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Biogeosciences Discussions

Interactive comment on "Direct observations of diel biological CO_2 fixation in the oceans" *by* H. Thomas et al.

H. Thomas et al.

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We are grateful for the reviewer comments, which helped improve the manuscript significant. We have chosen to acknowledge this accordingly.

Referee 2: 1. General comments While most past studies were focused on pCO2 variations over seasonal or longer time scales, this study explores the high frequency processes in controlling the carbon cycle in the surface waters of the Scotian Shelf region over a complete annual cycle. However, the authors did not spell out how such information may help improve our overall grasp of the human perturbed marine carbon cycle or achieve better understanding of the physiology of algal photosynthesis

Response: We have not targeted our paper primarily toward understanding human per-

turbations. Rather we intend to deepen our understanding of high frequency variability of the carbon cycle as observed from bulk parameters, in order to bridge physiological and in-situ studies. Based on the below comments, which we have adopted carefully, we feel that the paper is now clearer in this respect.

Referee 2: . This is an interesting study, but the authors need to better define their goals and explicitly expound implications of their discovery. This manuscript further investigates the CARIOCA data set, which has been partially presented by Shadwick et al. (2010 and 2011). It is OK to skip some detailed descriptions of methods and materials, but, since this is a separate manuscript, it is better to include brief descriptions of methods employed or, at least, refer to the other papers or original references when alluding to data processing.

Response: We have expanded the methods section accordingly.

Referee 2: 2. Specific comments Abstract: Line 3 on p. 2154: "through processes such as heat fluxes" Heat fluxes are not a process. Solar heating is.

Response: We do not understand this discrimination.

Referee 2: Lines 6-7 on p. 2154: "limited to a time span of several days to months, or exceptionally, for longer periods." It is not clear what "exceptionally" means in this context.

Response: Thank you very much. We have replaced the statement by: "in rare cases of".

Referee 2: Lines 7-8 on p. 2154: ", however corresponding investigations of the oceanic CO2 system are lacking." "however" is not the appropriate conjunction.

Response: Thank you very much. We have replaced the statement by: "but".

Referee 2: Line 11 on p. 2154: "and its effects on annual budgets." I do not find any discussion on "its effects on annual budgets." If this refers to Fig. 4, it needs

considerable elaboration.

Response: Thank you very much. This statement refers indeed to Fig. 4 (now Fig. 5). Since these data are computed or the integration of the hourly values (and not from other rather longer-term considerations), we feel that this statement is justified as for example evident from the seasonal differences in production rates as shown in (now Fig. 5).and the significant decline of production rates toward the end of the season. We have added a statement to the text.

Referee 2: Introduction:âĂĺ Line 15 on p. 2155: Replace the comma with a semicolon in ".....2011), however corresponding investigations of. . ."

Response: Thank you very much. Done.

Referee 2: Lines 2-11 on p. 2156: "Controls of the seasonal to interannual variability of the surface CO2 system . . ..The study, presented here, sheds light on the role of high frequency processes in controlling the carbon cycle in the surface waters of the Scotian Shelf region over a complete annual cycle." It is highly desirable to spell out what insights the authors expect to gain from the high frequency processes and how those may help us better understand the marine carbon cycle.

Response: Thank you very much. We have added the following statement to the text: In particular, we shall investigate the occurrence of processes with diel periodicity, and how their occurrence is controlled and how they contribute to seasonal and annual patterns of the surface water CO2 system on the Scotian Shelf.

Referee 2: Material and Methods:âĂĺ Lines 1-3 on p. 2157: "In an attempt to resolve the contribution of phytoplankton. . ., we derived chlorophyll a concentration . . . Nahorniak et al. (2001)." It is necessary to qualify "chlorophyll a concentration." Is it the chlorophyll a concentration at sea surface or certain specific depth or the average over certain depth range?

Response: Chlmod was derived from attenuation calculated between 5 and 6 m. This

depth interval was chosen to be as close to the CARIOCA sensors (2 m) as possible, whilst excluding noisy Ed data caused by surface light wave focussing. We have clarified this by modifying the passage as follows:

"In an attempt to resolve the contribution of phytoplankton to NCP during the warming period, we derived chlorophyll a concentration between 5 and 6 m from profiles of Seahorse Ed(ïĄň) using the model of Nahorniak et al. (2001). This depth range was chosen to be as close to the depth of the CARIOCA sensors (2 m) as possible, whilst preventing the inclusion of noisy Ed data due to surface light wave focussing. The model required that the attenuation of Ed at three wavelengths (412, 443, 555 nm) over a depth interval (5-6 m) be calculated, but since the sensor wavelengths (379.3, 442.9, and 491) did not exactly match the wavelengths required by the model, Ed(ïĄň) was first interpolated to model wavelengths. Modelled chlorophyll a (Chlmod; mg m-3) at an average depth of 5.5 m (i.e. half way between 5 and 6 m) was then calculated. . ."

Referee 2: Lines 11-14 on p. 2157: "Chlmod values were compared with discrete, . . . (RMSE) values of 0.89 and 0.83 mg m-3 (N = 8) respectively, were obtained." It would be better to present the validation plot, because the statistical parameters do not necessarily reflect the goodness of fit or the reliability of the modelled chlorophyll a values. One may argue that the range of chlorophyll a variation shown in Fig. 4 is considerably smaller than the RMSE (0.83 mg m-3), and, therefore, not meaningful.

Response: As per your suggestion, we have now included a plot of measured versus modelled Chl a. (Fig. 2c, attached). Please note that the statistics have changed compared with the original manuscript, as an error was found in the calculation code. Your point regarding the validity of the modelled values given the large RMSE is well made, and we discuss this in the Discussion section as shown below:

"In order to determine whether this reported periodicity in metrics of phytoplankton photosynthetic activity occurred at our study site, we bin averaged Chlmod over the 40-day warming period (days 160-200). This revealed a diel cycle with a difference of

$\sim$30% (0.13 mg m-3) between minimum and maximum values, and where the lowest values corresponded to low PAR levels during early morning and late afternoon, and maximum values to peak PAR at $\sim$midday (now Fig. 4d). It should be noted at this point that the daily Chlmod excursion is small compared with the RMSE of 4.31 mg m-3 (new Fig. 2c) indicating that quantitative interpretation of Chlmod results should be made with caution. However, even if not a truly quantitative estimate of Chl. a, the Chlmod pattern observed at our study site is very similar to those observed in other studies of optical signals that have been interpreted as the combined effects of processes that included daily primary production, phytoplankton sinking and zooplankton grazing (Gardner et al., 1993; Marra, 1997; Stramska and Dickey, 1992; Gernez et al., 2011)."

Referee 2: Results and Discussion: Lines 5-6 on p. 2158: "We corrected the observed pCO2 data (pCO2,obs) to a daily mean temperature to give pCO2,temp." Calculation of pCO2,temp is not trivial, but there is no mentioning of the method any where in the ms.

Response: Thank you very much. We agree that our explanation was too short. We have added a statement to the methods section.

Referee 2: Lines 7-10 on p. 2158: "The difference between pCO2,obs and pCO2,temp yielded pCO2 data that are governed by processes other than temperature within a 24-h period. Since we did not detect processes other than SST variability acting on the 24 h period, the remaining pCO2 10 variability can be ascribed to biological activity (pCO2,bio)." To what degree does air-sea exchange of CO2 affect pCO2? Will it interfere with the signal? If not, why not?

Response: Thank you very much for pointing to this omission. We have added the following statement: CO2 air sea fluxes play a very minor role on the surface layer DIC concentrations, such that the feedback between pCO2 and CO2 air-sea fluxes is negligible at the 24h time scale.

Referee 2: Lines 13-14 on p. 2158: "With the onset of the spring bloom, at approx-

imately day 90, the diel amplitude drastically increased (Fig. 3a)." It looks to me the spring bloom started after Day 95 instead of on Day 90, if it did occur as suggested by the authors. Is there any other evidence, such as Chl-a data, indicating the occurrence of the spring bloom?

Response: Thank you very much, we agree. This has been discussed by Shadwick et al. (2011, Mar Chem), and the bloom starts at around April 6th, which is around day 96. Surface Chl. A values have been shown in this paper in Fig. 16. We have added a reference to this paper in the text.

Referee 2: Lines 23-25 on p. 2158: "More importantly, a phase shift was detectable between pCO2,obs and pCO2,bio, with the latter occuring approximately 3 h earlier than the pCO2,obs (Fig. 3d)." It is not clear how Fig. 3d is constructed. Some description is necessary. Why the phase shift occurs only in this period but not in the other two deserves some explanation. "occuring" should be "occurring.".

Response: Thank you very much. Here we also intended to refer to Fig. 3c (now 4c) and to Fig 3d (now 4d). Also we have added a statement to the methods section, how the diel cycles were obtained.

Referee 2: Lines 7-8 on p. 2159: "NCP, indicated by a negative gradient in the pCO2 anomaly (Fig. 3d), dominates the system until dusk." "Gradient" is often referred to in a spatial sense rather than temporal sense. "Negative slope" may be a better term.

Response: Done.

Referee 2: Lines 11-13 on p. 2159: "The corresponding respiration rate, assumed to be constant throughout the day, is estimated to be 0.05 μmolC(l h)1; the rates of NCP and GPP are 0.26 μmolC(l h)1 and 0.31 μmolC(l h)1, respectively, both lasting approximately 10 h per day." It will be more convincing, if the estimated values are reasonable as compared to direct observations in the same area and the same season.

Response: Thank you very much. We have added now a comparison with the work by

Forget et al. (2007, MEPS), who report GGP rates of 1-3 μmol C (L d)-1.

Referee 2: Lines 2-5 on p. 2160: “we used the model of Nahorniak et al. (2001) to derive estimates of chlorophyll-a concentration (Chlmod; mg m3) every two hours during daylight from SeaHorse profiler measurements of multispectral downwelling irradiance, Ed().” The statement is redundant; the info has been given in Materials and Methods.

Response: This statement has now been deleted and the sentence modified to read, “In order to determine whether this reported periodicity in metrics of phytoplankton photosynthetic activity occurred at our study site, we bin averaged Chlmod over the 40-day warming period (days 160-200). This revealed a diel cycle with a difference of $\sim$30% (0.13 mg m-3) between minimum. . .”

Referee 2: Line 10 on p. 2160: “the change in gradient of pCO2,bio from positive to negative” “Gradient” should be slope.

Response: Done.

Referee 2: Lines 11-13 on p. 2160: “In other words, our data suggest that a threshold Chlmod must first be attained before the system achieves net CO2 drawdown.” “Chlmod” should be chlorophyll concentration. Since net CO2 drawdown still persisted after the Chl value dropped below the apparent “threshold value,” it is better to modify the statement by inserting “during the growth phase” after “attained.’

Response: Changed as suggested.

Referee 2: Lines 6-7 on p. 2161: “We have obtained the seasonal dynamics of NCP integrating the hourly pCO2,bio values (Fig. 4.). The maximum value of NCP is 3.4 molCm2, or 271 μmolC L1.” What is the time period pertaining to the NCP values mentioned here, “mol Cm2 d-1, and “μmolC L1 d-1”? Again some comparison with observations would make the estimates more convincing.

Response: These figures describe the accumulated effect of the diel pCO2,bio variability at a given time We inferred the rates from the slope of these figures. We have

added a statement to the caption of this figure. Also, we referred back to the work by Forget et al. (2007, MEPS), who report GGP rates of 1-3 μmol C (L d)-1. Furthermore, we discuss now the estimate by Charette et al. (2001).

Referee 2: C835 Conclusions: Lines 16-17 on p. 2161: “In summary, we observed a statistically significant diurnal periodicity of the CO2 system only during the period, when the water is warming.” It is worth some discussion why significant diurnal periodicity of the CO2 system occurs only during the warming period. Is mixing too strong during other periods, when strati- fication is weaker, so that the diel signal of pCO2 is obscured.

Response: We very much appreciate this comment. We now have added some thoughts about this in the results section when discussing Fig. 4 (formerly Fig. 3).

Referee 2: Figures: Fig. 1b. It should be specified in the legend that the blue crosses indicate the MLD.

Response: We have added a statement.

Referee 2: Fig. 2c “High coherence at the 24 h period occurs only during the period when the water is warming.” This plot takes considerable space but little is said about it. The figure caption is rather confusing. To me high coherence at the 24 hour period occurred from March to mid July, not just Day 160-200.

Response: We have inserted two statements in order to clarify this: in the methods section, and in the caption of (now) Fig 4.

Referee 2: Fig. 4. “Annual cycle of biological DIC uptake.” It is not clear how this plot was made or the meaning of it. If it is about DIC uptake, it should show units of rate. The caption mentions “mixed layer inventory,” which is confusing and needs explanation.

Response: We have added a statement to the caption of this figure (now 5).

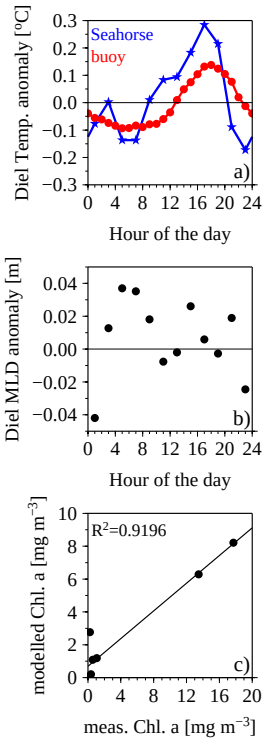

Fig. 1. added figure 2