A Coupled Two-dimensional Hydrodynamic and Terrestrial Input Model to Simulate CO_2 Diffusive Emissions from Lake Systems

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Abstract

Most lakes worldwide are supersaturated with carbon dioxide (CO_2) and consequently act as atmospheric net sources. Since CO_2 is a major greenhouse gas (GHG), the accurate estimation of CO_2 exchanges at air/water interfaces of aquatic ecosystems is vital in quantifying the carbon budget of aquatic ecosystems overall. To date, lacustrine CO_2 emissions are poorly understood, and lake carbon source proportions remain controversial, largely due to a lack of integration between aquatic and terrestrial ecosystems. In this paper a new process-based model framework (TRIPLEX-Aquatic) is introduced incorporating both terrestrial inputs and aquatic biogeochemical processes to estimate diffusive emissions of CO_2 from lake systems. The model was built from a two-dimensional hydrological and water quality model coupled with a new lacustrine CO_2 diffusive flux model. For calibration and validation purposes, two years of data collected in the field from two small boreal oligotrophic lakes located in Québec (Canada) were used to parameterize and test the model by comparing simulations with observations for both hydrodynamic and carbon process accuracy. Model simulations were accordant with field measurements in both calibration and verification. Consequently, the TRIPLEX-Aquatic was used to estimate the annual mean CO_2 diffusive flux and predict terrestrial dissolved organic carbon (DOC) impacts on the CO_2 budget for both lakes. Results show a significant fraction of the CO_2 diffusive flux (~30-45%) from lakes was primarily attributable to the input and mineralization of terrestrial DOC, which indicated terrestrial organic matter was the key player in the diffusive flux of CO_2 from oligotropical lake systems

in Québec, Canada.

Keywords: boreal lake; carbon dioxide; diffusive flux; hydrodynamic model; aquatic carbon cycle; terrestrial DOC

1. Introduction

Lakes account for more than 3% of land surface area (Downing et al., 2006) and are an important component in terrestrial carbon cycling. Substantial evidence indicates that the transfer of terrestrial carbon to lake ecosystems is considerably larger than the carbon flux to marine systems and approximately coequal to estimates of the net ecosystem productivity (NEP) of the terrestrial biosphere (Richey et al., 2002; Cole et al., 2007; Battin et al., 2009). In addition, a significant fraction of terrestrial carbon can be mineralized in lake systems (Kling et al., 1991; Cole et al., 1994; Hope et al., 1996; del Giorgio et al., 1997; Striegl et al., 2001; Algesten et al., 2003; Sobek et al., 2003; Rantakari and Kortelainen, 2005; Cole et al., 2007). Lake surveys carried out worldwide have demonstrated that boreal, temperate, and tropical lakes are typically supersaturated with CO_2 and consequently release significant amounts of CO_2 into the atmosphere (Kling et al., 1991; Cole et al., 1994, 2007; Sobek et al., 2003; Roehm et al., 2009; Battin et al., 2009).

The northern latitude biomes have been identified as important for CO_2 exchange

67 between ecosystems and the atmosphere, with a net sink of CO_2 for temperate forests
68 (Chapin III, et al., 2000; Dunn et al., 2007). However, there are few quantitative
69 estimates of lake emission in relation to current assessments of the CO_2 balance. To
70 date, the lake CO_2 emissions over space are poorly understood (Duchemin et al., 2002;
71 Sobek et al., 2003; Cardille et al., 2007; Roehm et al., 2009; Tedoru et al., 2009;
72 Demarty et al., 2011), and lake carbon source proportions in different ecosystems
73 remain controversial (del Giorgio et al., 1999; Cole et al., 2000; Jonsson et al., 2001,
74 2003; Prairie et al., 2002; Algesten et al., 2003; Hanson et al., 2003, 2004; Karlsson et
75 al., 2007; McCallister and del Giorgio, 2008). Therefore, estimates of the fraction of
76 terrestrial organic carbon that is exported to lakes and then routed into atmospheric
77 CO_2 and the evaluation of the role of lakes in regional carbon budget require the
78 integrated studies of the entire lake-watershed system (Algesten et al., 2003; Jenerette
79 and Lal, 2005; Cole et al., 2007; Battin et al., 2009; Buffam et al., 2011).

80 Identifying CO_2 emissions from lakes is challenging and tends to be fraught with
81 uncertainty since complex links exist between terrestrial and aquatic ecosystems
82 (Hutjes et al., 1998; Wagener et al., 1998; Kalbitz et al., 2000; Smith et al., 2001;
83 McDowell, 2003; Hanson et al., 2004; Jenerette and Lal, 2005; Cole et al., 2007;
84 Buffam et al., 2011). In addition, water bodies exhibit significant multidimensional
85 variations caused by interactions among hydrodynamic, biological, and chemical
86 processes (Cole and Wells, 2006). Although lacustrine biogeochemistry is an
87 integrative discipline, previous terrestrial and lake models have developed somewhat
88 independently of each other (Grimm et al., 2003; Jenerette and Lal, 2005; Hanson et

al., 2004; Cole et al., 2007; Cardille et al., 2007; Debele et al., 2008; Jones et al., 2009). Therefore, understanding the connectivity between each process and scaling up biogeochemical information must rely on coupled terrestrial and aquatic carbon cycle models essential in reducing uncertainty in carbon fluxes from and into lake systems (Grimm et al., 2003; Jenerette and Lal, 2005; Chapin III, 2006; Cole et al., 2007; Battin et al., 2009; Buffam et al., 2011).

In this paper a new process-based two-dimensional model framework (TRIPLEX-Aquatic) was developed to investigate lake carbon cycles with a particular emphasis on CO_2 diffusion. This model incorporates both terrestrial inputs and an aquatic carbon cycle model with exceptional spatial and temporal resolution. Thus, the model constitutes an improved tool to investigate the primary processes involved in aquatic carbon cycling (including CO_2 diffusive exchanges between air and water bodies). Here, we seek to address two questions: 1. Is the TRIPLEX-Aquatic able to capture the dynamics of CO_2 diffusive flux in boreal lakes? 2. What is the contribution of terrestrial DOC to lake CO_2 emission?

2. Model description and methods

To achieve the objectives of this study, the model need to capture the principal hydrological characteristics, the detailed carbon cycle accounting for inputs of DOC from the watershed in lake carbon processing, and the accurate CO_2 diffusive flux simulation to the atmosphere.

Figure 1 provides a schematic of the applied method based upon hydrological, carbon submodels, and CO_2 diffusive exchanges between air and water in the lake. The first model, hydrological submodel simulates the hydrodynamic conditions in lake. It is important in modeling carbon cycle since hydrology controls physical mixing processes between different spatial components of lake, factors that can directly or indirectly control biotic and abiotic processes. The second model, the lake carbon processes focus primarily on the prediction of organic/inorganic pools via photosynthesis and respiration, and their effects on dissolved oxygen and conventional cycles of nitrogen and phosphorus. This approach represents a substantial progression in lacustrine biogeochemical models since the 1970s (Harris, 1980; Beck, 1985; Ambrose et al., 1993; Kayombo et al., 2000; Chapelle et al., 2000; Omlin et al., 2001; Cole and Wells, 2006). In this paper, lake hydrodynamic and carbon simulations follow the approach of the CE-QUAL-W2 model (Cole and Wells, 2006) since the model has coupled between two-dimensional hydrodynamics and carbon cycle simulations with the same time steps and spatial grid, as well as it having already been successfully applied to rivers, lakes, reservoirs, and estuaries for several decades in the past. The CE-QUAL-W2 model is available at http://www.ce.pdx.edu/w2, and its program code is not changed in this study.

The third model, the simulation of CO_2 diffusive fluxes at the air/water interface uses a new boundary layer model developed by Vachon and Prairie (2013) for the CO_2 diffusive flux in temperate lakes. Because this simulation in CE-QUAL-W2 model was simply designed the gas transfer coefficient for CO_2 is related to that of oxygen

132 transfer using a factor of 0.923 (Cole and Wells, 2006), and most of these CO_2 transfer
133 velocities are lower (Fig. 2) than the measurements that collected from aquatic
134 systems of different size lakes (Vachon and Prairie, 2013), whereas some of velocities
135 (e.g., Eq-1, Eq-5, Eq-8, Eq-13) are much higher than the observations under high
136 wind speed. As a result, these transfer velocities make it impossible to reliably
137 simulate CO_2 diffusive fluxes from lakes. The new model is named as TRIPLEX-
138 Aquatic, which is more suitable in predicting CO_2 diffusive emission from lake
139 systems. The program code of new CO_2 diffusive flux submodel (Vachon and Prairie,
140 2013) was developed using the Fortran language as in the CE-QUAL-W2 model.

141 The inputs of TRIPLEX-Aquatic model and file format are same as the
142 CE-QUAL-W2 model, including climate data (e.g. air average temperature, dew point
143 temperature, wind speed and direction, cloud cover), inflow and constituent
144 concentrations (e.g. DOC, dissolved inorganic carbon (DIC), phosphate (PO_4^{3-}),
145 ammonium (NH_4^+), nitrate (NO_3^-), and dissolved oxygen (DO)), and bathymetric and
146 geometric data of lake. The model outputs represent the characteristics of hydrology
147 (e.g. water velocity, density, temperature) and carbon processes (e.g. DOC, DIC,
148 bicarbonates, carbonates, CO_2 concentration in water) in the lake, especially the CO_2
149 diffusive fluxes to the atmosphere. A brief overview of the TRIPLEX-Aquatic
150 model is presented below.
151

152 **2.1 The hydrodynamic submodel**

153 The hydrodynamic simulation is able to characterize time variable
154 longitudinal/vertical distributions of thermal energy in water bodies, based upon a
155 finite difference solution applied to laterally averaged equations of fluid motion
156 including momentum balance, continuity, constituent transport, free surface elevation,
157 hydrostatic pressure, and equation of state (Cole and Wells, 2006).
158 The model quantifies the free surface elevation, pressure, and density as well as the
159 horizontal and vertical velocities (Cole and Wells, 2006). Explicit numerical schemes
160 are also used to compute water velocities that affect the spatiotemporal distribution of
161 temperature and biological/chemical constituents. The model simulates the average
162 temperature for each model cell based upon water inflows/outflows, solar radiation,
163 and surface heat exchanges. The term-by-term formulation was used to characterize
164 the surface heat exchange. Spatial and temporal variations are permitted for
165 longitudinal diffusion. The model computes the vertical diffusion coefficient from the
166 vertical gradient of longitudinal velocities, water densities, and decay of surface wind
167 shear. A full description of the model is offered by Cole and Wells (2006).
168
169 **2.2 The carbon cycle submodel**

170 The carbon submodel explicitly depicts organic and inorganic carbon processes in
171 lake system. The organic carbon process includes four interacting systems:
172 phytoplankton kinetics, nitrogen cycles, phosphorus cycles, and the dissolved oxygen
173 balance (Fig. 3). The model accepts inputs in terms of different pools of organic
174 matter (OM) and various species of algae. OM is partitioned into four pools according

175 to a combination of its physical state (dissolved – DOM versus particulate – POM)
176 and reactivity (labile – L versus refractory – R) characterizing the
177 mineralization/decay rate of organic compounds. Labile OM (LDOM and LPOM) is
178 more readily mineralized (i.e., having faster decay rates) whereas refractory OM
179 (RDOM and RPOM) is less readily mineralized (i.e., having slower decay rates). All
180 OM decay and decomposition processes in the model follow first order kinetics with
181 temperature-dependent coefficients. The inorganic carbon processes include carbon
182 dioxide input and output the inorganic carbon pool among carbonate species via two
183 major pathways: atmospheric and biological exchange processes.

184 The hydrodynamic and carbon dynamics have been well documented and are
185 described in detail in the CE-QUAL-W2 (Cole and Wells, 2006). The scope of this
186 study was only to describe CO_2 diffusion across the air/water interface and the newly
187 redesigned TRIPLEX-Aquatic.

188

189 **2.3 The CO_2 diffusive flux submodel**

190 CO_2 diffusion across the air/water interface (F_{CO_2}) is driven by the concentration
191 gradient between the atmosphere and surface water and regulated by the gas exchange
192 velocity *K*. Hence:

193 $$F_{CO2} = K_{CO2}(\Phi_{CO2} - pCO_{2_{atm}} K_H) \quad (1)$$

194 where K_{CO_2} is the piston velocity (cm/h); Φ_{CO_2} is the CO_2 concentration in water
195 (g/m^3); and ($pCO_{2atm}K_H$) is the CO_2 concentration in equilibrium with the atmosphere.

196 pCO_{2atm} represents the CO_2 partial pressure in the atmosphere, and K_H is the Henry's

197 constant corrected for water temperature.

198 K_{CO_2} is the piston velocity constant for CO_2 calculated as follows:

199 $$K_{CO2} = K_{600}(\frac{600}{Sc_{CO2}})^n \quad (2)$$

200 n, the exponent, was used the value 0.5, which is appropriate for low-wind systems

201 (Jahne et al., 1987). K_{600}, the piston velocity measured with SF_6 and normalized to a

202 Schmidt number of 600, was used the recently function (Vachon and Prairie, 2013) for

203 temperate lakes in Canada that determined according to lake area (LA) together with

204 wind speeds. Comparison to the power function developed for low-wind speed

205 conditions by Cole and Caraco (1998) that focused on wind speed alone, this equation

206 provided a more complete predictive model of gas transfer velocities in lakes because

207 the ecosystem size acts as the main modulator of the effect of wind speed on gas

208 exchange (Read et al., 2012).

209 $$K_{600} = 2.51 + 1.48U_{10} + 0.39U_{10}\log_{10} LA \quad (3)$$

210 where U_{10} is the wind speed (m/s) at a height of 10 m. Sc_{CO2}, representing the Schmidt

211 number for carbon dioxide, is calculated according to Equation 4 (Wanninkhof,

212 1992):

213 $$Sc_{CO2} = 1911.1 - 118.11T_W + 3.4527T_W{}^2 - 0.04132T_W{}^3 \quad (4)$$

214 where T_W is the water surface temperature (ºC).

215

216 ## 3. Model input and test data

The computational grid of the two-dimensional lake model was developed based upon the bathymetric and geometric data collected from the unperturbed oligotrophic Lake Mary (46.26º N, 76.22º W) and Lake Jean (46.37º N, 76.35º W) in Québec, Canada, with a surface area of 0.58 and 1.88 km^2, respectively. The watershed areas are 1.19 km^2 for Lake Mary and 5.43 km^2 for Lake Jean. The region has an average altitude of 230 m, and is characterized by an average temperature of approximately 5ºC, with 1000 mm of annual precipitations. Dominant tree species are red pine and yellow birch in mature. Soils are Brunisolic Luvisols. The lake areas were divided into 24 horizontal segments and 10 vertical layers. Longitudinal segments were 50 m in length for Lake Mary and 160 m in length for Lake Jean. The vertical layers were 2 m thick for both lakes (Fig. 4).

Time-varying boundary conditions at the surface of the lakes were set up with regard to meteorological influences. Hourly meteorological data, such as air average temperature, dew point temperature, wind speed and direction as well as cloud cover were obtained from weather monitoring station (Maniwaki Airport, Québec) located closet to the sites (17 km for Lake Mary, and 29 km for Lake Jean), although the meteorological data may be less accurate because it is not the local weather station. Daily inflow and constituent concentrations of DOM at branch—estimated by the TRIPLEX-DOC model (Wu et al., 2013) that is capable of estimating DOC and hydrologic dynamics in forest soils by incorporating both ecological drivers and biogeochemical processes in the age-sequence of temperate forests, then multiplyed the watershed forest landscape areas of Lake Mary and Lake Jean. They were adapted

239 to TRIPLEX-Aquatic formats—were used as time-series inflow boundary conditions.
240 Other inflow constituents—included POM, DIC, phosphate (PO_4^{3-}), ammonium
241 (NH_4^+), nitrate (NO_3^-), and DO—were compared to data from the nearby tributary in
242 Eastern Canada with sampled data (Wang and Veizer, 2000; Hélie et al., 2002; Hélie
243 and Hillaire-Marcel, 2006; Teodoru et al., 2009) because these have not been sampled
244 in the present study.

245 Hydraulic parameters governing horizontal dispersion and bottom friction were set
246 to default values using the Chezy friction model (Cole and Wells, 2006). Parameters
247 affecting constituent kinetics are also required by the model. Initially, kinetic
248 coefficients were set to default values (Cole and Wells, 2006) but subsequently tuned
249 during the aquatic carbon process calibration so that the model output agreed with the
250 field data. Kinetic coefficients were adjusted within acceptable ranges based upon
251 data in published literature (Table 1). Although site-specific data are preferable, the
252 paucity of details on hydraulic and kinetic coefficients in the lakes under study made
253 it difficult to rely on site-specific data alone.

254 To test the model, four times campaigns were conducted in the two lakes from 2006
255 to 2007 because of the remote region, during periods following ice breakup in May
256 2006 (16 sampling time points in 6 days) and 2007 (15 sampling time points in 2
257 days), summer stratification in July 2006 (10 sampling time points in 2 days) and
258 when fall overturn occurred in October 2006 (14 sampling time points in 3 days) for
259 the center of Lake Mary, and during periods in July2006 (27 sampling time points in 2

260 days), October 2006 (1 sampling time point in 1 day), May 2007 (14 sampling time
261 points in 1 day), July2007 (20 sampling time points in 2 days) for the center of Lake
262 Jean. During each field trip, surface layer samples and information on water
263 temperature, dissolved CO_2 concentrations (pCO_2) as well as DOC at 15 cm depth
264 was collected in pelagic sites of lake. An about 10 m depth profile of temperature, pH,
265 DO and pCO_2 was also carried out at the central point of lake.

266 To determine pCO_2, three 30-mL water samples were collected in 60-mL
267 polypropylene syringes from each depth and carried out within 6 h of return to the
268 field laboratory. They were equilibrated with an equal volume (30 mL) of ultrapure
269 nitrogen (N_2) by vigorous shaking for two minutes. Water was then flushed gently and
270 the gaseous phase finally injected into the gas chromatograph (GC) (Star-3400CX;
271 Varian, Palo Alto, CA, USA). Equilibrated CO_2 concentrations in the gaseous phase
272 were calculated according to their solubility coefficients as a function of laboratory
273 temperature (Flett et al. 1976). The CO_2 diffusive fluxes were therefore estimated
274 from CO_2 saturation measured in the lakes in conjunction with wind speed. DOC
275 concentration was analyzed in 0.2 μm filtered water samples in an OI-1010 Total
276 Carbon Analyzer (OI Analytical, TX, USA) using wet persulafate oxidation. In
277 addition, water temperature, DO, and pH profiles were taken with a YSI-6600 probe.
278

279 ## 4. Model calibration and validation

280 Calibration of the TRIPLEX-Aquatic model in middle segment (the center of lake)

281 was carried out by tuning appropriate model parameters to match the predicted and
282 measured data from Lake Mary in 2007 to obtain the best possible fit within
283 acceptable ranges specified by Cole and Wells (2006) (Table 1). The model was
284 verified against more data measured at Lake Mary in 2006 during which it was
285 subjected to different ambient weather and flow conditions from those prevailing
286 during model calibration in 2007, in order to test if the model was capable of
287 accurately simulating the hydrodynamic regime and aquatic carbon dynamics under
288 climatic conditions differing from those used for calibration. The model was also
289 validated against measurements taken in Lake Jean from 2006 to 2007. System
290 coefficients used in the model were the same as those determined during model
291 calibration. Measurements serve to validate model results related to water temperature,
292 pH, DO, pCO_2, DOC, and the CO_2 diffusive flux.
293

294 **4.1 Temperature, pH, dissolved oxygen, and pCO_2**

295 Hydrodynamic calibration is typically performed by examining vertical and
296 longitudinal concentration gradients of conservative constituents. Cole and Wells
297 (2006) recommend the use of temperature gradients as a first step for hydrodynamic
298 calibration. The prediction of surface water temperature for 2007 was in agreement
299 with the measured data from Lake Mary (Fig. 5a) despite high variability in the
300 calibration data. The root mean squared error **(**RMSE) for the calibration period was
301 0.95ºC. The verification of surface layer water temperature during 2006 for Lake
302 Mary and from 2006 to 2007 for Lake Jean (Fig. 5) shows sufficient agreement

between the model simulations and field measurements. The water temperature RMSE was 0.9ºC during all simulation periods in both lakes.

With regard to the validation of the vertical simulation of lake hydrodynamics and carbon cycle, the water temperature**,** pH, DO, and pCO_2 between model reconstructions and measurements were examined. Figure 5 shows that model simulation results with respect to depth were also accordant with the recorded observations: the RMSE were 0.28ºC for temperature, 0.09 for pH, 3.5 for DO (%), and 4.7 for pCO_2 during fall turnover (Fig. 6a, c, e, g), and 0.96ºC for temperature, 0.44 for pH, 11.1 for DO, and 5.3 for pCO_2 during spring stratification in Lake Mary (Fig. 6b, d, f, h). However, predicted values showed lower gradients than measured values during the spring period, especially for DO (Fig. 6f). The model also tended to underestimate water DO (%) by approximately 9% for complete profile during fall turnover (Fig. 6e).

Differences between simulated and measured DO concentration, could partly be explained by lower tributary dissolved oxygen loads, because data was compared from the nearby tributary where may region-specific differences. For thermocline had lower gradients in predicted values than actual, because the stratification is a complex integration of multiple forcing components such as mixing rates, vertical dimensions of layer, layer temperature, basin morphometry, hydrology and, most important, meteorological conditions (Harleman, 1982; Owens and Effler, 1989), thus, it is difficult to accurately simulate the thermocline without intensive meteorological data,

while the data used in this study are measured at only one nearby meteorological station. On the other hand, uncertainties resulting from the daily inflow of TRIPLEX-DOC model simulations in the upland watershed likely propagated into the simulations by way of the TRIPLEX-Aquatic model computation for waterbody, since outputs from the TRIPLEX-DOC model were used to run the TRIPLEX-Aquatic model.

Although it is importance of water temperature and thermal stratification dynamics for temporal variation of surface water CO_2 in boreal lake (Aberg et al., 2010), the RMSE of surface temperature, pCO_2 in model simulation lead to approximately 12% and 15% mean errors in CO_2 diffusive flux respectively, they had only minor impacts on lake CO_2 emission.

4.2 Dissolved organic carbon

Dissolved organic carbon, a substrate for microbial respiration, is a key constituent in aquatic carbon dynamics and could be the source of significant variations in lake pCO_2 (Hope et al., 1996; Sobek et al., 2003). Figure 6 offers a comparison between simulated and observed daily DOC concentrations from 2006 to 2007 in Lake Mary. Although the DOC values in different sampling times during daily period have significant variation while the simulated values were relative stable, simulated values were reasonably distributed in the middle of the daily observational period (RMSE=0.71). This agreement obtained during 2006 demonstrates that the model is

capable of modeling daily DOC carbon-process properties within Lake Mary.

4.3 CO_2 diffusive flux

In this study, a zero CO_2 flux was assumed during the ice cover period for the simulations. During the ice-free period, there were considerable seasonal variations in the magnitude of the CO_2 diffusive flux and a distinct seasonal cycle in both Lake Mary and Lake Jean (Fig.8). Peak fluxes occurred in the month of May following ice breakup and reached a brief, temporary minimum in early July. This minimum was followed by a second peak in late fall associated with autumnal mixing.

In comparing simulated results with observational daily data from 2006 for Lake Mary and from 2006 to 2007 for Lake Jean, the model successfully reproduced the observed distributions of CO_2 flux in both lakes, except for a daily value in autumn 2006 in Lake Jean that may be due to a single measurement. Although more systematic measurements were absent in this study, such reasonable agreement between simulated and observed hydrodynamic plots and aquatic carbon dynamic parameters demonstrates that TRIPLEX-Aquatic was able to model various hydrodynamic and aquatic carbon cycle processes within the lake systems. It can thus be applied to simulate the CO_2 diffusive flux for lakes.

5. Terrestrial DOC and lake CO_2 emissions

5.1 Seasonal and annual mean lake CO_2 diffusive flux

366 The most current estimates of the annual CO_2 emission budgets of lakes, based
367 upon measurements, only consider CO_2 produced during ice-free periods. However,
368 CO_2 produced during winter months may accumulate under the ice cover and be
369 subsequently released into the atmosphere once ice break-up occurs in spring (Striegl
370 et al., 2001; Duchemin et al., 2006; Demarty et al., 2011). This early spring CO_2
371 release accumulated during the winter should be accounted for in order to develop a
372 more realistic annual CO_2 emission budget for boreal lakes.

373 At the end of the winter season, the TRIPLEX-Aquatic model was well-calibrated
374 to capture the principal characteristics of a high CO_2 flux episode just after ice melt
375 over a period of approximately ten days (Fig. 8a, b). During this period the model
376 estimated that approximately 80% of the CO_2 contained in the water column of Lake
377 Mary and Lake Jean was emitted into the atmosphere. The values for early spring CO_2
378 emissions ranged from 5% to 8% of the annual CO_2 diffusive emission budget for
379 both lakes during the 2006 and 2007 period, which are thus an important portion in
380 the annual CO_2 budget.

381 For Lake Mary and Lake Jean, variations in daily CO_2 flux were greatest during
382 spring and fall and smallest during summer stratification (Fig. 8a, b). The average
383 summer (from July to August) values were approximately 22% to 57% lower than the
384 average calculated values for the entire open water period in both lakes, a typical
385 situation for northern temperate dimictic lakes (Hesslein et al., 1990).

386 Although there is a reasonable agreement between model simulations and field

measurements for daily CO_2 diffusive flux (Fig. 8), when comparisons are based on seasonal CO_2 diffusive flux in Lake Mary (Fig. 9a), it was noted that the observations made during the autumn of 2006 were much higher than those in the simulation. For Lake Jean (Fig. 9b) measurements taken in the summer of 2006 were lower than those in the model simulations.

5.2 Impact of terrestrial DOC on lacustrine CO_2 diffusive emissions

A large body of literature suggests net heterotrophy is the key factor responsible for the often observed supersaturation of CO_2 in lake systems (del Giorgio et al., 1999; Cole et al., 2000; Jonsson et al., 2001, 2003; Prairie et al., 2002; Algesten et al., 2003; Hanson et al., 2003, 2004; Sobek et al., 2003; Karlsson et al., 2007; McCallister and del Giorgio, 2008), but this inference is tempered by uncertainties in the magnitude of the carbon load to lakes, and the relative contributions to lake CO_2 emission (Hanson et al., 2004; Karlsson et al., 2007; McCallister and del Giorgio, 2008).

To evaluate impacts of terrestrial DOC on the lake CO_2 emission regime, a comparison between DOC inputs and CO_2 fluxes was performed where the DOC data was simulated by way of the TRIPLEX-DOC model. Figure 10 shows a positive relationship between terrestrial DOC and CO_2 flux in both Lake Mary (CO_2 flux = 15.32DOC + 132.37, $R^2 = 0.42$, $P<0.0001$) and Lake Jean (CO_2 flux = 12.68DOC + 201.9, $R^2 = 0.50$, $P<0.0001$), underlining the important role of DOC inputs in seasonal CO_2 diffusive flux variations.

To further estimate the impact of terrestrial DOC on aquatic CO_2 diffusive flux, a sensitivity analysis was carried out on the modeled results for 2006 to 2007 for both lakes by setting the terrestrial DOC inputs to zero while keeping other variable inputs at normal values, mimicking a situation in which the terrestrial DOC input would be nil. Results showed the annual mean CO_2 diffusive flux from lakes under no-DOC-input conditions were much lower (approximately 15% to 29% lower) than values with DOC inputs (Fig. 11a, b).

6. Discussion and conclusion

6.1 Comparison model with earlier approaches

There are presently only a handful of model studies (Hanson et al., 2004; Cardille et al., 2007; Buffam et al., 2011) that have tried to link terrestrial watershed carbon inputs to their aquatic components for CO_2 emission. However, integration is still pending. In this study a comprehensive process-based aquatic carbon model (TRIPLEX-Aquatic) incorporating both terrestrial inputs, an aquatic carbon cycle, and detailed hydrodynamic simulation was developed and applied to investigate aquatic CO_2 diffusion in lake ecosystems within Québec, Canada.

Although recent lake carbon models (Hanson et al., 2004; Cardille et al., 2007) integrate inputs of terrestrial DOC from watersheds, such models have no or very low hydrodynamic spatial resolution. In addition, these models do not include real-time meteorological conditions, while using constants to represent physical mixing

428 processes between spatial components. The mass balance model (Jones et al., 2009)
429 accounts for real-time metrological data for lake carbon simulation, but does not
430 include inputs of terrestrial DOC from catchments. Accordingly, the lake
431 hydrodynamic routine is less realistic than the simulation carried out in this study.
432 Moreover, previous photosynthetic estimates are based upon empirical models
433 whereas simulations in this study were based on a process-based model.

434 A previous numerical CO_2 emission model developed by Barrette and Laprise
435 (2002) illustrate the relevant approach to modeling physical processes in the water
436 column based upon an extension of the lake water column model. It was used to study
437 the temporal and spatial distribution of the dissolved CO_2 concentration profile and
438 the CO_2 diffusive flux at the air/water interface. However, this particular model does
439 not include the autotrophic and heterotrophic production of organic matter based upon
440 variables such as water temperature, dissolved oxygen, nutrient salts, and terrestrial
441 organic matter from catchments. All were included in the model used in the present
442 study.

443 For the CO_2 diffusive flux submodel in TRIPLEX-Aquatic model, although a few
444 studies have indicated that CO_2 diffusive fluxes obtained with the boundary layer
445 technique might have been underestimated (Anderson et al., 1999; Jonsson et al.,
446 2008) in comparison with the eddy covariance technique that is a direct measurement
447 of the CO_2 flux, while the studies of Eugster et al. (2003) and Vesala et al. (2006)
448 showed a good agreement. The boundary layer model of Vachon and Prairie (2013)

449 also provided no bias estimations of CO_2 evasion based on experiment in aquatic
450 systems of different size in Canada under a low-wind environment, which is similar to
451 the lakes in this study. Even though the Vachon and Prairie (2013) model in this study
452 is relatively simple, it is reasonable for estimating the CO_2 diffusive flux, partly
453 because there has been little evidence that incorporation of comprehensive surface
454 forcing provides a better flux field than simple wind speed algorithms (Wanninkhof et
455 al., 2009).
456

457 **6.2 Impact of terrestrial DOC on CO_2 emission**

458 Based on model validation, the agreement between observations and simulated
459 results indicates the model is able to capture the principal hydrological characteristics
460 and carbon dynamic processes in lake systems, it thus provides a realistic CO_2
461 diffusive flux simulation.

462 For the early spring CO_2 emissions, our model can successfully simulate the high
463 CO_2 flux episode following ice breakup events. Such emission peaks were also
464 identified by measurements in boreal lakes (Riera et al., 1999; Duchemin et al., 2006;
465 Huotari et al., 2009; Demarty et al., 2011). Duchemin et al. (2006) estimated during
466 the week following ice breakup 95% of the dissolved CO_2 contained in the water
467 column was released into the atmosphere. CO_2 emitted during this short period would
468 account for 7% to 52% of total annual emissions (Duchemin et al., 2006; Huotari et
469 al., 2009; Demarty et al., 2011). Our results are within the lower end of their estimates,

and reveal a significant CO_2 contribution during the ice break-up periods to the annual CO_2 budget of aquatic ecosystems in boreal lakes.

Concerning the seasonal and annual CO_2 emission, the differences between simulated and measured CO_2 diffusive flux values may result, in part, from the absence of systematic (or continuous) measurements of highly variable daily emissions: there are only a few daily observations for each season and these cannot accurately represent the natural CO_2 emission, thus resulting in a substantial overestimation or underestimation of seasonal, or annual flux values. On one hand, for the analysis of seasonal or annual variability, we should, in the future, use the eddy covariance measurements, which provide more frequent sampling and more accurate estimates of the CO_2 emission (Vesala et al., 2006; Jonsson et al., 2008; Huotari et al., 2011). On the other hand, it is our hope that the model simulation could contribute to the development of more effective sampling strategies, based on the characteristics of the simulated temporal CO_2 emission pattern associated with each lake.

For the impact of terrestrial DOC on lake CO_2 emission, results from this study reveal that approximately 15% to 29% of the annual CO_2 diffusive flux is due to terrestrial DOC input. Our study agree with the work ranged from 3% to 80% CO_2 flux from terrestrial organic carbon in lakes of the southern Quebec, Canada (McCallister and del Giorgio, 2008), the boreal Scandinavia (Algesten et al., 2003), and of the Wisconsin, UAS (Cole et al., 2002; Hanson et al., 2004). Our results thus support the hypothesis that a significant fraction of aquatic CO_2 diffusive flux is

491 attributable to allochthonous organic carbon inputs from lake catchments (del Giorgio
492 et al., 1999; Cole et al., 2000, 2007; Jonsson et al., 2001, 2003; Prairie et al., 2002;
493 Algesten et al., 2003; Hanson et al., 2003, 2004; Karlsson et al., 2007; McCallister
494 and del Giorgio, 2008; Battin et al., 2009; Buffam et al., 2011).

495 Sediment respiration is also an important source of CO_2 in lake system (Algesten et
496 al., 2005; Kortelainen et al., 2006; Brothers et al., 2012). To investigate the potential
497 effects of sediment dynamics on the CO_2 emission from the lake, we performed a
498 sensitivity experiment with sediment oxygen demand levels ranging from 1 to 0 g m^{-2}
499 d^{-1} in Lake Mary and Lake Jean. The mean contribution of benthic metabolism to
500 surface CO_2 diffusive emission was approximately 23% to 47%. This result is in good
501 agreement with the observed studies (Jonsson et al., 2001; Brothers et al., 2012) that
502 revealed the benthic respiration in boreal lakes representing approximately 23% to
503 50% of the total carbon production.

504 There is generally a net uptake of CO_2 from the atmosphere in boreal forests
505 (Chapin III, et al., 2000; Dunn et al., 2007), whereas, lake ecosystems seems to
506 process a large amount of terrestrial derived primary production and alter the balance
507 between carbon sequestration and CO_2 release. It demonstrates that lake ecosystems
508 contribute significantly to regional carbon balances.
509

510 **6.3 Future improvements to the** TRIPLEX-Aquatic

511 A major challenge for developing a new process-based model is the validation

512 phase. Results presented in this study demonstrate that the TRIPLEX-Aquatic
513 model is able to provide the potential to predict the hydrodynamic and carbon
514 processes in two selected boreal oligotrophic lakes (Lake Mary and Lake Jean).
515 However, our model calibration and validation are still limited by the number of
516 sample available in this study and should be improved by using more sensor network
517 data in future. Moreover, additional system verification and model testing should be
518 conducted when applying the model to lakes with different characteristics in different
519 climatic zones.

520 In addition, the aquatic carbon approach is relatively simple in the current version
521 of TRIPLEX-Aquatic. Decomposition processes of organic carbon follow first order
522 kinetics of temperature-dependent coefficients for bacterial degradation. In fact,
523 mineralization of allochthonous organic carbon occurs primarily, if not exclusively, by
524 way of bacterial degradation (Jonsson et al., 2001). Photochemical degradation
525 (Granéli et al., 1996) and its interaction with bacterial mineralization (Bertilsson and
526 Tranvik, 1998) may add substantially to overall lake mineralization. Moreover,
527 groundwater inflow (Kling et al., 1991; Striegl and Michmerhuizen, 1998) and surface
528 water (Dillon and Molot, 1997; Cardille et al., 2007) enriched in inorganic carbon
529 derived from weathering and soil respiration could be an important factor in some
530 lakes.

531 There is also increasing evidences that gas transfer near the air/water interface
532 cannot be adequately quantified using simple wind speed and lake area. Studies have

shown that other factors, such as friction velocity, bubbles, buoyancy, energy dissipation, fetch, surface slicks, rain, and chemical enhancement (Asher and Pankow, 1986; Wallace and Wirick, 1992; Erickon, 1993; Ho et al., 2000; Zappa et al., 2001; McNeil and d'Asaro, 2007; Wanninkhof et al., 2009; MacIntyre et al., 2010), can also affect the gas transfer velocities. Disregarding these factors will undoubtedly add to the analytical uncertainty in relation to the aquatic carbon cycle. These shortcomings will be addressed and minimized in the future.

It is important to point out that the TRIPLEX-Aquatic model, incorporating robust process-based hydrodynamic components, could be feasibly adapted to reservoirs in the future in spite of the fact that their hydrodynamic and biogeochemical characteristics differ from those observed in lake systems. The model can also be coupled with land surface and ecosystem models at various horizontal resolutions or forced with GCM outputs to investigate the potential impact of climate and land use changes on lake carbon cycles. It is hoped that reassessment and future investigation will generate an improved and integrative understanding of carbon flux in lakes and reservoirs as well as a better integration between aquatic and terrestrial components.

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Figure Captions

Figure 1: Modular structure of the TRIPLEX-Aquatic model. DOC: dissolved organic carbon, POC: particulate organic matter, DIC: dissolved inorganic carbon, and DO: dissolved oxygen.

Figure 2: Comparison of the CO_2 transfer velocities at the air/water interface with wind speed (Eq.1-13) at 20^{o}C in the CE-QUAL-W2 model (Cole and Wells, 2006) and in Vachon and Prairie (2013) model (Eq.14) in this study. The function of Eq.1 from Broecker et al. (1978), Eq.2 from Gelda et al. (1996), Eq.3 from Banks and Herrera (1977), Eq.4 from Wanninkhof et al. (1991), Eq.5 from Kanwisher (1963), Eq.6 from Cole and Buchak (1995), Eq.7 from Banks (1975), Eq.8 from Smith (1978), Eq.9 from Liss (1973), Eq.10 from Downing and Truesdale (1955), Eq.11 from Kanwisher (1963), Eq.12 from Yu et al. (1977), and Eq.13 from Weiler (1974).

Figure 3: Flow diagram showing key pools and flux of carbon, nitrogen, and phosphorus simulation in the lake ecosystem from the CE-QUAL-W2 model (Cole and Wells, 2006). T: temperature, P: precipitation, DOM: dissolved organic matter, POM: particulate organic matter, L: labile, R: refractory, DO: dissolved oxygen, DIC: dissolved inorganic carbon.

Figure 4: Map of the study lakes and the grid arrangement with model segment identification numbers for Lake Mary (a) and Lake Jean (b). The dark circle is sample site.

Figure 5: Observed versus predicted water surface temperatures from 2006 to 2007

for Lake Mary (a) and Lake Jean (b).

Figure 6: Measured versus simulated vertical temperature, pH, dissolved oxygen (DO), dissolved CO_2 (pCO_2) profiles in Lake Mary during autumn (21 October 2006) (a, c, e, g) and spring (14 May 2007) (b, d, f, h) periods.

Figure 7: Time series plots of measured versus simulated daily DOC concentrations in Lake Mary. Error bars represent standard deviations.

Figure 8: Time series plots of measured versus simulated daily CO_2 diffusive fluxes from Lake Mary (a) and Lake Jean (b). Error bars represent standard deviations.

Figure 9: Comparison between measurements and simulations of seasonal CO_2 diffusive fluxes for Lake Mary (a) and Lake Jean (b). Boxes indicate interquartile intervals (25^{th} and 75^{th} percentiles) while bars represent 90% intervals (5^{th} and 95^{th} percentiles).

Figure 10: Relationship between terrestrial DOC input and the CO_2 diffusive flux from Lake Mary (a) and Lake Jean (b).

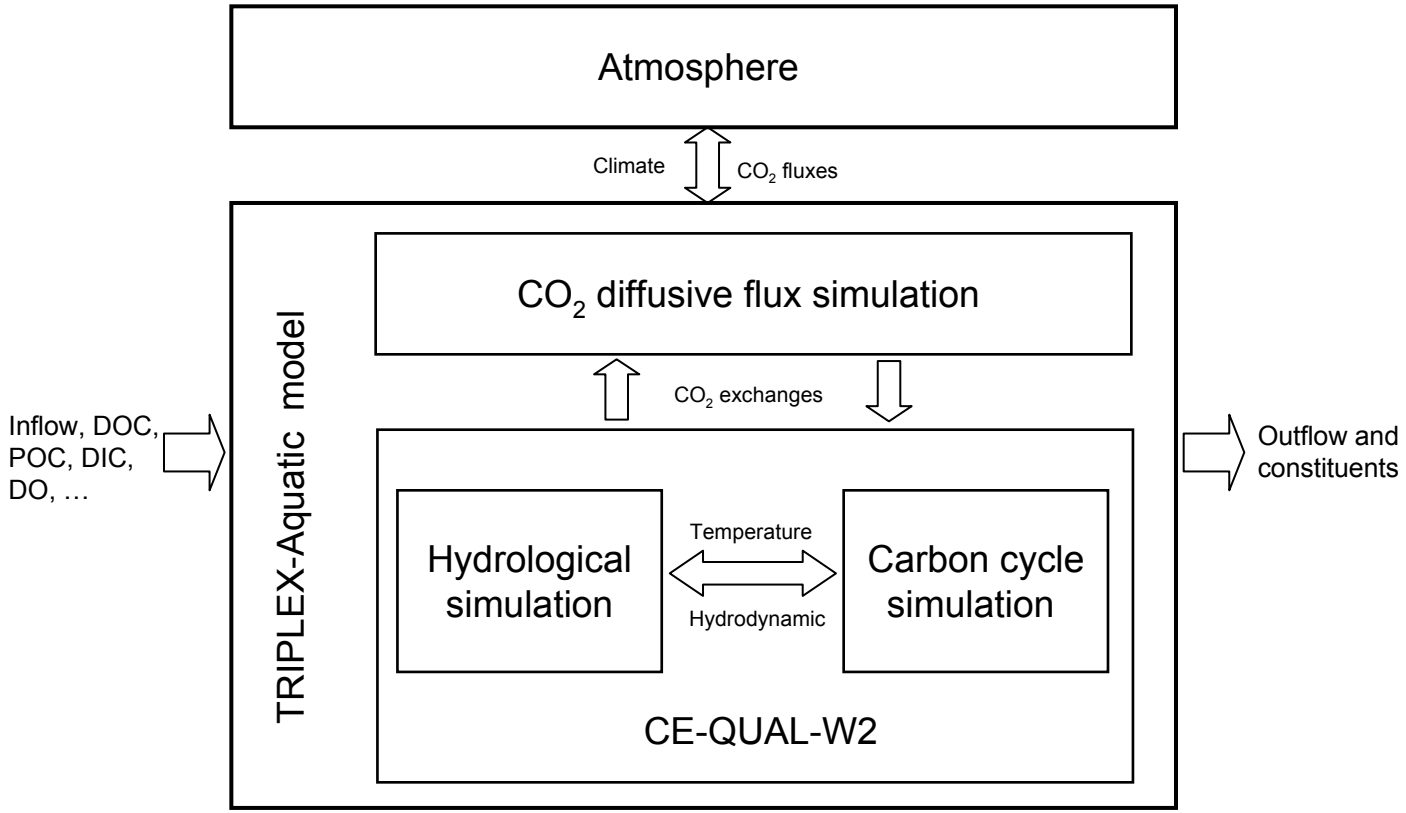
Figure 11: Sensitivity analysis for the effect of terrestrial DOC inputs on the annual mean CO_2 diffusive flux from Lake Mary (a) and Lake Jean (b). Bars represent standard errors.

907 **Table 1** Final calibration values for hydrodynamic and ecological input variables.
908

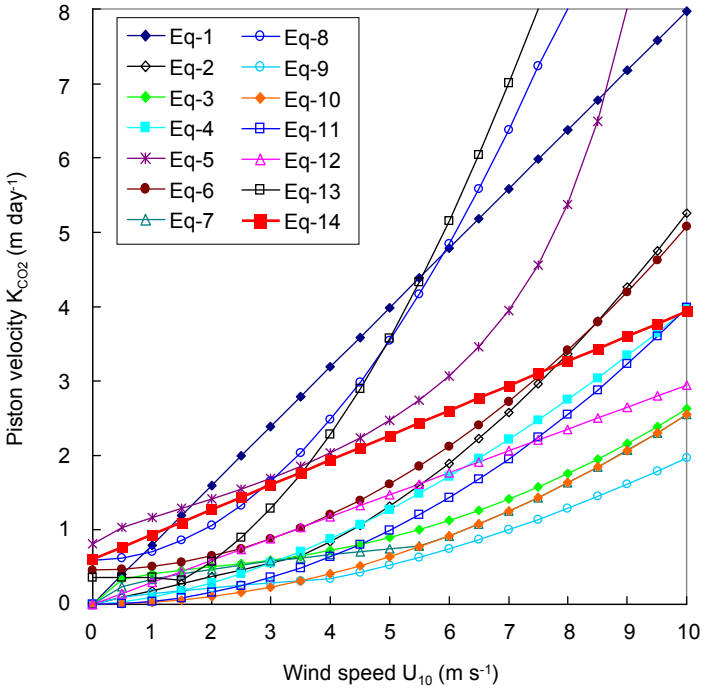
Kinetic parameters	**Units**	**Value**	**Suggested value** (*Cole and Well*, 2006)
Horizontal eddy viscosity	m^2/s	1.0	1.0
Horizontal eddy diffusivity	m^2/s	1.0	1.0
Bottom frictional resistance	m^2/s	70	70
Solar radiation fraction absorbed at the water surface	–	0.45	0.45
Solar radiation extinction – water	m^{-1}	0.45	0.25-0.45
Solar radiation extinction – detritus	m^{-1}	0.2	0.1
Solar radiation extinction – algae	m^{-1}	0.2	0.2
Wind sheltering coefficient	–	1.0	0-1.0
Zero-order sediment oxygen demand	$g\ m^{-2}\ day^{-1}$	1.0	0.1-1.0
Algal growth rate	day^{-1}	2.0	1.1-2.0
Algal dark respiration rate	day^{-1}	0.04	0.02-0.04
Algal excretion rate	day^{-1}	0.04	0.01-0.04
Algal mortality rate	day^{-1}	0.1	0.01-0.1
Algal settling rate	day^{-1}	0.1	0.1-0.14
Phosphorus half-saturation coefficient	$g\ m^{-3}$	0.003	0.003-0.009
Nitrogen half saturation coefficient	$g\ m^{-3}$	0.014	0.014, 0.03
Light saturation	$W\ m^{-2}$	50	75
Lower temperature for minimum algal rates	ºC	5	5
Lower temperature for maximum algal rates	ºC	12	25
Upper temperature for maximum algal rates	ºC	20	35
Upper temperature for minimum algal rates	ºC	30	40
Lower temperature rate multiplier for minimum algal growth	–	0.1	0.1
Lower temperature rate multiplier for maximum algal growth	–	0.99	0.99
Upper temperature rate multiplier for maximum algal growth	–	0.99	0.99
Upper temperature rate multiplier for minimum algal growth	–	0.1	0.1
Phosphorus-to-biomass ratio	–	0.005	0.005
Nitrogen-to-biomass ratio	–	0.08	0.08
Carbon-to-biomass ratio	–	0.45	0.45
Algae-to-chlorophyll a ratio	–	130	145
Ammonium decay rate	day^{-1}	0.3	0.12
Sediment release rate of ammonium	fraction of SOD	0.001	0.001
Lower temperature for ammonium decay	ºC	5.0	5.0
Upper temperature for ammonium decay	ºC	25.0	25.0
Lower temperature rate multiplier for ammonium decay	–	0.1	0.1
Upper temperature rate multiplier for ammonium decay	–	0.99	0.99
Sediment release rate of phosphorus	fraction of SOD	0.001	0.001-0.03
Stochiometric ratio of phosphorus in organic matter	–	0.005	0.005
Stochiometric ratio of nitrogen in organic matter	–	0.08	0.08

Nitrate decay rate	day^{-1}	0.05	0.05-0.15
Lower temperature for nitrate decay	ºC	5.0	5.0
Upper temperature for nitrate decay	ºC	25.0	25.0
Lower temperature rate multiplier for nitrate decay	–	0.1	0.1
Upper temperature rate multiplier for nitrate decay	–	0.99	0.99

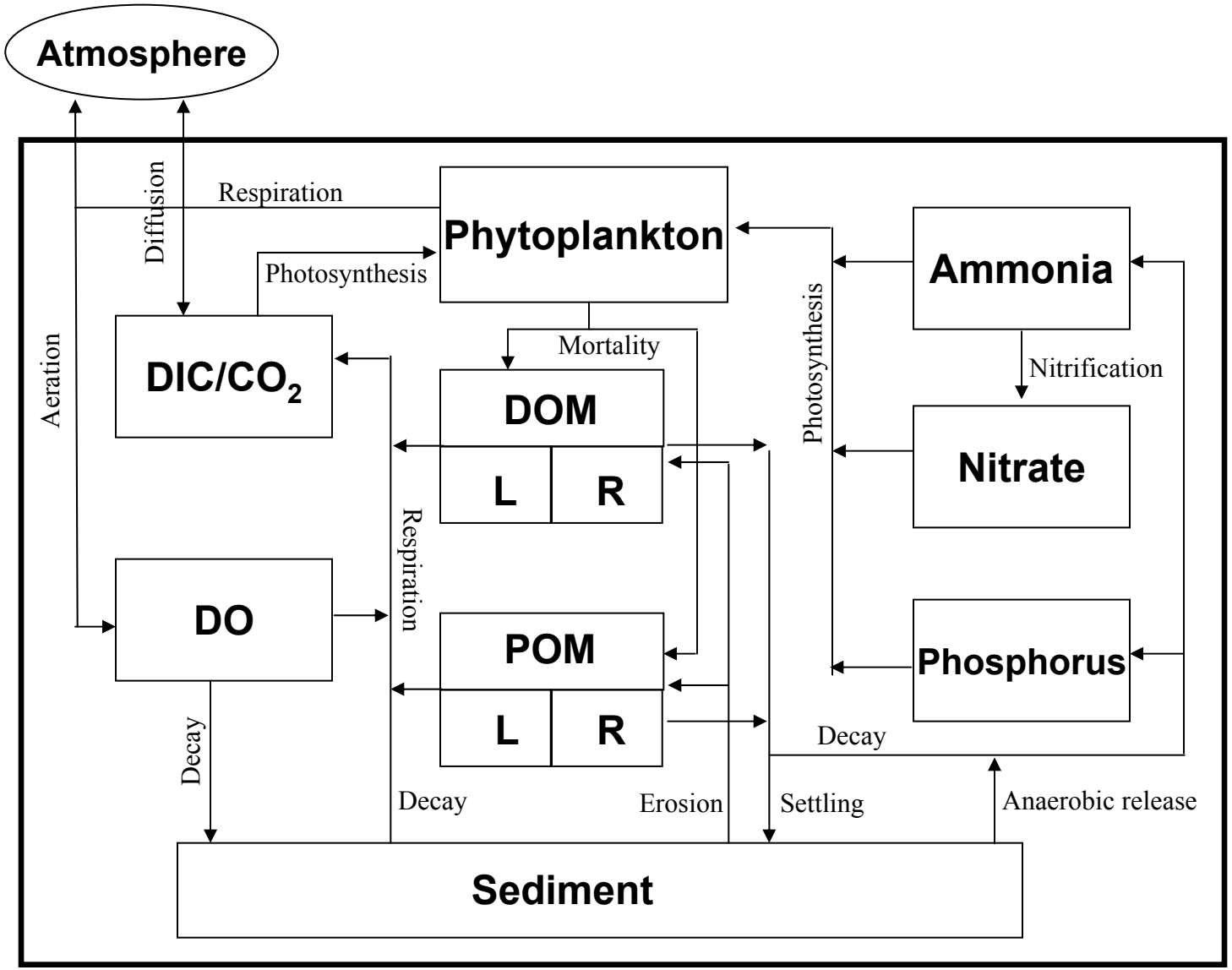
909


Atmosphere
Climate
CO_2 fluxes
TRIPLEX-Aquatic model
CO_2 diffusive flux simulation
CO_2 exchanges
Inflow, DOC, POC, DIC, DO, …
Outflow and constituents
Hydrological simulation
Temperature
Hydrodynamic
Carbon cycle simulation
CE-QUAL-W2

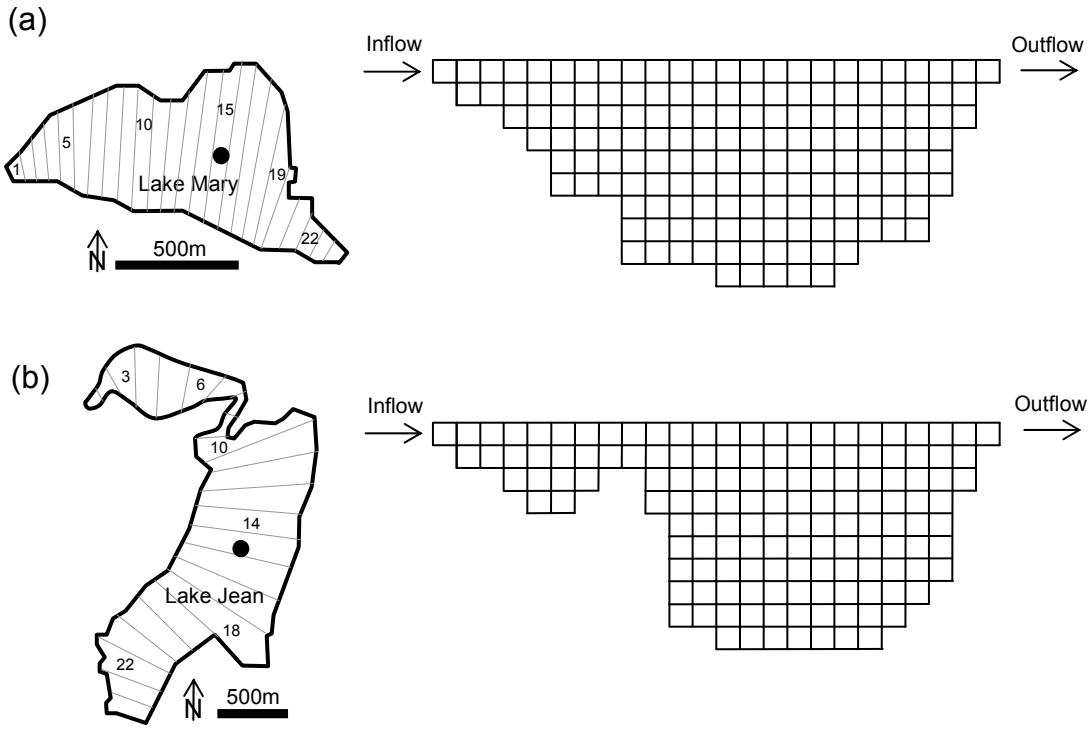
Wu et al., Fig.1


Eq-1
Eq-2
Eq-3
Eq-4
Eq-5
Eq-6
Eq-7
Eq-8
Eq-9
Eq-10
Eq-11
Eq-12
Eq-13
Eq-14
Piston velocity K_{CO2} (m day^{-1})
Wind speed U_{10} (m s^{-1})
0
1
2
3
4
5
6
7
8
9
10

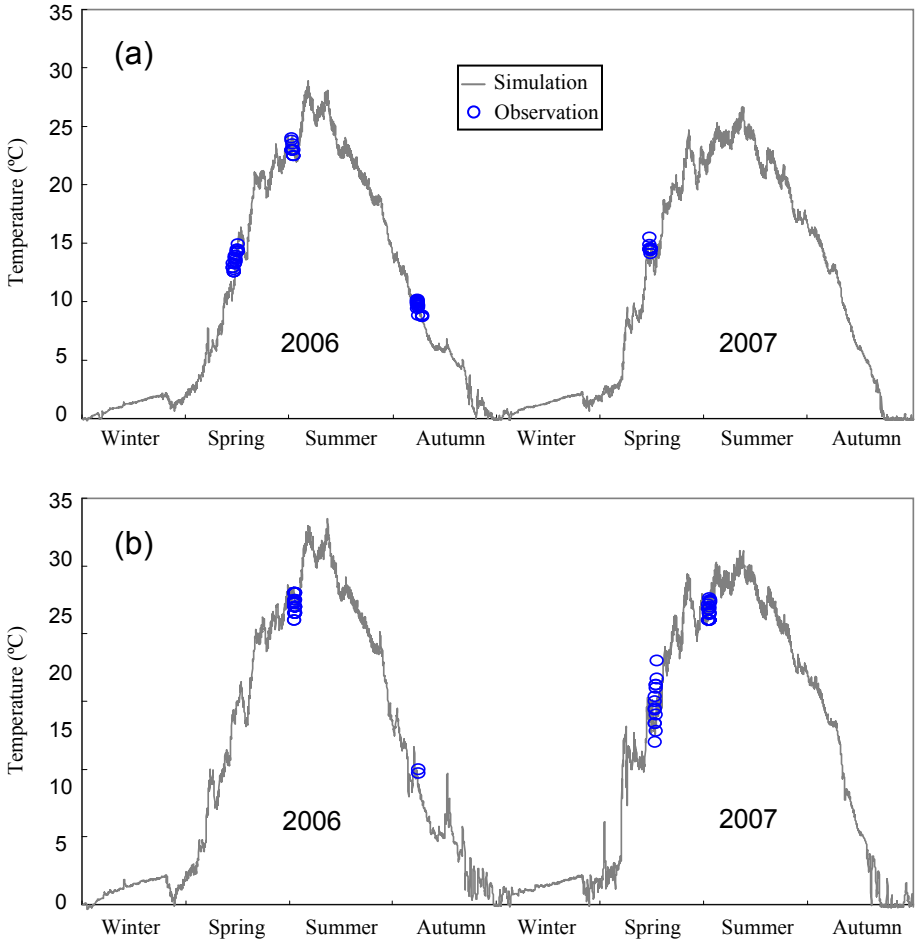
Wu et al., Fig.2


Atmosphere
Diffusion
Respiration
Phytoplankton
Photosynthesis
Ammonia
Aeration
DIC/CO2
Mortality
Nitrification
DOM
L
R
Photosynthesis
Nitrate
Respiration
DO
POM
L
R
Phosphorus
Decay
Decay
Decay
Erosion
Settling
Anaerobic release
Sediment

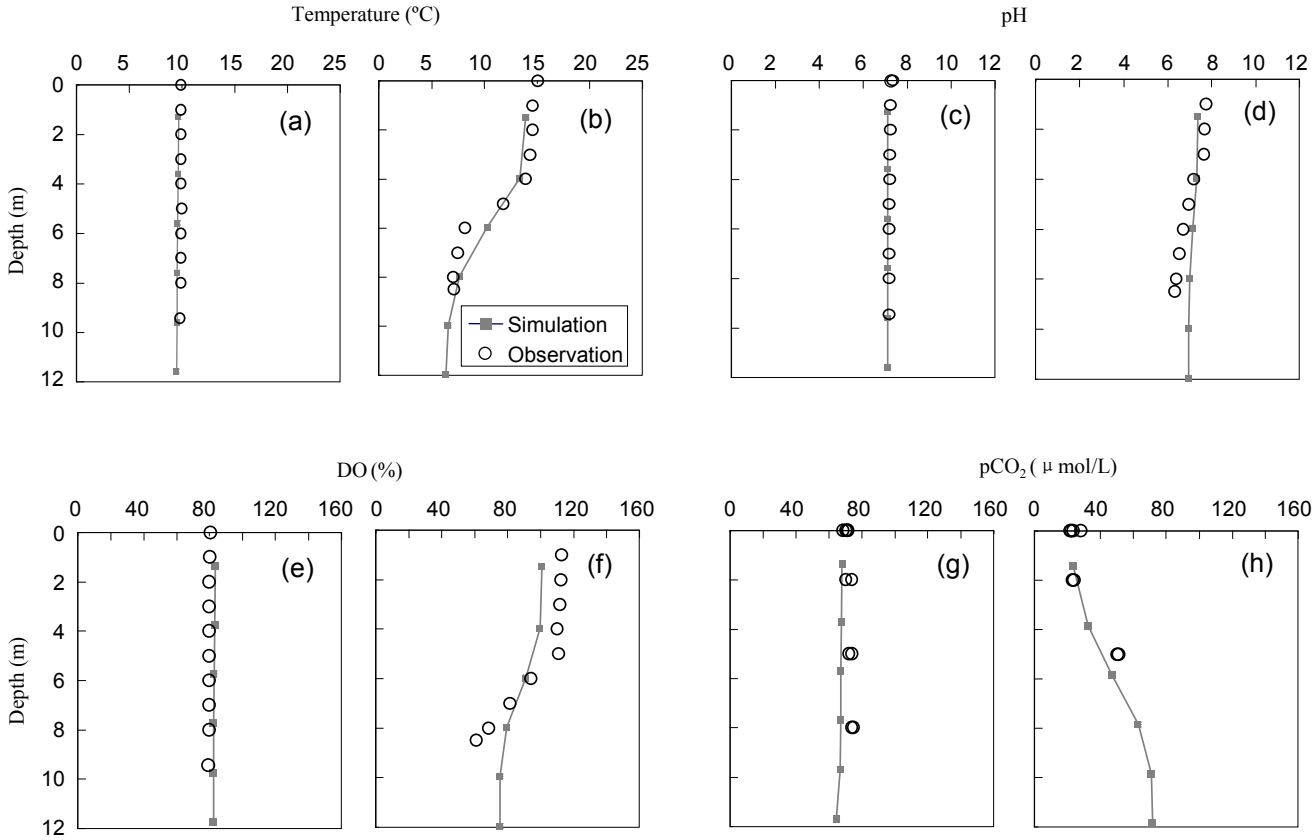
Wu et al., Fig. 3


(a)
Inflow
Outflow
1
5
10
15
19
22
Lake Mary
500m
(b)
Inflow
Outflow
3
6
10
14
18
22
Lake Jean
500m

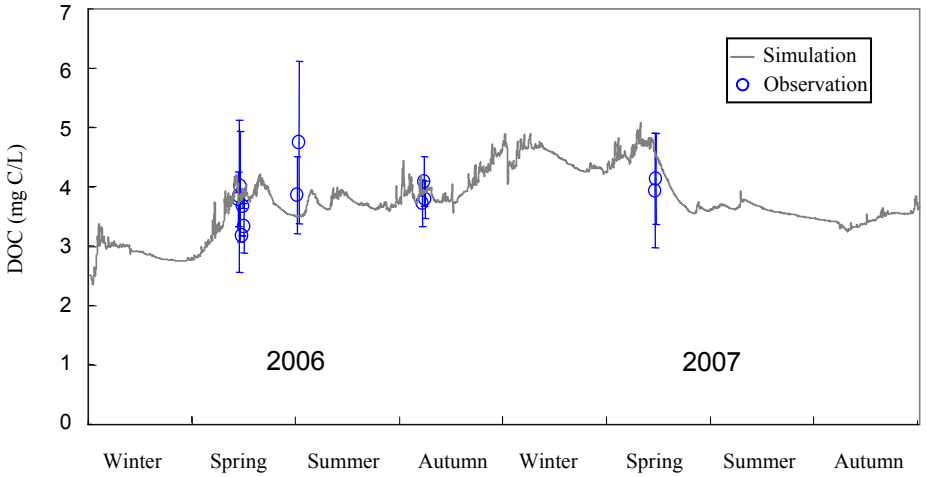
Wu et al., Fig. 4


(a)
Simulation
Observation
Temperature (ºC)
35
30
25
20
15
10
5
0
2006
2007
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn
(b)
Temperature (ºC)
35
30
25
20
15
10
5
0
2006
2007
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn

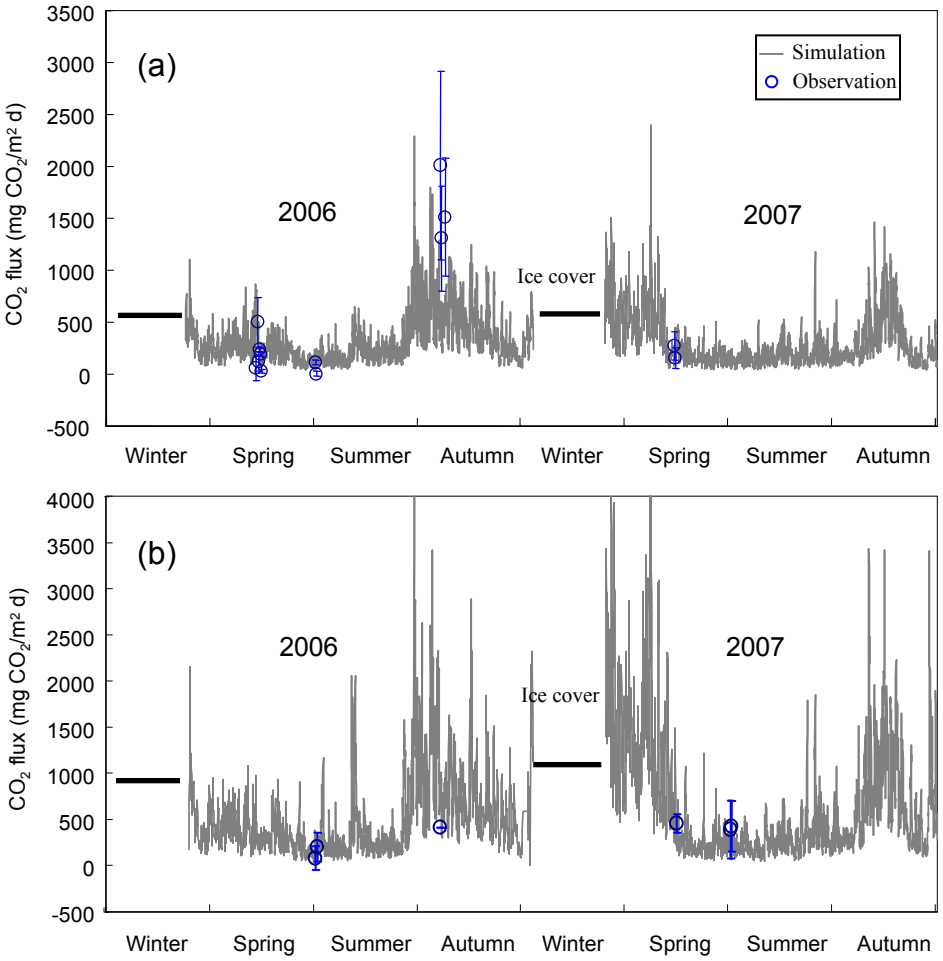
Wu et al., Fig.5


Temperature (ºC)
pH
DO (%)
pCO2 (μ mol/L)
Depth (m)
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
Simulation
Observation

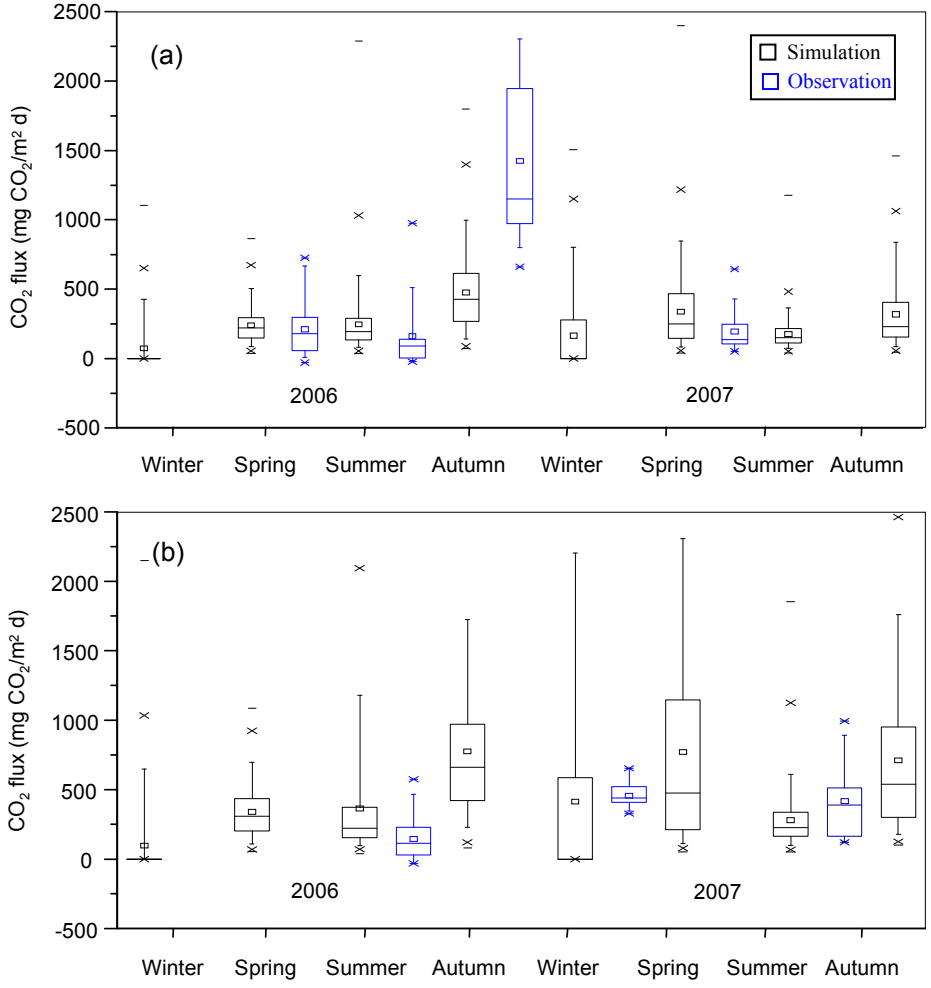
Wu et al., Fig.6


DOC (mg C/L)
0
1
2
3
4
5
6
7
Simulation
Observation
2006
2007
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn

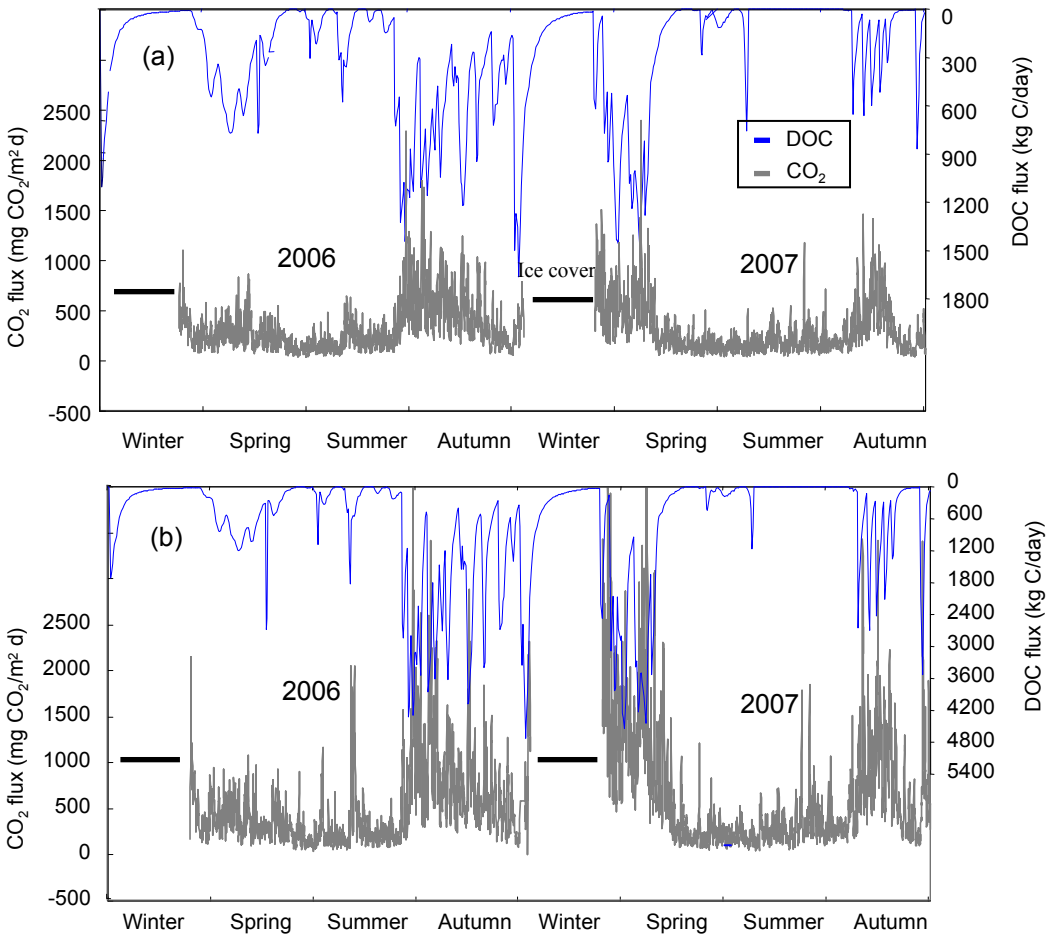
Wu et al., Fig.7


(a)
Simulation
Observation
2006
2007
Ice cover
CO_2 flux (mg CO_2/m² d)
3500
3000
2500
2000
1500
1000
500
0
-500
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn
(b)
2006
2007
Ice cover
CO_2 flux (mg CO_2/m² d)
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn

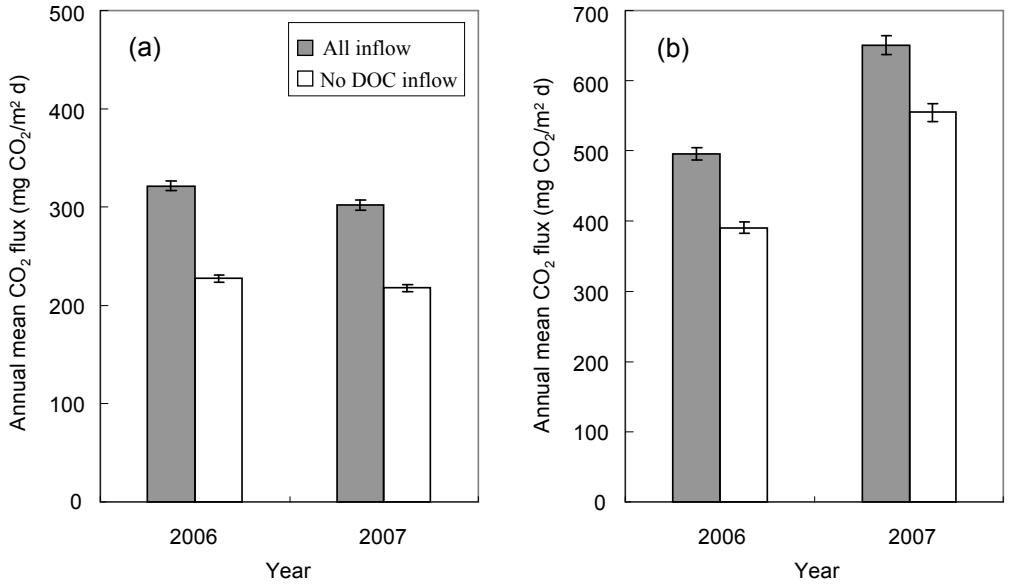
Wu et al., Fig.8


(a)
Simulation
Observation
CO_2 flux (mg CO_2/m² d)
2500
2000
1500
1000
500
0
-500
2006
2007
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn
(b)
CO_2 flux (mg CO_2/m² d)
2500
2000
1500
1000
500
0
-500
2006
2007
Winter
Spring
Summer
Autumn
Winter
Spring
Summer
Autumn

Wu et al., Fig.9



Wu et al., Fig. 10



Wu et al., Fig. 11