Geoscientific
Model Development

Supplement of

Numerical study of the seasonal thermal and gas regimes of the largest artificial reservoir in western Europe using the LAKE 2.0 model

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1 Representation of biogeochemical processes in LAKE model

1.1 Governing equations for dissolved gases and organic carbon in a water column

Evolution and vertical distribution of three dissolved gases are considered in the LAKE2.0 model, which are methane CH_4, oxygen O_2 and carbon dioxide CO_2. However, dissolved carbon dioxide is supposed to be always in carbonate equilibrium, so that it contributes to concentration of dissolved inorganic carbon (DIC), $C_{DIC} = C_{CO_2} + C_{HCO_3^-} + C_{CO_3^{2-}}$, and it is the change of DIC that reflects the number of carbon atoms in CO_2 molecules added to (or lost by) a solution from (to) atmosphere, bubbles, respiring organisms or decaying organical matter (see Section 1.2).

In addition, the content of dissolved organic carbon (DOC), particulate organic carbon (both living, POCL, and dead, POCD) are calculated. POCL includes carbon atoms contained in phytoplankton and zooplankton.

The species listed above obey the following equation system:

$$\frac{\partial C_{CH_4}}{\partial t} = \text{Dif}_A(C_{CH_4}) + B_{CH_4} - O_{CH_4}, \tag{1}$$

$$\frac{\partial C_{O_2}}{\partial t} = \text{Dif}_A(C_{O_2}) + B_{O_2} + P_{O_2} - R_{O_2} - D_{O_2} - S_{O_2} - O_{O_2}, \tag{2}$$

$$\frac{\partial C_{DIC}}{\partial t} = \text{Dif}_A(C_{DIC}) + B_{CO_2} - P_{CO_2} + R_{CO_2} + D_{CO_2} + S_{CO_2} + O_{CO_2}, \tag{3}$$

$$\frac{\partial \rho_{DOC}}{\partial t} = \text{Dif}(\rho_{DOC}) + E_{POCL} - D_{DOC}, \tag{4}$$

$$\frac{\partial \rho_{POCL}}{\partial t} = \text{Dif}(\rho_{POCL}) + P_{POCL} - R_{POCL} - E_{POCL} - D_{h,POCL}, \tag{5}$$

$$\frac{\partial \rho_{POCD}}{\partial t} = \text{Dif}(\rho_{POCD}) - \frac{\partial(w_g \rho_{POCD})}{\partial z} - D_{POCD} + D_{h,POCL}. \tag{6}$$

where $\text{Dif}_A(\bullet) \equiv \frac{1}{A}\frac{\partial}{\partial z}\left(A k_s \frac{\partial \bullet}{\partial z}\right)$, $\text{Dif}(\bullet) \equiv \frac{\partial}{\partial z}\left(k_s \frac{\partial \bullet}{\partial z}\right)$ are diffusion operators, w_g is a sedimentation velocity of POCD particles. Equations (4)-(6) do not contain A, because they are not derived by horizontal averaging, but follow from assumption of horizontal homogeneity of respective biogeochemical variable. This is caused by uncertainty of estimating the flux of these substances at the

sloping interface between water and sediments. The r.h.s of these equations represent diffusion (assuming $k_s = k_{s,t} + k_{s,m}$ with the same eddy diffusivity $k_{s,t}$ and molecular diffusivity $k_{s,m}$ for all species; molecular dissusivity is not included in POCL and POCD equations), sources and sinks due to the following processes:

- dissolution/exsolution of gases at the bubble-water interface (B_{CH_4}, B_{O_2} and B_{CO2});

- photosynthesis (P_{O_2}, P_{CO_2}, P_{POCL});

- respiration (R_{O_2}, R_{CO_2}, R_{POCL});

- biochemical oxygen demand in the water column (D_{O_2}, D_{CO_2}, D_{DOC}, D_{POCD});

- sedimentary oxygen demand (S_{O_2}, S_{CO_2});

- methane aerobic oxidation in the water column (O_{CH_4}, O_{O_2}, O_{CO_2});

- death of living species ($D_{h,POCL}$)

All variables in the above list are positive definite, excepting B_{CH_4}, B_{O_2} and B_{CO2} that may be either positive or negative. All concentrations in (1)-(3) are expressed in mol/m^3 that allows for simple relations of sinks and sources in different equations based on stoichiometry of the respective reactions. Organic carbon variables DOC, POCL and POCD in (4)-(6) are molar concentrations of carbon atoms contained in these organic groups. Terms B_{CO_2}, P_{CO_2}, R_{CO_2}, D_{CO_2}, S_{CO_2}, O_{CO_2} in (3) possess "CO$_2$" subscript because carbon atoms are supplied to or removed from DIC of a solution in a form of CO$_2$.

In the following, the parameterizations of processes related to O$_2$ and CO$_2$ dynamics are described, whereas formulations for CH$_4$ processes are presented in (Stepanenko et al., 2016).

The formulations for photosynthesis, respiration, biochemical oxygen demand and sedimentary oxygen demand basically adopted from (Stefan and Fang, 1994) and (Hanson et al., 2004).

1.2 Carbonate equilibrium

Carbonate equilibrium means the equilibrium in the following reactions:

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-, \tag{7}$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}. \tag{8}$$

Involving kinetic constants of these reactions yields, that the DIC reads

$$C_{DIC} \equiv C_{CO_2} + C_{HCO_3^-} + C_{CO_3^{2-}} = C_{CO_2} \left[1 + k_1 10^{pH} + k_1 k_2 10^{2pH} \right]. \tag{9}$$

Here, the constants are given by Arrhenius equation:

$$k_i = k_{i0} \exp \left[-\frac{E_{act,i}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \ i = 1, 2, \tag{10}$$

R – universal gas constant, $k_1 = 4.3*10^{-7}$ mol/l, $k_2 = 4.7*10^{-11}$ mol/l, $E_{act,1} = 7.66 * 10^3$ J/mol, $E_{act,2} = 1.49 * 10^4$ J/mol. Thus, C_{CO_2} is readily calculated given C_{DIC} value, and vice versa, where pH is an external parameter.

Carbon atoms are added or removed from carbonate equilibrium system in a form of CO_2 during respiration, photosynthesis and organic chemical and physical processes, hence the change of C_{DIC} equals to number of CO_2 consumed or produced. This explains the sense of terms in equation (3). For obtaining CO_2 flux across bubble surface or CO_2 diffusive flux to the atmosphere, C_{CO_2} is needed and is calculated from (9).

1.3 Boundary conditions for dissolved gases in a water column

The top boundary condition (at the lake-atmosphere interface) for any dissolved gas concentration in the case of open water has the form:

$$\frac{k_s}{h} \frac{\partial C}{\partial \xi} \bigg|_{\xi=0} = F_C, \tag{11}$$

where C is C_{CH_4}, C_{O_2} or C_{CO_2}, and F_C is the diffusive flux of a gas into the atmosphere, positive upwards. This flux is calculated according to the widely used parameterization:

$$F_C = k_{ge}(C|_{\xi=0} - C_{ae}), \tag{12}$$

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with C_{ae} being the concentration of the gas in water equilibrated with the atmospheric concentration and described by Henry law and k_{ge}, m/s, denoting the gas exchange coefficient, the so-called "piston velocity". The latter is written as:

$$k_{ge} = k_{600}\sqrt{\frac{600}{Sc(T)}}, \tag{13}$$

with the Schmidt number $Sc(T)$ having individual values for different gases and being temperature-dependent. The k_{600} coefficient has been a subject of numerous studies, and a number concepts have been put forward to quantify it (Donelan and Wanninkhof, 2002). The proper computation of this coefficient should account for the effects of a number of factors such as turbulence in adjacent layers of water and air, wave development and breaking, cool skin dynamics. The surface renewal model (MacIntyre et al., 2010; Heiskanen et al., 2014), used in LAKE2.0 model, "integrates" those effects through the near-surface dissipation rate of turbulent kinetic energy:

$$k_{600} = \frac{C_{1,SR}(\epsilon|_{\xi=0}\nu_w)^{\frac{1}{4}}}{\sqrt{600}}, \tag{14}$$

where ν_w designates molecular viscosity of water, $C_{1,SR} = 0.5$ is an empirical constant. TKE dissipation rate is available directly from $k - \epsilon$ closure.

When a lake is covered by ice, $F_C = 0$, which neglects contribution of diffusion through ice cracks.

1.4   Photosynthesis

The intensity of photosynthesis in terms of oxygen molecules production is expressed as:

$$P_{O_2} = \frac{P_{max}L_{min}\rho_{Chl-a}}{H_{sec}\mu_{O_2}}. \tag{15}$$

The denominator here serves co convert units in the r.h.s. from mg/(l*h) to mol/(m^3 s). The P_{max} value expresses limitation of oxygen production by temperature in a form:

$$P_{max} = C_P\theta_P^{(T-T_0)}, \tag{16}$$

so that C_P is a value of P_{max} at the reference temperature $T = T_0$. The limitation of oxygen production by the available photosynthetically active

radiation PAR (S_{PAR}) is given by the Haldane kinetics:

$$L_{min} = \frac{S_{PAR}(1 + 2\sqrt{C_{Lmin,1}/C_{Lmin,2}})}{S_{PAR} + C_{Lmin,1} + S_{PAR}^2/C_{Lmin,2}}. \tag{17}$$

The PAR intensity delivering maximum to a limiter L_{min} (=1) is $S_{PAR} = \sqrt{C_{Lmin,1}C_{Lmin,2}}$. In the model, these coefficients are specified as (Stefan and Fang, 1994; Megard et al., 1984):

$$C_{Lmin,1} = C_{PAR}\theta_{PAR}^{(T-T_0)}, \tag{18}$$
$$C_{Lmin,2} = \mathrm{H}(T - T_{00})C_{Lmin,2,>T_{00}} + [1 - \mathrm{H}(T - T_{00})]C_{Lmin,2,<T_{00}}, \tag{19}$$

with $\mathrm{H}(\bullet)$ denoting a Heavyside function, and T_{00} standing for another reference temperature. It is seen from (17), that $L_{min} \to 0$ if $S_{PAR} \to 0$ and $S_{PAR} \to \infty$, i.e. PAR ihnibits photosynthesis at both low and high values of its intensity. The PAR instensity S_{PAR} is expressed in a number of photons per square meter per hour, so that:
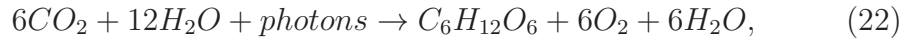
$$S_{PAR} = H_{sec}T_{J\to Eins}S_{PAR}^*, \tag{20}$$

where $H_{sec} = 3600$ s and S_{PAR}^* is PAR intensity in W/m². The coefficient transforming from J to Einstein (Einstein is an energy of Avogadro number of photons), $T_{J\to Eins}$, is estimated assuming the uniform distribution of energy in PAR region, which yields:

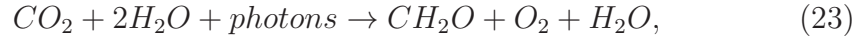$$T_{J\to Eins} = \frac{\lambda_{PAR}}{N_A h_P c}, \tag{21}$$

with N_A, h_P, c denoting Avogadro number, Planck constant and the light speed in vacuum, respectively, all in SI units.

The treatment of chlorophyll-a concentration ρ_{Chl-a} is given in Section 1.10.

Finally, from the gross photosynthesis reaction:

$$6CO_2 + 12H_2O + photons \to C_6H_{12}O_6 + 6O_2 + 6H_2O, \tag{22}$$

or, in a shortened form:

$$CO_2 + 2H_2O + photons \to CH_2O + O_2 + H_2O, \tag{23}$$

we see that the carbon dioxide consumption equals oxygen production, i.e. $P_{CO_2} = P_{O_2}$.

Equation (22) also implies that $P_{POCL} = P_{CO_2}$.

Table 1: Constants in photosynthesis model

Constant	Units	Value
C_P	h^{-1}	9.6
θ_P	n/d	1.036
T_0	°C	20
T_{00}	°C	10
μ_{O_2}	g/mol	32
H_{sec}	s	3600
C_{PAR}	Einstein/(m^2*h)	0.687
θ_{PAR}	n/d	1.086
$C_{Lmin,2,>T_{00}}$	Einstein/(m^2*h)	15.
$C_{Lmin,2,<T_{00}}$	Einstein/(m^2*h)	5.
λ_{PAR}	m	$5.5 * 10^{-7}$ (550 nm)

1.5 Respiration

P.Hanson et al. (Hanson et al., 2004) assume, that respiration is performed by "living particles", i.e. POCL, only in epilimnion, and may be scaled by gross primary production (i.e., photosynthesis rate), $R_{POCL} = \alpha_{POCL}P_{POCL}$, $\alpha_{POCL} = 0.8$. In contrast, we assume that this process happens at all depths where enough oxygen *in situ* to be used in respiration is available, with the same scaling. Evidently,

$$R_{O_2} = R_{CO_2} = \alpha_{POCL}P_{POCL}. \tag{24}$$

1.6 Biochemical oxygen demand (BOD)

We treat biochemical oxygen demand as a consumption of oxygen during degradation of dead organic particles (POCD) D_{POCD} and dissolved organic carbon (DOC) D_{DOC}, following (Hanson et al., 2004); they suggest that $D_{POCD} = \rho_{POCD}/\tau_{POCD}$, $D_{DOC} = \rho_{DOC}/\tau_{DOC}$ with time scales $\tau_{POCD} = 20D_{sec}$, $\tau_{DOC} = 200D_{sec}$ (D_{sec} is a number of seconds in a day). Thus, the BOD rate is:

$$D_{O_2} = D_{CO_2} = \left(\frac{\rho_{POCD}}{\tau_{POCD}} + \frac{\rho_{DOC}}{\tau_{DOC}} \right). \tag{25}$$

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1.7 Sedimentary oxygen demand (SOD)

The sedimentary oxygen demand appears as a sink in (2) and in essence is the contribution of the vertical flux of O_2 at the lake's bottom to the horizontally averaged oxygen concentration:

$$S_{O_2} = -\frac{F_{SOD}}{A}\frac{\partial A}{\partial z}. \tag{26}$$

Basing on the argument that SOD is controlled by both diffusion (governed by Fickian law) and biochemical consumption (described by Michaelis-Menthen kinetics), (Walker and Snodgrass, 1986) derive:

$$F_{SOD} = \mu_\beta\frac{C_{O_2}}{k_{O_2,SOD} + C_{O_2}} + k_c C_{O_2}, \tag{27}$$

where μ_β is proportional to organics oxidation potential rate in sediments, and k_c is the mass transfer coefficient. Both are thought to be exponentially dependent on temperature:

$$\mu_\beta = \mu_{\beta,0}\theta_{\mu_\beta}^{T-T_{\mu_\beta}}, k_c = k_{c,0}\theta_{k_c}^{T-T_{k_c}}. \tag{28}$$

The stoichiometry of SOD is assumed to be close to that of BOD (??), therefore, $S_{CO_2} = S_{O_2}$. Additionally, the flux of O_2 due to SOD at the lake bottom, F_{SOD}, is used as the bottom (lake deepest point) boundary condition for the oxygen equation (2).

Table 2: Constants in sedimentary oxygen demand model

Constant	Units	Value
θ_{μ_β}	n/d	1.085
θ_{k_c}	n/d	1.103
T_{μ_β}	K	25
T_{k_c}	K	20
$\mu_{\beta,0}$	mol/(m²*s)	$0.5/(\mu_{O_2}D_{sec})$, $[\mu_{O_2}] = g/mol$
$k_{c,0}$	m/s	$0.045/D_{sec}$

1.8 Exudates and death rate of POCL

Hanson et al. suggest exudation to be scaled with photosynthesis rate, $E_{POCL} = \beta_{POCL} P_{POCL}$, $\beta_{POCL} = 0.03$ and the death rate to be defined as $D_{h,POCL} = \frac{\rho_{POCL}}{\tau_{Dh}}$, where time scale τ_{Dh} ranges from $1.1 D_{sec}$ in hypolimnion to $33 D_{sec}$ in epilimnion.

1.9 Sedimentation of organic particles

In the current model version we use the Stokes sedimentation velocity below the mixed layer:

$$w_s = \frac{4}{3A} \frac{\Delta g d^2}{\nu_m},\qquad (29)$$

and the high-Reynolds-number limit of this variable

$$w_s = \sqrt{\frac{4}{3B}\Delta g d}\qquad (30)$$

in the mixed layer. Here, $\Delta = \rho_p/\rho_{w0} - 1$, ρ_p is a particle's density, and d – its diameter, the typical values for constants may be chosen as $A = 30.0$, and $B = 1.25$ (Song et al., 2008), and the density of organic particles as $1.25\ g/cm^3$ (Avnimelech et al., 2001).

1.10 Chlorophyll-a dynamics

The chlorophyll-a dynamics in the model follows a simple scheme suggested in (Stefan and Fang, 1994), where chlorophyll-a density is calculated as:

$$\rho_{Chl-a} = \rho_{Chl-a,0} \mathrm{H}(H_a - z),\qquad (31)$$

where the active layer, H_a, is a maximum value between mixed-layer depth, H_{ML}, and the photic zone depth, H_{PZ}. The mixed-layer depth is defined as the depth of maximum Brunt-Väisälä frequency, and the photic zone depth is estimated as the depth at which the PAR irradiance drops to 10% of its surface value. The mean chlorophyll-a concentration in the active layer, $\rho_{Chl-a,0}$, is assigned according to a trophic status of the lake: $2 * 10^{-3}$ mg/l for oligotrophic lakes, $6 * 10^{-3}$ mg/l for mesotrophic lakes and $15 * 10^{-3}$ mg/l for

eutrophic lakes. In turn, the trophic status is formally defined from the water turbidity. The Secchi disk values of 2 m and 3.5 m are used to distinguish between eutrophic and mesotrophic, mesotrophic and oligotrophic states, respectively. These thresholds are expressed in the model through light extinction coefficient values, α, using Poole and Atkins formula (Poole and Atkins, 2009):

$$\alpha = \frac{k_{PA}}{z_{SD}},\qquad(32)$$

where z_{SD} is the Secchi disk depth and $k_{PA} = 1.7$. The above chlorophyll-a scheme is identical to that of (Stefan and Fang, 1994), excepting for it does not take into account the annual cycle of $\rho_{Chl-a,0}$.
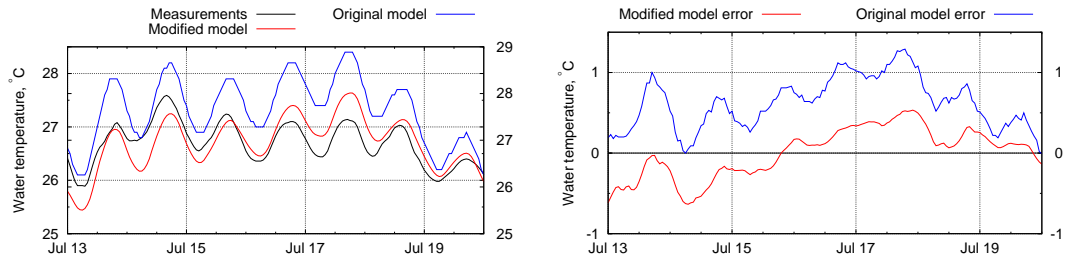
2 Sensitivity tests

Figure S1: ML water temperature, original and modified model results and their errors when compared to the observations.
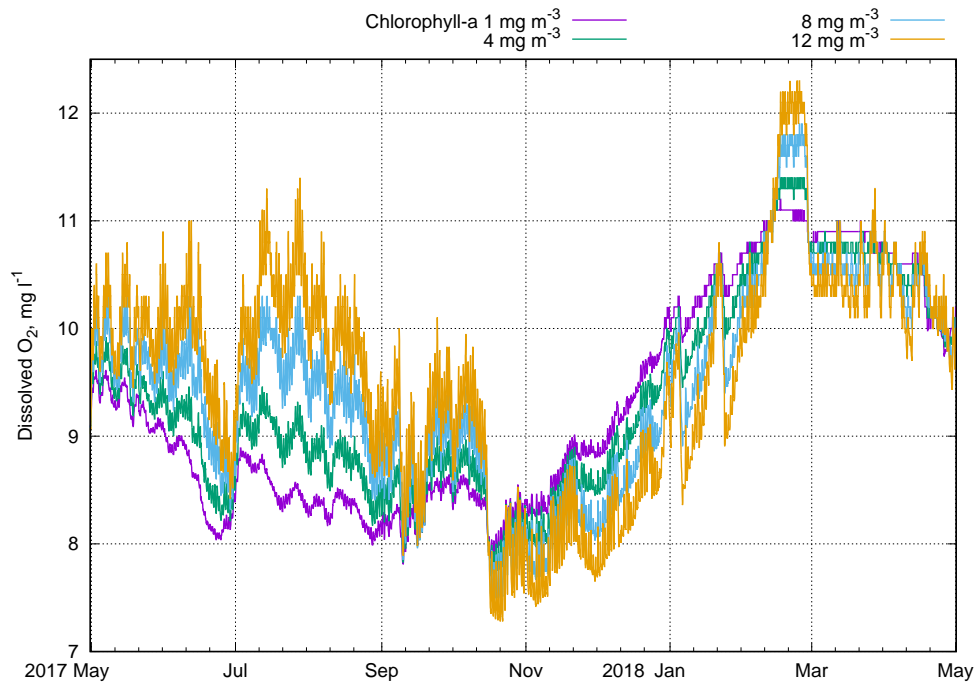

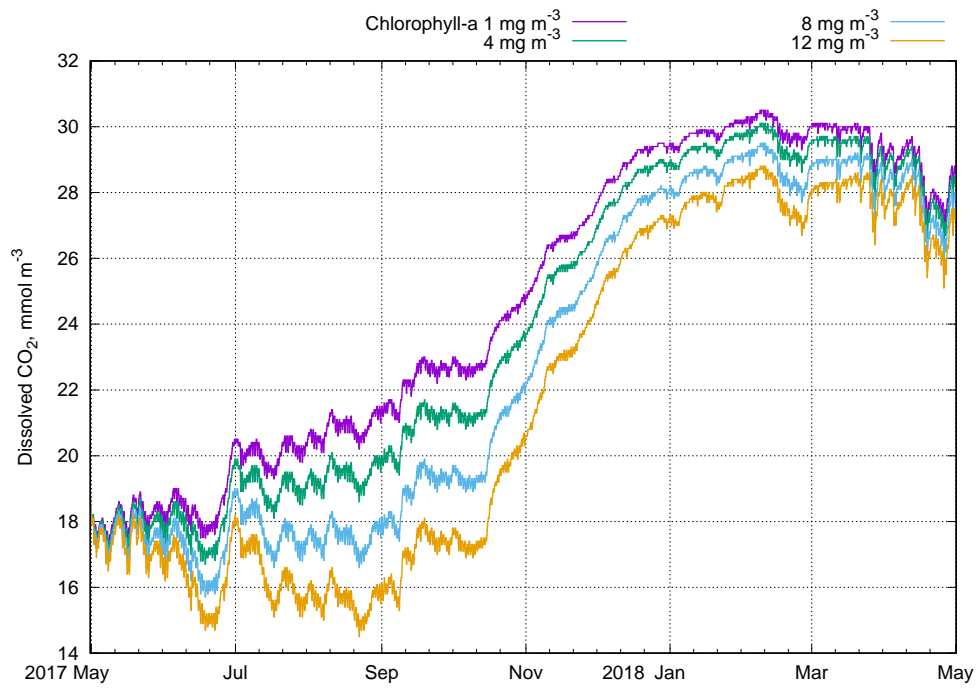Figure S2: DO concentration at different chlorofill-a concentration values.

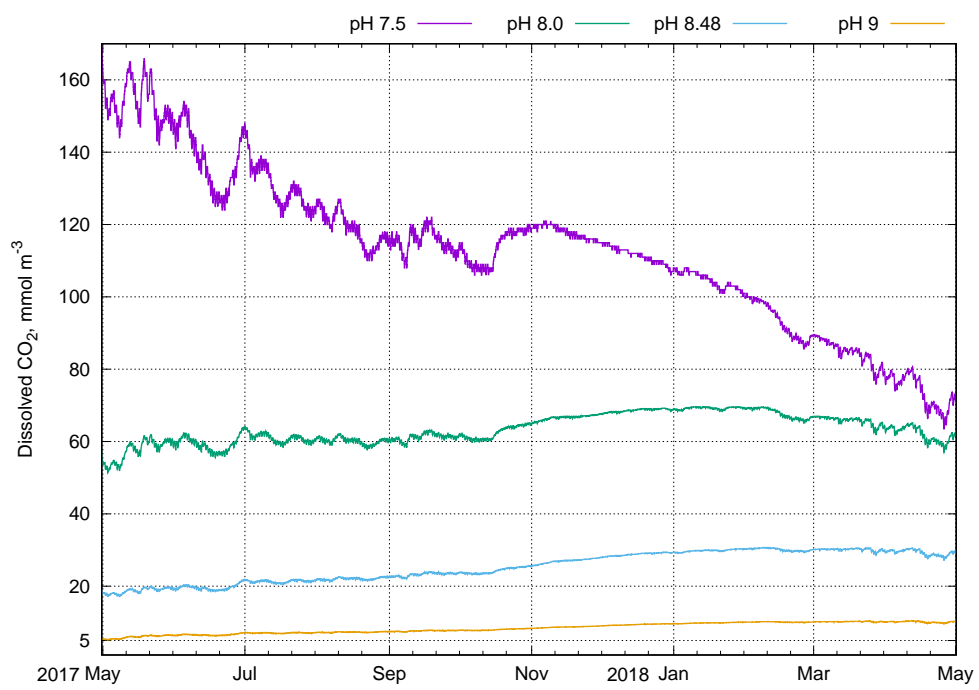Figure S3: CO_2 concentration at different chlorofill-a concentration values.

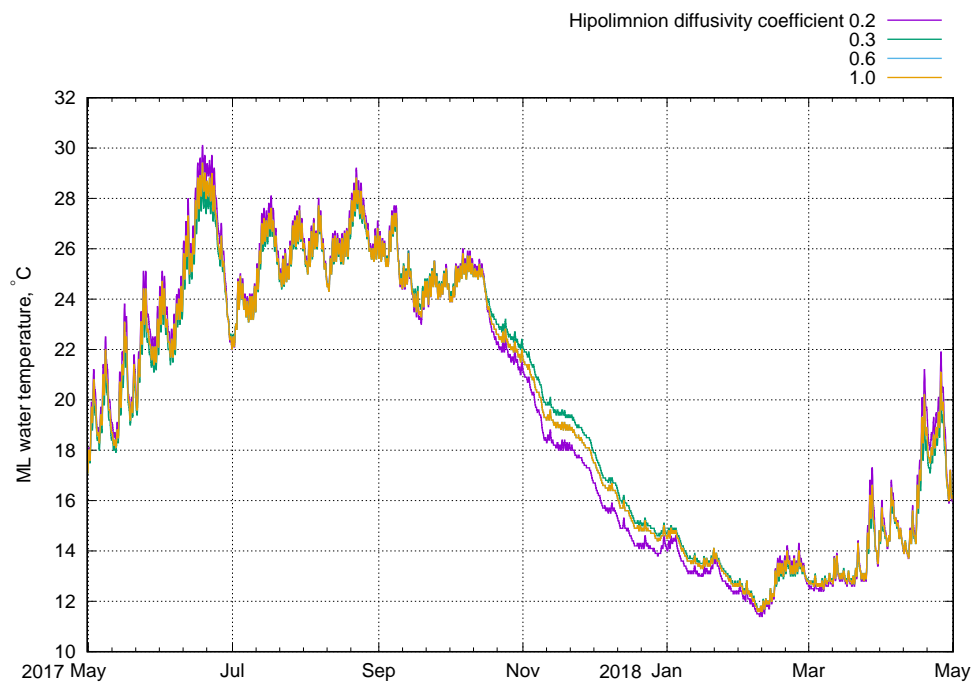Figure S4: Dissolved CO_2 concentrations at different pH values.

Figure S5: ML temperature at different hypolimnetic diffusivity coefficient values.

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