4.2.4 Process model: Photosynthesis and respiration	5
4.2.5 Process model: Ordinary differential equations	6
4.2.6 Parameter Model: Priors	9
4.3 Results	10
4.3.1 Carbon chemistry iterative solution	10
4.3.2 Posteriors	15
A LiBbi model code	19
Bibliography	29

Chapter 4

A data assimilating state-space model for algal growth under controlled conditions within a photobioreactor

4.1 Introduction

Microalgae are tiny organisms..

4.2 Methods

4.2.1 Data Model: Data description and collection methods

O₂, pH, DIC and alk observations collected over 4 days.

Gas, temperature, light and dilution rate were used as forcings.

4.2.2 Process model: Carbon chemistry

To calculate the carbon chemistry of the photo-bioreactor, we would ideally use CO2SYS [4] to calculate HCO_3^- , CO₂, CO₃ and pH. CO2SYS is a program developed for CO₂ system calculations (CO2SYS) that calculates and returns a detailed state of the carbonate system of oceanographic water samples in seawater and freshwater [4]. It uses two of the four measurable carbonate system parameters (total alkalinity, total inorganic CO₂, pH, and either fugacity fCO₂ or partial pressure of CO₂) to calculate the other two parameters at a set of input conditions (temperature and pressure).

To incorporate CO2SYS into LiBbi for solving carbon chemistry on the timescale of the microalgae model, we explicitly define 2 iterations of the Newton-Raphson

method for finding approximations to roots of real valued functions. The Newton-Raphson method is an iterative process considering a function, its derivative and an initial starting value. Vital to the convergence of the Newton-Raphson method is a good starting value. To provide a good starting value, we randomly sample from a range of CO2SYS input parameters (temperature = 20-30, salinity = 30-40, DIC = 200-2500, and alkalinity = 1500-3000) and fit an approximating equation to pH as a function of DIC, S and T (alk?). This gives us a close initial starting value for the Newton-Raphson method.

Converges in 2-3 iterations

Choice of H₂CO₃ and HCO₃⁻ dissociation constants K₁ and K₂ was Mehrbach (refit BY DICKSON AND MILLERO) [BM: After the iterative approach is finalised, the K₁ and K₂ constants are adjusted based on measurements taken during the experiment, K₁*1.23 and K₂*0.53 measured during experiment] temperature: 2-35, salinity: 20-40, Seawater scale, Artificial seawater.

The CO2SYS Matlab version [6] was used to produce values of CO₂ and HCO₃⁻ across DIC range 200-2500. Approximating equations were fit

Total inorganic CO₂ (TCO₂) is the sum of the dissolved CO₂, the carbonate (CO₃²⁻), and the bicarbonate (HCO₃⁻).

4.2.3 Process model: Gas transfer equilibrium concentrations for O₂ and CO₂

The equilibrium concentration for CO₂ solubility in water CO_{2H} (μmol/L) is calculated using Henry's law,

$$CO_{2H} = K_{CO_2} * fCO_2 * 1.0220 * 1e6 \quad (4.1)$$

where fCO₂ (atm) is the fugacity or approximately the partial pressure of CO₂, 1.0220 is the density of seawater (kg/L) at salinity 34 ppt and temperature 27°C

[5] [2]. K_{CO_2} (mol/kg_{soln}/atm) is the solubility of gas in seawater [BM: ask Chris: solubility of gas? is this right] and is calculated from the fitted van't Hoff equation and the logarithmic Setchenow salinity dependence [7],

$$K_{CO_2} = \exp(-60.2409 + 93.4517(100/T_K) + 23.3585 * \ln(T_K/100) + S(0.023517 - 0.023656(T_K/100) + 0.0047036(T_K/100)^2)) \quad (4.2)$$

where T_K is the temperature (K) and S is salinity (ppt).

Similarly the equilibrium concentration for O_2 solubility in water O_{2H} is calculated using Henry's law,

$$O_{2H} = K_{O_2} * f_{O_2} * 1.0220 * 1e - 6 \quad (4.3)$$

where f_{O_2} (atm) is the fugacity or approximately the partial pressure of O_2 , 1.0220 is the density of seawater (kg/L) at salinity 34 ppt and temperature 27°C [5] [2], and K_{O_2} (mol/kg_{soln}/atm) is the solubility of oxygen in seawater with an adjusted salinity dependence [1],

$$K_{O_2} = (\exp(-1282.8704 + 36619.96/T_K + 223.1396 * \log(T_K) - 0.354707 * T_K + S * (5.957e - 3 - 3.7353/T_K) + 3.68e - 6 * S^2))/0.2094e - 6 \quad (4.4)$$

where T_K is the temperature (K) and S is salinity (ppt).

The equilibrium concentrations for O_2 and CO_2 are modelled together with the gas turning on and off during the experiment, as

$$kLA_{O_2}\xi(O_{2H} - O_2) \quad (4.5)$$

$$0.893kLA_{O_2}\xi(CO_{2H} - CO_2) \quad (4.6)$$

where ξ is the gas state (1= on, 0= off), and kLA_{O_2} is the mass transfer coefficient for air (d⁻¹), and 0.893 is the ratio between measured O_2 and CO_2 mass transfer constants [3].

4.2.4 Process model: Photosynthesis and respiration

Net photosynthesis

$$dDIC/dt = -P_1 * I * mm + R_1 \quad (4.7)$$

$$dO_2/dt = \frac{P_1 * I * mm - R_1}{R_Q} \quad (4.8)$$

Photosynthesis (P_1) and respiration (R_1) are both modelled as random walks, by taking P and R , previously constant parameters, and replacing them by $P_1(t)$ and $R_1(t)$. Here, we take $P_1(t)$ and $R_1(t)$ to be such that

$$P_1(t + \Delta t) = P_1(t) + r_P$$

$$R_1(t + \Delta t) = R_1(t) + r_R$$

where $r_P \sim N(0, \sigma_{r_P})$, $r_R \sim N(0, \sigma_{r_R})$, and Δt is the length of discrete time-step. For the purpose of the Bayesian analysis here, σ_{r_P} and σ_{r_R} are treated as a parameter to be inferred.

R_Q is the respiratory quotient, the ratio of CO_2 produced and O_2 consumed by a cell.

PAC is Photosynthetically Active Carbon, this is the type of carbon that the microalgae use for photosynthesis. This can be CO_2 , HCO_3^- , or a combination of both, eg $PAC = CO_2 + HCO_3^-$ if the microalgae are using both carbon dioxide and bicarbonate for photosynthesis.

$$PAC = HCO_3^- \quad (4.9)$$

$$mm = \frac{PAC}{K_m + PAC} \quad (4.10)$$

4.2.5 Process model: Ordinary differential equations

Ode's:

$$\begin{aligned} \frac{\partial DIC}{\partial t} = & \quad \text{Rate} \quad \text{flux into cells} \quad \text{gas transfer} \quad \text{dilution} \\ & -(P - R) + \hat{Q}^{air} kLa_{CO_2}^{air} (CO_2^{air} - CO_2) + \frac{Q^M}{V} (DIC^M - DIC) \\ & + \hat{Q}^{co2} kLa_{CO_2}^{co2} (CO_2^{co2} - CO_2) \end{aligned} \quad (4.11)$$

$$\begin{aligned} \frac{\partial O_2}{\partial t} = & \frac{1}{R_Q} (P - R) + \hat{Q}^{air} kLa_{O_2}^{air} (O_2^{air} - O_2) + \frac{Q^M}{V} (O_2^M - O_2) \\ & + \hat{Q}^{co2} kLa_{O_2}^{co2} (O_2^{co2} - O_2) \end{aligned} \quad (4.12)$$

$$\begin{aligned} \frac{\partial TA}{\partial t} = & R_R (P - R) + \frac{Q^M}{V} (TA^M - TA) \end{aligned} \quad (4.13)$$

	Symbol	Description	Prior / Value	Unit
State variable initial conditions	DIC^0	Dissolved inorganic carbon		$\mu\text{M/L}$
	O_2^0	Oxygen		$\mu\text{M/L}$
	TA^0	Total alkalinity		$\mu\text{M/L}$
	P^0	Rate of photosynthesis		$\mu\text{M/L/day}$
	R^0	Rate of respiration		$\mu\text{M/L/day}$
	pH^0	-		$\log_{10}(-\text{mol/L H}^+)$
	CO_2^0	Carbon dioxide		$\mu\text{M/L}$
	HCO_3^{-0}	Bicarbonate		$\mu\text{M/L}$
	CO_3^{2-0}	Carbonate		$\mu\text{M/L}$
Gas transfer terms	\hat{Q}^{air}	indicator for flow in air line	0 or 1	-
	$x_{CO_2}^{air}$	mole fraction of CO_2 atmosphere	400	ppm
	CO_{2H}	Equilibrium CO_2 concentration	Eq. 4.1	$\mu\text{M/L}$
	CO_2^{air}	sat CO_2 conc with atmosphere	$x_{CO_2}^{air} CO_{2H}$	
	$kLa_{CO_2}^{air}$	Mass transfer coefficient for CO_2	$0.893 kLa_{O_2}^{air}$	day^{-1}
	$x_{O_2}^{air}$	mole fraction of O_2 atmosphere	0.2094	atm

	O_{2H}	Equilibrium O ₂ concentration	Eq. 4.3	$\mu\text{M/L}$
	O_2^{air}	sat O ₂ conc with atmosphere	$x_{O_2}^{air} O_{2H}$	
	τ	half-life of $kLa^{air}_{O_2}$	range(2-20)	min^{-1}
	$kLa^{air}_{O_2}$	Mass transfer coefficient for O ₂	$\ln(2) * 24 * 60 / \tau$	day^{-1}
Dilution terms	Q^M	rate		ml/day
	V	Volume of the reactor	500	ml
	DIC^M	Media dissolved inorganic carbon	1724.20	$\mu\text{M/L}$
	O_2^M	Media oxygen concentration	226.65	$\mu\text{M/L}$
	TA^M	Media total alkalinity	1797.90	$\mu\text{M/L}$
Other dilution terms	\hat{Q}^{CO_2}	indicator for dilution	0 or 1	-
	$x_{O_2}^{CO_2}$	mole fraction of	0	-
	$O_2^{CO_2}$	sat CO ₂ conc with CO ₂	$x_{O_2}^{CO_2} O_{2H}$	
	$kLa_{O_2}^{CO_2}$	mass transfer coefficient		day^{-1}
	$O_2^{CO_2}$			
	$x_{CO_2}^{CO_2}$	mole fraction of	1	ppm
	$CO_2^{CO_2}$	sat CO ₂ conc with CO ₂	$x_{CO_2}^{CO_2} CO_{2H}$	
	$kLa_{CO_2}^{CO_2}$	mass transfer coefficient	$0.893 kLa_{O_2}^{CO_2}$	day^{-1}
	$CO_2^{CO_2}$			

Symbol	Variable	Units
DIC	Dissolved inorganic carbon concentration	$\mu\text{mol/L}$
O ₂	Oxygen	$\mu\text{mol/L}$
pH	-	$\log_{10}(-\text{mol/L H}^+)$
CO ₂	Carbon dioxide	$\mu\text{mol/L}$
HCO ₃ ⁻	Bicarbonate	$\mu\text{mol/L}$
CO ₃ ²⁻	Carbonate	$\mu\text{mol/L}$
PAC	Photosynthetically active carbon	$\mu\text{mols/L}$
mm	-	-
kLA _{O2}	Mass transfer coefficient for O ₂	d ⁻¹
CO _{2H}	Equilibrium CO ₂ concentration	$\mu\text{mols/L}$
K _{O2}	Solubility of gas	mol/kg _{soln} /atm
K _{CO2}	Solubility of gas	mol/kg _{soln} /atm
TA	Total alkalinity	$\mu\text{mols/L}$
S	Salinity	ppt
fCO2	Fugacity/CO ₂ partial pressure	atm
fO2	Fugacity/O ₂ partial pressure	atm
K _m	Carbon restriction	$\mu\text{mols/L}$
P	Photosynthesis rate	$\mu\text{mols/L/day}$
R	Respiration rate	$\mu\text{mols/L/day}$
R _R	Redfield ratio	-
R _Q	Respiratory quotient	-

Table 4.2 : Table of variables and parameters.

Symbol	Variable	Units
I	Light Intensity	normalised to 0-1
T	Temperature	◦ C
T_K	Temperature	K
ξ	gasflow	on/off (1,0)

Table 4.3 : Table of Forcings

4.2.6 Parameter Model: Priors

Decide whether the parameters vary in time or not.

Parameter	Prior	Proposal
S	34	*
fCO2	397e-6	*
fO2	0.21	*
kLA_{O_2}	$\text{LogNormal}(\log(200.0), 0.5)$	$\text{LogNormal}(\log(kLA_{O_2}), 0.5\text{prop}_{std})$
K_m	$\text{LogNormal}(\log(200.0), 0.8)$	$\text{LogNormal}(\log(K_m), 0.8\text{prop}_{std})$
R_R	$\text{Uniform}(0.0001, 0.2)$	$\text{TrunNormal}(R_R, 0.2\text{prop}_{std}, 0.0001, 0.2)$
R_Q	$\text{Uniform}(0.66, 1)$	$\text{TrunNormal}(R_Q, 0.2\text{prop}_{std}, 0.66, 1.0)$
σ_P	$\text{Normal}(0.05, 0.01)$	$\text{Normal}(\sigma_P, 0.01\text{prop}_{std})$
σ_R	$\text{Normal}(0.01, 0.001)$	$\text{Normal}(\sigma_R, 0.001\text{prop}_{std})$

Table 4.4 : Table of Parameters, their priors and proposal distributions. * indicates the parameter was held fixed. ($\text{prop}_{std}=0.1$)

4.3 Results

4.3.1 Carbon chemistry iterative solution

Total Sulfur

$$\begin{aligned}
 TS &= \frac{0.14}{96.062} * \frac{S}{1.8065} \\
 IS &= 19.924 * \frac{S}{(1000.0 - 1.005 * S)} \\
 KS_{int} &= -\frac{4276.1}{T_K} + 141.328 - 23.093 * \log(T_K) + \left(-\frac{13856.0}{T_K} + 324.57 \right. \\
 &\quad \left. - 47.986 * \log(T_K)\right) * \sqrt{IS} + \left(\frac{35474}{T_K} - 771.54 + 114.723 * \log(T_K)\right) * IS \\
 &\quad - \frac{2698}{T_K} * IS^{1.5} + \frac{1776}{T_K} * IS^2 \\
 KS &= \exp(KS_{int}) * (1 - 0.001005 * S)
 \end{aligned}$$

Fluorine

$$\begin{aligned}
 TF &= 0.000067 * S / 18.9984 / 1.80655 \\
 KF &= \exp\left(-\left(-\frac{874.0}{T_K} - 0.111 * \sqrt{S} + 9.68\right)\right) \\
 SWS_{2T} &= \frac{\left(1 + \frac{TS}{KS}\right)}{\left(1 + \frac{TS}{KS} + \frac{TF}{KF}\right)} \\
 Free_{2T} &= 1 + \frac{TS}{KS}
 \end{aligned}$$

H2O dissoc

$$KW = \exp(148.9802 - \frac{13847.26}{T_K} - 23.6521 * \log(T_K) + (\frac{118.67}{T_K} - 5.977 + 1.0495 * \log(T_K)) * \sqrt{S} - 0.01615 * S)$$

Boron

$$KB = \exp((-8966.90 - 2890.53 * \sqrt{S} - 77.942 * S + 1.728 * S * \sqrt{S} - 0.0996 * S^2)/T_K + 148.0248 + 137.1942 * \sqrt{S} + 1.62142 * S - (24.4344 + 25.085 * \sqrt{S} + 0.2474 * S) * \log(T_K) + 0.053105 * \sqrt{S} * T_K)$$

$$TB = 0.0004326 * \frac{S}{35}$$

Carbon eq constants

$$K1 = 10^{(-(\frac{3633.86}{T_K} - 61.2172 + 9.6777 * \log(T_K) - 0.011555 * S + 0.0001152 * S^2))} * 1.23$$

$$K2 = 10^{(-(\frac{471.8}{T_K} + 25.9290 - 3.16967 * \log(T_K) - 0.01781 * S + 0.0001122 * S^2))} * 0.53$$

1.23 and 0.53 were experiment specific and measured

Initial guess at the pH

$$pH_{init} = 12.26 - 0.0030605 * DIC - 0.043752 * T - 0.013625 * S + 0.00011315 * TA + 1.3463e - 5 * DIC * T + 5.2215e - 7 * DIC * TA$$

Iterations

$$\begin{aligned}
h &= 10^{-pH_{init}} \\
h_{free} &= \frac{h}{Free_{2T}} \\
f0 &= (DIC * 1e - 6 * \frac{K1 * h + 2 * K1 * K2}{h * h + K1 * h + K1 * K2} \\
&\quad - h_{free} + \frac{KW}{h} - Alk * 1e - 6 + \frac{TB}{1 + \frac{h}{KB}}) * 1e6 \\
df0 &= (DIC * 1e - 6 * \frac{K1 + 2 * K1 * K2}{h^2 + K1 * h + K1 * K2} \\
&\quad - DIC * 1e - 6 * \frac{(K1 * h + 2 * K1 * K2)}{(h^2 + K1 * h + K1 * K2)^2} * (2 * h + K1) \\
&\quad - TB * \frac{1}{(1 + \frac{h}{KB})^2} / KB \\
&\quad - \frac{KW}{h^2} - \frac{1}{Free_{2T}}) * 1e6 * (-\log(10) * 10^{-pH}) \\
pH &= pH - \frac{f0}{df0} \\
H &= 10^{-pH} \\
denom &= H^2 + K1 * H + K1 * K2 \\
CO2 &= \frac{DIC * H^2}{denom} \\
HCO3 &= \frac{DIC * H * K1}{denom} \\
CO3 &= \frac{DIC * K1 * K2}{denom}
\end{aligned}$$

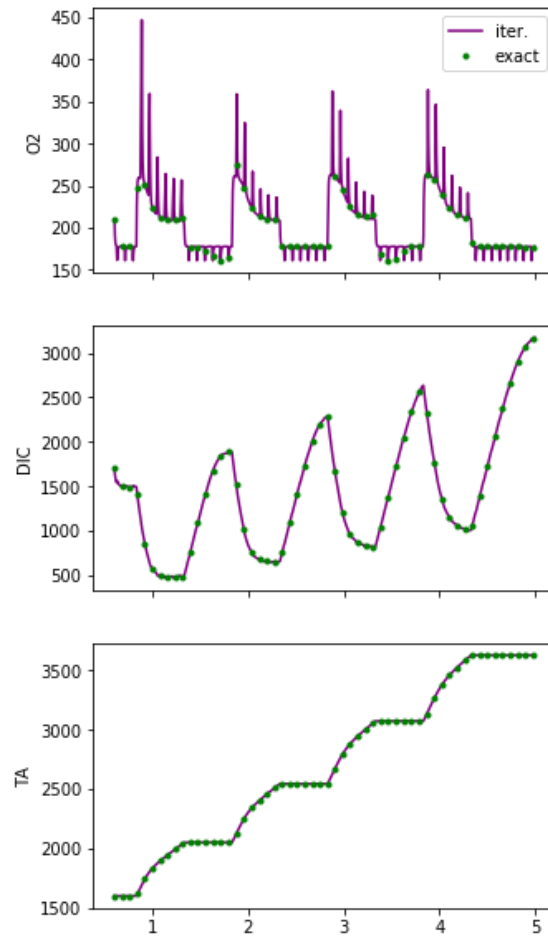


Figure 4.1 : Iterative vs exact solution for state variables O_2 , DIC , and TA .

Variable	Iter. 1	Iter. 2	Iter. 3	Iter. 4	Iter. 5
O_2	0.308389964	0.016044284	4.18E-05	6.89E-05	7.59E-05
DIC	16.78775711	0.958511825	0.005229318	0.002305054	0.002333411
TA	2.607767674	0.160897272	0.000688102	0.001257725	0.001218981
pH	0.036092734	0.002355758	1.41E-05	6.93E-06	6.93E-06
CO_2	2.109401968	0.145719349	0.001222812	0.000866728	0.000866727
HCO_3	19.81869214	1.21021115	0.008016765	0.001025002	0.001025139
CO_3	20.89660704	1.307061652	0.00867642	0.001102278	0.001102434

Table 4.5 : RMSE for 5 iterations of the Newton-raphson carbon chemistry iterative solution.

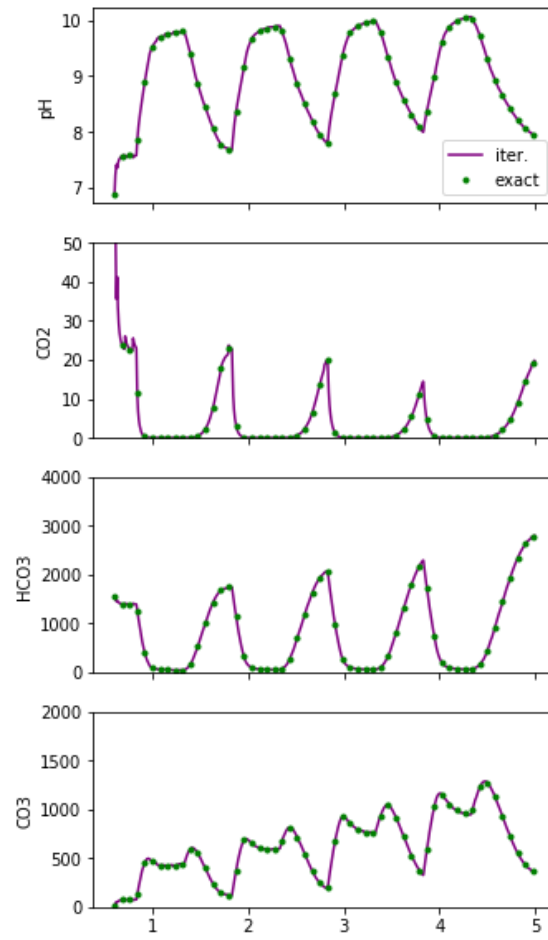


Figure 4.2 : Iterative vs exact solution for carbon chemistry CO_2 , HCO_3 , CO_3 , and pH .

4.3.2 Posteriors

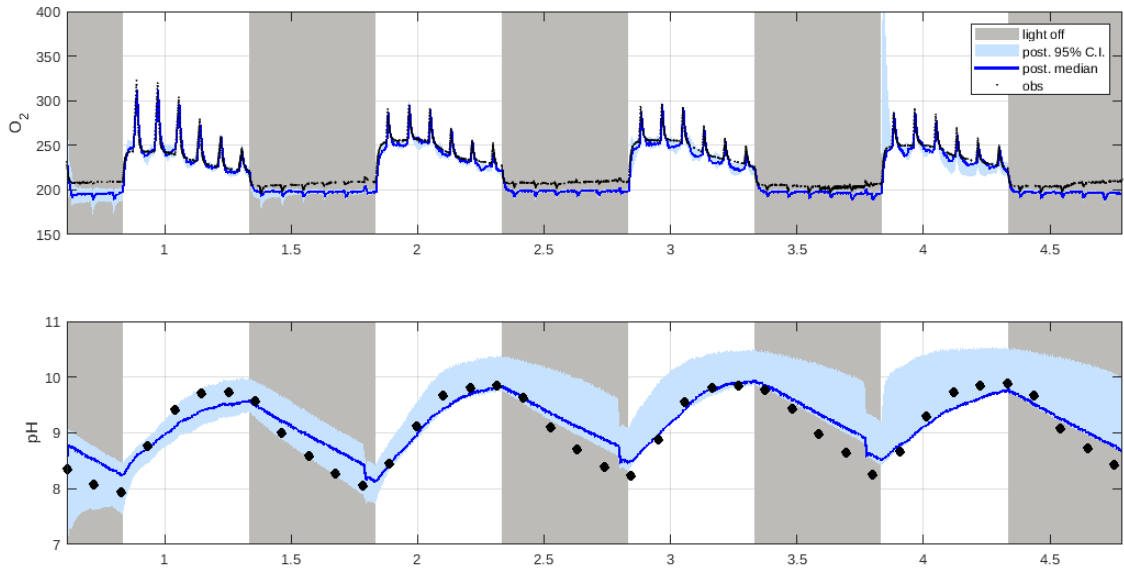


Figure 4.3 : Posteriors for O_2 and pH .

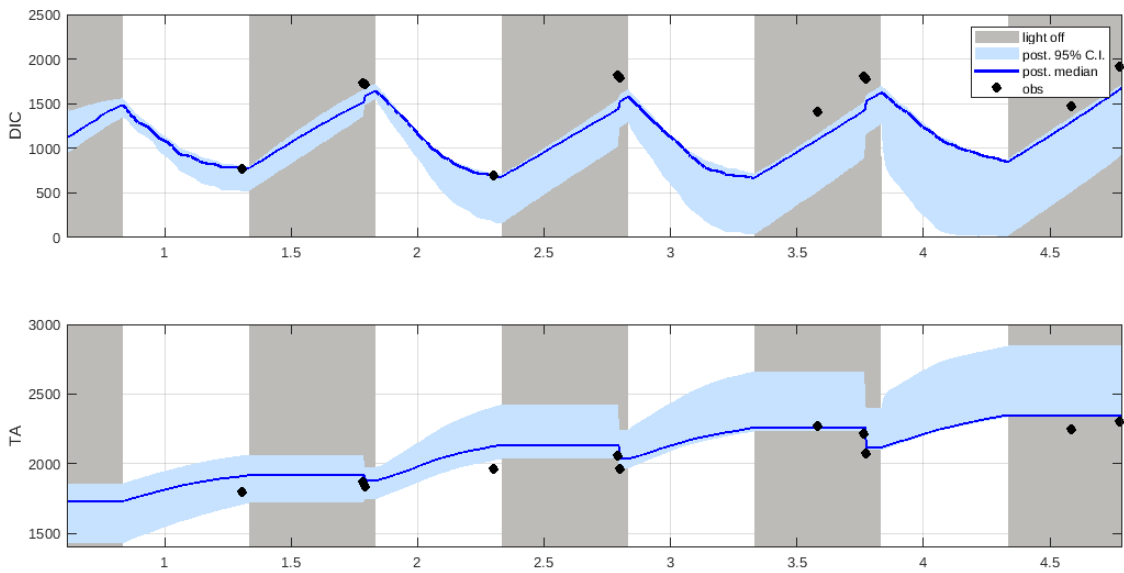


Figure 4.4 : Posteriors for DIC and TA .

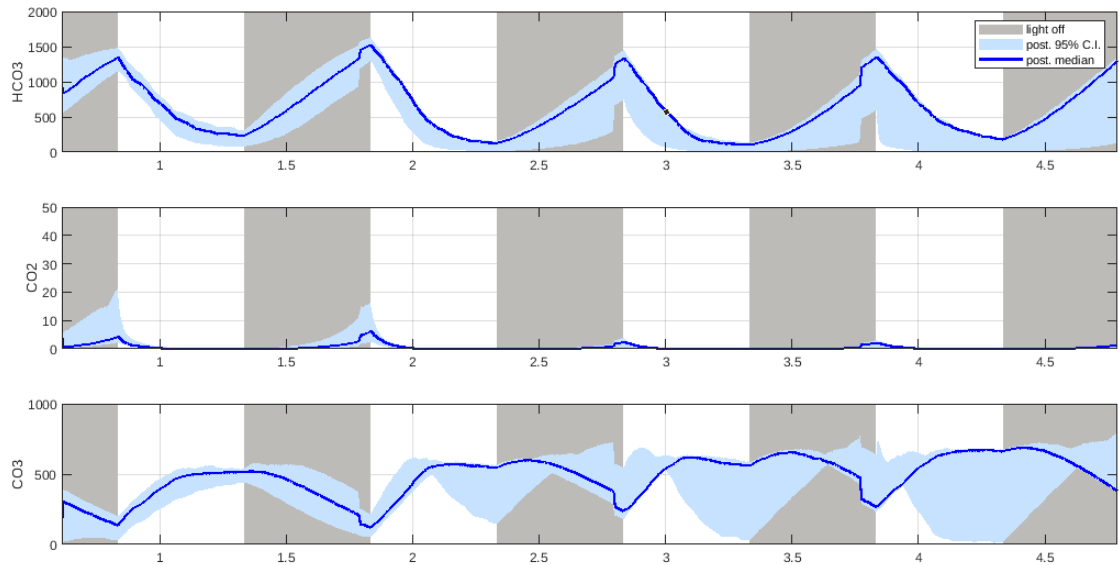


Figure 4.5 : Posteriors for carbon chem.

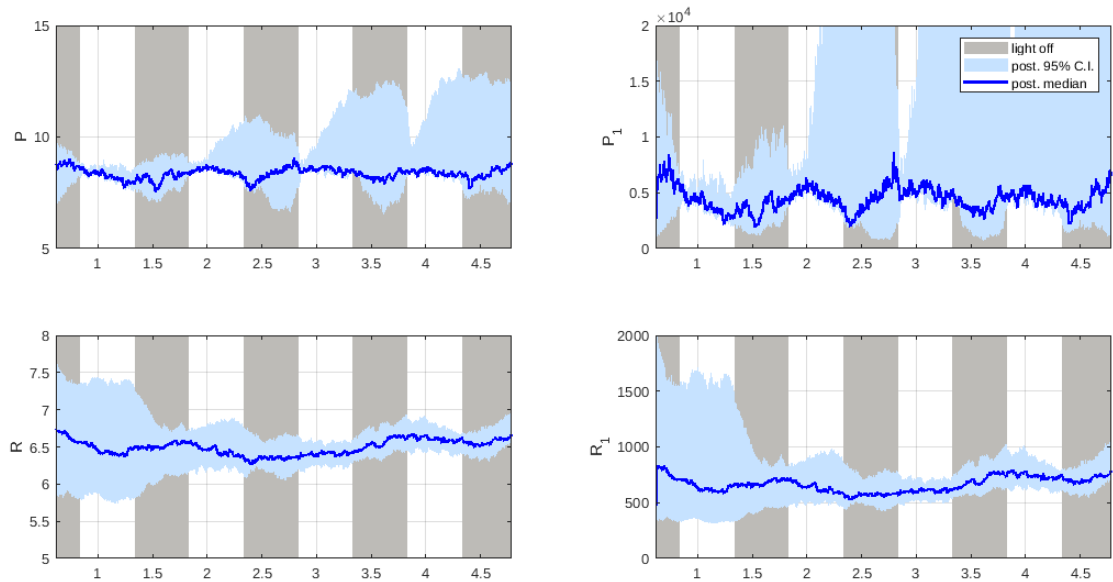


Figure 4.6 : Posteriors for photosynthesis and respiration.

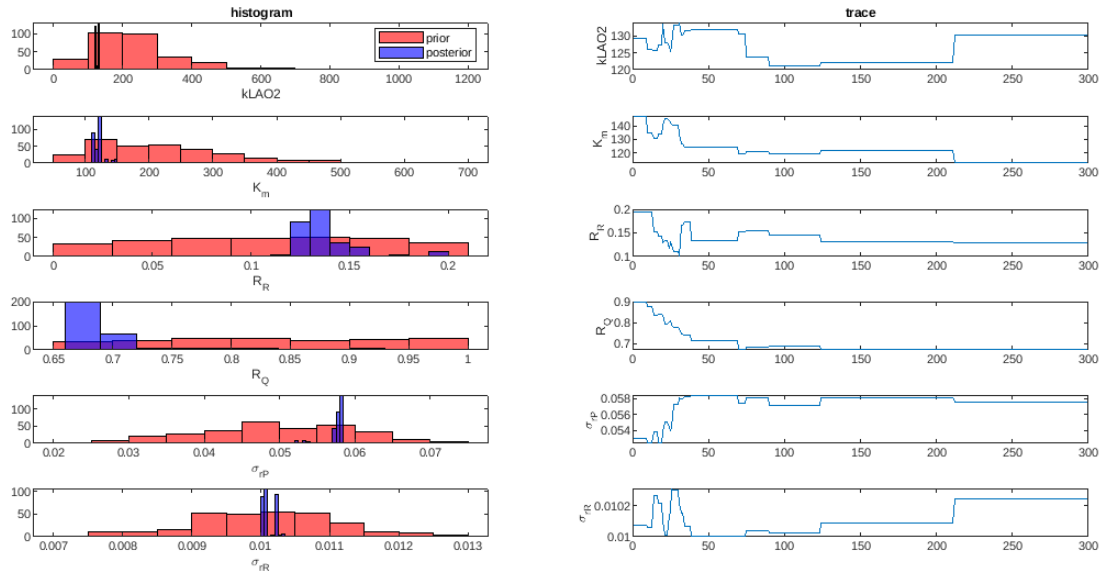


Figure 4.7 : Priors, posteriors and traces for model parameters.

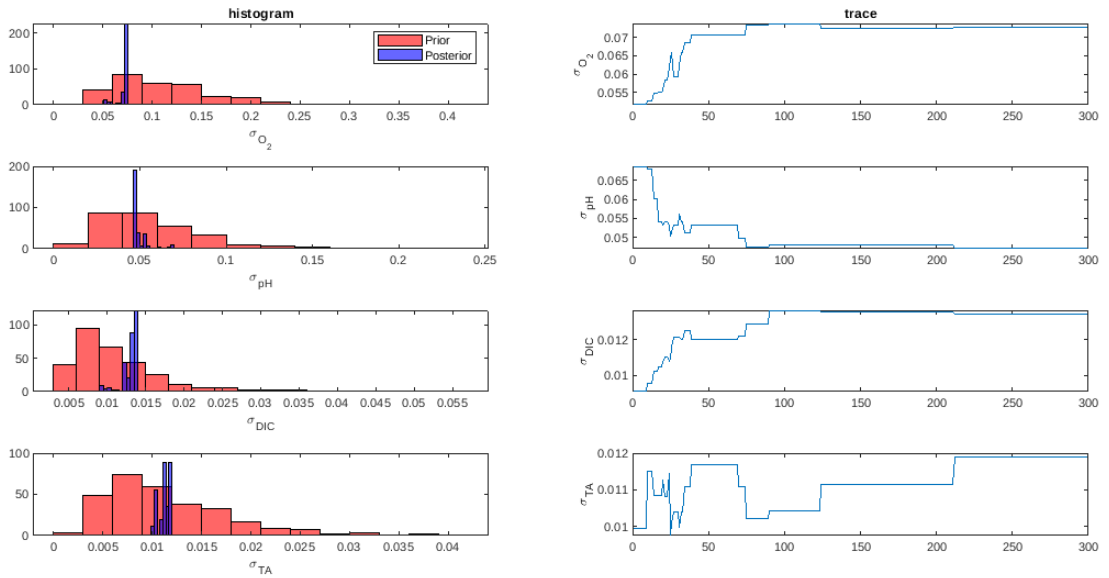


Figure 4.8 : Priors, posteriors and traces for obs. error parameters.

Appendix A

LiBbi model code

Model file: micro_iterative.bi

```
/*
 * Microalgae model.
 * ode solver every minute, obs and input files are in days
 * iterative solution using newton raphson for the CO2SYS solutions
 */
model micro_iterative {

  const F02  = 0.2094
  const FC02 = 397e-6
  const S    = 34

  param kLA02
  param Km
  param RR
  param RQ

  input I // light intensity
  input T //temperature (C)
  input gas //gas on/off

  state DIC // state variables
```

```
state O_2
state pH
state O2H_pr
state CO2H_pr
state R
state R1
state P
state P1
state alk
state CO2
state HCO3
state CO3
state O_2H
state CO2H

noise r_R
noise r_P

/* random walk parameter */
param sigma_r_R
param sigma_r_P

obs O2_obs
obs pH_obs
obs DIC_obs
obs alk_obs
```

```
sub parameter { /* prior distribution over parameters */
```

```
Km ~ log_normal(log(200.0), 0.8)
```

```
kLA02 ~ log_normal(log(200.0), 0.5)
```

```
RR ~ uniform(0.0001, 0.2)
```

```
RQ ~ uniform(0.66, 1.0)
```

```
sigma_r_R ~ normal(0.01, 0.001)
```

```
sigma_r_P ~ normal(0.05, 0.01)
```

```
}
```

```
const prop_std = 0.1;
```

```
sub proposal_parameter {
```

```
Km ~ log_normal(log(Km), 0.8*prop_std)
```

```
kLA02 ~ log_normal(log(kLA02), 0.5*prop_std)
```

```
RR ~ truncated_normal(RR, 0.2*prop_std, lower = 0.0001, upper = 0.2)
```

```
RQ ~ truncated_normal(RQ, 0.2*prop_std, lower = 0.66, upper = 1.0)
```

```
sigma_r_R ~ normal(sigma_r_R, 0.001*prop_std)
```

```
sigma_r_P ~ normal(sigma_r_P, 0.01*prop_std)
```

```
}
```

```
sub initial { /* prior distribution over initial conditions, given parameters */
```

```
// specify the initial condition model
```

```
R ~ normal(log(500.0), 0.6)
```

```
R1 ~ log_normal(log(500.0), 0.6)
```

```
P ~ normal(log(5000.0), 0.8)
```

```

P1 ~ log_normal(log(5000.0), 0.8)
alk ~ log_normal(log(1700.0), 0.1)

DIC ~ log_normal(log(1200.0), 0.2)
O_2 ~ log_normal(log(230.0), 0.2)
pH ~ log_normal(log(8.5), 0.2)
CO2 ~ log_normal(log(3.0), 0.4)
HCO3 ~ log_normal(log(1000.0), 0.3)
CO3 ~ log_normal(log(300.0), 0.4)
O_2H ~ log_normal(log(200.0), 0.2)
CO2H ~ log_normal(log(10.0), 0.2)
}

```

```

sub transition(delta = 0.0023) { // obs are in days ie delta=1.0 for daily solving

```

```

/* processes */

```

```

inline TK      = T + 273.0 // temp in kelvin

```

```

inline K0_CO2 = exp(-60.2409 + 93.4517*(100.0/TK) + 23.3585*log(TK/100.0)+ S*(0.0

```

```

CO2H          <- K0_CO2*FCO2*1.0220*1e6

```

```

inline K0_O2  = (exp(-1282.8704 + 36619.96/TK + 223.1396*log(TK) -0.354707*TK +

```

```

O_2H          <- K0_O2*FO2*1.0220*1e-6

```

```

inline PAC    = HCO3    //PAC=photosynthetically active carbon. if the phyto are j
inline mm     = PAC/(Km+PAC)

// CO2SYS iterative solution
// set up all the constants

inline logTK  = log(TK)
inline S2     = S*S
inline sqrtS  = sqrt(S)

// total sulphur

inline TS     = (0.14/96.062)*(S/1.80655)
inline IS     = 19.924*S/(1000.0 - 1.005*S)

inline KS_int = -4276.1/TK + 141.328 - 23.093*logTK + (-13856.0/TK + 324.57 - 4
inline KS     = exp(KS_int)*(1 - 0.001005*S)

// Fluorine

inline TF     = 0.000067*S/18.9984/1.80655
inline KF     = exp(-(-874.0/TK - 0.111*sqrtS + 9.68))
inline SWS_2_T = (1.0 + TS/KS)/(1.0 + TS/KS + TF/KF)
inline Free_2_T = 1.0 + TS/KS

// H2O dissoc

```

```

inline KW = exp(148.9802 - 13847.26/TK - 23.6521*logTK + (118.67/TK - 5.977 + 1.

// Boron

inline KB = exp((-8966.90 - 2890.53*sqrtS - 77.942*S + 1.728*S*sqrtS - 0.0996*S2)
inline TB = 0.0004326*S/35.0

// Carbon eq constants

inline K1 = 10**(-(3633.86/TK - 61.2172 + 9.6777 *logTK - 0.011555*S + 0.0001152*
inline K2 = 10**(-( 471.8/TK + 25.9290 - 3.16967*logTK - 0.01781*S + 0.0001122*S

// end all the constants

// intial guess at the pH (use the approximating equation)

// inline pH_init = 9.5803 - 0.0027089*DIC - 0.018089*T - 0.012068*S + 0.0016329*
inline pH_init = 12.26 -0.0030605*DIC -0.043752*T -0.013625*S+ 0.00011315*alk + 1

// iteration 1

inline h_1 = 10.0**(-pH_init)
inline h_free_1 = h_1/Free_2_T
inline f0_1 = (DIC*1e-6*(K1*h_1 + 2.0*K1*K2)/(h_1*h_1 + K1*h_1 + K1*K2) - h_free
inline df0_1 = (DIC*1e-6*(K1 + 2.0*K1*K2)/(h_1**2.0 + K1*h_1 + K1*K2) - DIC*1e-6
inline pH_1 = pH_init - f0_1/df0_1

```



```
// iteration 2
```

```
inline h = 10.0**(-pH_1)
```

```
inline h_free = h/Free_2_T
```

```
inline f0 = (DIC*1e-6*(K1*h + 2.0*K1*K2)/(h*h + K1*h + K1*K2) - h_free + KW/h -
```

```
inline df0 = (DIC*1e-6*(K1 + 2.0*K1*K2)/(h**2.0 + K1*h + K1*K2) - DIC*1e-6*(K1*h
```

```
pH <- pH_1 - f0/df0
```

```
// calculate the final concentrations
```

```
inline H = 10.0**(-pH)
```

```
inline H2 = H*H
```

```
inline denom = (H2 + K1*H + K1*K2)
```

```
C02 <- DIC*H2/denom
```

```
HCO3 <- DIC*H*K1/denom
```

```
C03 <- DIC*K1*K2/denom
```

```
// end C02SYS iterative solution
```

```
/* R and P as random walks */
```

```
r_R ~ normal(0.0, sigma_r_R)
```

```
R <- R + r_R
```

```
R1 <- exp(R)
```

```

r_P ~ normal(0.0, sigma_r_P)

P  <- P + r_P

P1  <- exp(P)

ode(h = 0.1, atoler = 1.0e-6, rtoler = 1.0e-6, alg = 'RK4(3)'){
  dDIC/dt  =  -P1*I*mm + R1  + gas*0.893*kLA02*(C02H - C02)    // DIC = Dissolved Inorganic Carbon
  dO_2/dt  =  (P1*I*mm - R1)/RQ  + gas*kLA02*(O_2H - O_2)
  // O_2 = Dissolved Oxygen
  dalk/dt  =  RR*P1*I*mm
}

}

sub observation {

O2_obs ~ log_normal(log(O_2), 0.3)
pH_obs ~ log_normal(log(pH), 0.3)
DIC_obs ~ log_normal(log(DIC), 0.3)
alk_obs ~ log_normal(log(alk), 0.3)
}

}

Prior sampling file: prior.conf

--target prior
--model-file micro_iterative.bi
--nsamples 500
--start-time 0.61304

```

```
--end-time 4.7866  
--noutputs 6049  
--input-file data/input_all_2018_normalised.nc  
--output-file results/prior_micro_iterative.nc
```

Posterior sampling file: posterior.conf

```
--target posterior  
--model-file micro_iterative.bi  
--input-file data/input_all_2018_normalised.nc  
--obs-file data/obs_all_2018.nc  
--nsamples 500  
--nparticles 1024  
--start-time 0.61304  
--end-time 4.7866  
--noutputs 6049  
--output-file results/posterior_micro_iterative.nc  
--with-transform-initial-to-param
```

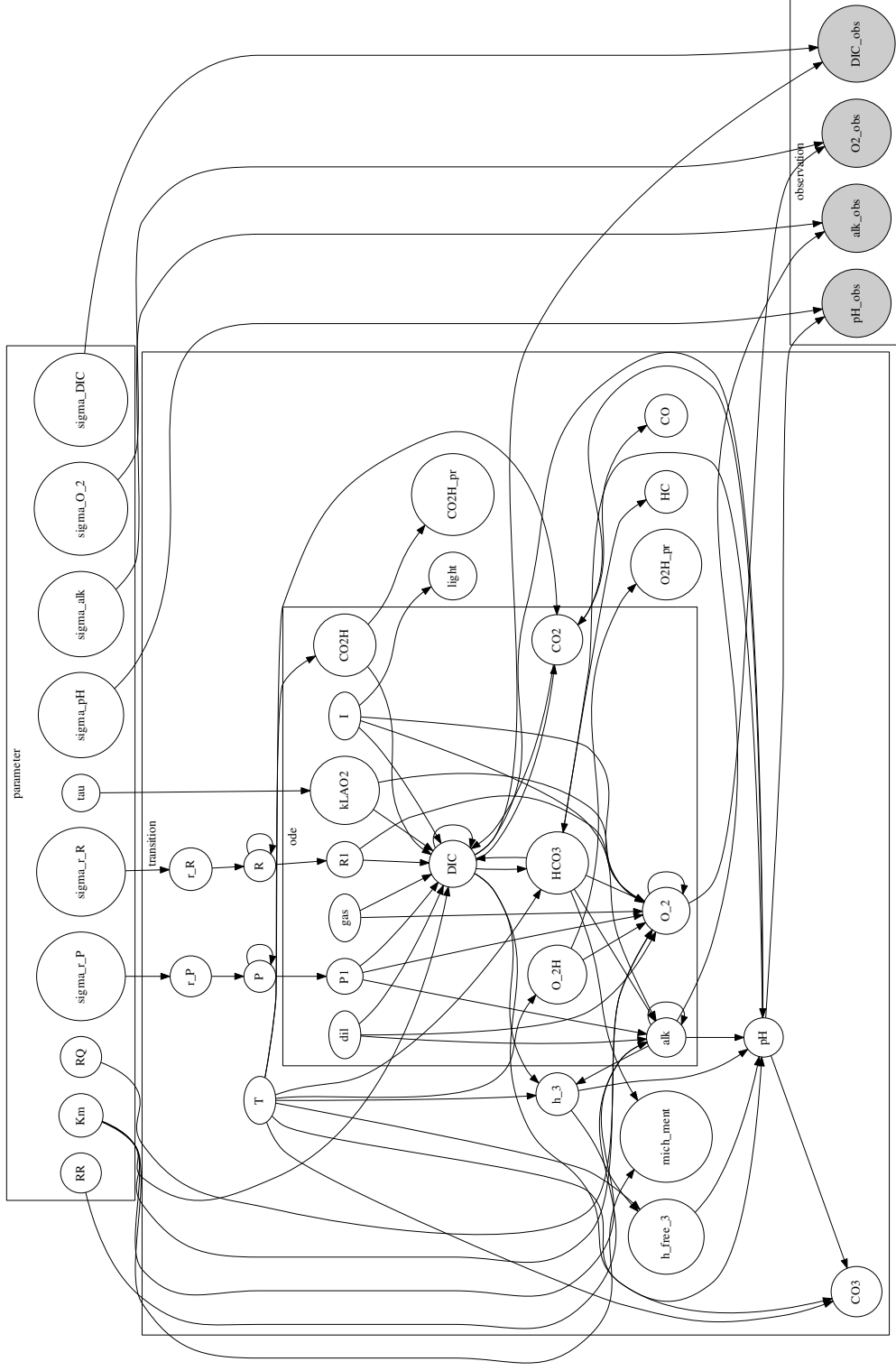


Figure A.1 : Directed Acyclic Graph of the LiBbi model file micro.bi

Bibliography

- [1] Rubin Battino, Timothy R Rettich, and Toshihiro Tominaga. The solubility of oxygen and ozone in liquids. *Journal of physical and chemical reference data*, 12(2):163–178, 1983.
- [2] Arnold E Greensberg, LS Clesceri, Andrew D Eaton, and MAH Franson. Standard methods for the examination of water and wastewater. *American Public Health Asociation, Whashington, DC*, 1992.
- [3] E Molina Grima, JA Sánchez Pérez, F Ía Garc Camacho, and A Robles Medina. Gas-liquid transfer of atmospheric co₂ in microalgal cultures. *Journal of Chemical Technology & Biotechnology*, 56(4):329–337, 1993.
- [4] Ernie Lewis, Doug Wallace, and Linda J Allison. Program developed for co {sub 2} system calculations. Technical report, Brookhaven National Lab., Dept. of Applied Science, Upton, NY (United States . . . , 1998.
- [5] Niels Ramsing and Jens Gundersen. Seawater and gases. *Limnol. Oceanogr*, 37:1307–1312, 2011.
- [6] SMAC Van Heuven, D Pierrot, JWB Rae, E Lewis, and DWR Wallace. Matlab program developed for co₂ system calculations. *ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee*, 530, 2011.
- [7] R.F Weiss. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine chemistry*, 2(3):203–215, 1974.