Response to Anonymous referee #1

We thank the referee for his/her comments on the article. We acknowledge that these comments helped to improve the manuscript significantly. We reply to each comment separately. The referee comments are shown with black text in italics. The response is given in blue color. The page, chapter and row numbers used here refer to the original manuscript, as the revised manuscript will not be available in the discussions section.

General comments

The paper presents and discuss one year of continuous measurements of marine CO2 concentrations, gathered at the marine monitoring station of Utö island, in the northern area of the Baltic sea. Overall this article addresses a timely topic and the results presented can substantially contribute to improving estimates of the CO2 emitted and absorbed by the Baltic Sea.

Marine data are mainly gathered by a flow through system that pumps seawater from 5 m depth and 250 m from the coast, allowing continuous measurements of the basic physical parameters as well as dissolved oxygen, fluorescence and CO2 partial pressure (pCO2) also during harsh wintry conditions. The marine dataset is completed with direct measurements of air-sea CO2 fluxes gathered by a flux tower on the seashore and high quality atmospheric CO2 measurements acquired at the nearby meteorological station, making this dataset new and extremely valuable.

The data are analyzed to highlight the seasonal variability, the diurnal pCO2 cycle and to identify its main drivers. Finally, the authors estimate the bias that can be introduced calculating annual budget of the Baltic CO2 air-sea fluxes without taking into account this daily variability.

The main point where the paper needs a substantial improve is the overall writing and presentation of the methods and the results. I also recommend a revision of English style.

The authors agree that the writing and presentation require polishing in order to make the manuscript more approachable. We carefully went thought the manuscript again. Additionally, as we have no native English speakers amongst the authors, the manuscript underwent a professional English proofreading.

Methods used look generally adequate but are poorly written: you have to go back and forth the pages to understand what has been measured and where, and they often lack of detailed information on accuracy both on measured and calculated parameters. The model proposed to separate the different drivers of CO2 variability needs a better discussion mentioning also the variability that can derive from the advection of different water masses. Some trends presented in figure 6 and 7 are unexpected and need a better discussion.

We made multiple changes in the methods section. These changes include:

- We revised the structure by dividing it into the flow-through measurements, other measurements and calculated data.
- We added more information on the measurements including accuracies.
- We added a map and short introduction of the study site.

In the results, we added discussion on the discrepancies between the modelled and observed pCO2 changes, including the effects of air-sea exchange of oxygen, mixing processes and estimation of the mixed layer depth.

More information on these updates is given in the replies below.

The conclusions can be improved adding a comparison with other coastal areas / previous studies, where similar data are available.

A comparison to different coastal areas was added in the conclusions section. These include the following:

P20R1:

"Multiple processes affecting the diurnal pCO2 variability at Utö were distinguished and their interplay depended on season discussed, similarly as found for the East of Gotland by Wesslander et al. (2011)"

P20R2:

"The diurnal pCO2 pattern was not clearly observed in winter time, which is in agreement to the observations in the Baltic Proper (Lanso et al., 2017)."

P20R3:

"Thus, on average, the magnitude and the timing of the diurnal pCO2 variability at Utö are similar to the ones of the pelagic conditions in the Baltic Proper, found in other studies (Wesslander et al., 2011, and Lanso et al., 2017). However, the large diurnal pCO2 signals created by upwelling indicates the stronger coastal influence at our study site."

Specific comments

Please, revise the title: the paper discus the daily variability of pCO2, and related airsea CO2 fluxes, not of other parameters of the CO2 system as carbonate saturation state, DIC, pH...

The title was changed accordingly to "The diurnal cycle of the pCO2 in a coastal region of the Baltic Sea".

Section 2 "Controls on the partial pressure of CO2"

This section is rather confusing. It summarizes some basic aspects of carbon chemistry and, at the same time, explains which can be neglected in the study area. I would suggest to present here the basic of carbon chemistry, with clear references to the pendix, and move the considerations on which process is important for the area, after the presentation of the study site, where the calculation performed are explained.

Only the basics of carbon chemistry is now briefly introduced in this section. The site-specific considerations (Chapter 2.4) were moved to a new chapter, 3.8 "The included processes controlling pCO2".

3 Materials and methods

Please, add a map with the location of Utö island, the station and the different sampling locations mentioned in the paper. The reference (Laasko et al 2018) includes mainly a description of the atmospheric station. This paper could be a good opportunity to present the Utö marine station with a table summarizing instrument type, variable measured, frequency etc.

A map showing the sampling locations was added (see the next figure and its caption) in the beginning of the methods section.



Sampling locations at Utö Atmospheric and Marine Research Station. The grid size (distance between plus signs) is 1 km. The smaller figure on the upper right corner shows the location of Utö (orange star). The National Land Survey of Finland is acknowledged for providing the map.

The different marine stations are now shortly introduced in the beginning of the methods section: "The marine observations include, but are not limited to, CTD casts carried out northwest from the island, flow-through analyses at the Marine station and thermistor measurements in the vicinity of the inlet of the seawater inlet (Fig 1)."

Also, a reference to the up-to-date observation list was added in P4R20: "For the complete list of observations, visit Finnish Meteorological Institute's web site (https://en.ilmatieteenlaitos.fi/uto-observations). Site bathymetry and other information about the study site are given by Laakso et al. (2018) and Kraft et al. (2021)."

The description of the instrumental setup and the whole method section is quite confusing and needs a reorganization where the description of measured data is clearly separated from calculated parameters and experimental considerations. I would suggest the following:

Improve the description of the study site providing general physical and biogeochemical settings of the study area. Describe the different stations where data are gathered and sampling strategy of all the data presented and discussed in the paper.

* Measurements from the flow-through system: instrument used, parameters acquired, frequency, accuracy, etc.

* Measurements from other stations: manual samplings, laboratory analysis, method, accuracy.

* Assessment of data quality etc.. you could add a separate section or add a sentence where there is the description of data acquisition.

* Calculated data: describe how you calculated all the derived parameters and estimate the uncertainty on derived carbonate system variables.

The methods section was divided into the following sections as suggested by the reviewer: flowthrough measurements, measurements from other sampling locations and calculated data. The methods section starts now with a short introduction to the different components of the marine station: a map of the sampling sites and additional text describing the sites were added. Information of the data accuracy and quality of each variable was added after the introduction of each variable.

The description of the biogeochemical setup was added in the beginning of methods section P4R14: "As the whole Baltic Sea, our study site is affected by climate change induced increase of sea water temperature (Laakso et al., 2018). Besides the warming trend, also stratification has strengthened affecting the connectivity between water layers separated by seasonal thermocline and halocline (Liblik and Lips 2019). Long-term trends in alkalinity show increase throughout the Baltic Sea, partly compensating CO2-induced acidification (Müller et al, 2016). Within our study region, phytoplankton blooms are a recurrent phenomenon due to eutrophication (e.g. Kraft et al., 2021).

The following references were added:

Liblik, T., and Lips, U.: Stratification has strengthened in the Baltic Sea – An analysis of 35 years of observational data, Front. Earth Sci., 7, 174, doi: 10.3389/feart.2019.00174, 2019.

Kraft, K., Seppälä, J., Hällfors, H., Suikkanen, S., Ylöstalo, P., Anglès, S., Kielosto, S., Kuosa, H., Laakso, L., Honkanen, M., Lehtinen, S., Oja, J., and Tamminen, T.: First application of IFCB high-frequency imaging-in-flow cytometry to investigate bloom-forming filamentous cyanobacteria in the Baltic Sea, Front. Mar. Sci., 8, 594144, doi: 10.3389/fmars.2021.594144, 2021.

P8 The description of the calculation done is rather hard to follow. The DIC derived from mixing with other water masses is not considered in your model. Why? If you consider that this is a minor component of DIC variability in the study area, you should explain and justify your choice.

Mixing is an important process that alters the DIC, but the estimation of its magnitude is challenging. For this reason, we added the following in the chapter that deals with the included processes controlling pCO2:

"In general, the tidal force is the most prominent process to generate a diurnal pattern on the mixing of the DIC. In this location of the non-tidal Baltic Sea, the effect of tidal currents on the water masses are

very small and thus we can neglect their effect. However, several other processes such as coastal upwelling can also generate mixing. The driving force of upwelling (or downwelling) is steady wind over the sea from suitable direction, and at our study site, close to open sea which contains very small islands, sea-breeze cannot be completely neglected but is not expected to be strong. However, there is a possibility that the density driven mixing has a diurnal cycle due to the strong diurnal pattern of solar irradiation.

The mixing component of the diurnal DIC variations can be large occasionally. For instance, there was clear indications of the mixing of water masses on July 22, 2018; the pCO2 varied 503 uatm while the water cooled by 8 °C. However, there is not always that clear indicators hinting to the mixing events. In order to analyze the effect of the mixing of DIC precisely, one has to know the 3D field of DIC and the water currents. This would require an array of carbonate system measurements, which we do not have. The analysis of the mixing of DIC is beyond the scope of this paper."

We reckon that the mismatch between the observed and modelled hourly pCO2 variations (as seen in Fig. 8) may be partly due to the effect of mixing of water masses with differing DIC content. There is a clear seasonal pattern visible in the slopes between the observed and modelled hourly pCO2 changes. For this reason, we added the following in P18R16:

"Also, our crude estimation of mixed layer depth may introduce an error in the modelled pCO2 change. It is possible that in spring, the mixing of DIC may be incomplete and the calculated mixed layer thus too deep. This causes the gas exchange of oxygen to be underestimated through Eq. 4, which further causes the biological pCO2 component to be too low. In autumn, the calculated mixed layer depth might be too shallow to represent the real mixing of carbon, as it is defined as the bottom layer depth in the cases when the mixed layer at the CTD location was found deeper than the bottom layer depth in the inlet location. It is possible that there is lateral mixing with the deeper areas. This would cause the gas exchange to be overestimated and the biological pCO2 component to be too high."

We also changed the figure 8 that shows the modeled vs observed pCO2 change to density plot that shows more clearly how the observations are distributed. This plot highlights that most observations are packed close to origo.

The most variation in our model originates from the biological component we added more discussion on the possible effects of air-sea exchange of oxygen on the biological component. The following were added in P18R16:

"It is possible that the seasonal slope changes in Fig.10 are due to the fact that the oxygen concentration change by the O2 flux is not well-described. There can be a lag between the air-sea O2 flux and the O2 concentration change at 5 m depth. It is likely that the wind speed-parameterization of O2 flux gives good estimate of the flux, but the flux at the surface is challenging to translate into the O2 concentration changes at 5 m depth at one hour resolution. In summer, the oxygen flux is directed from the sea to atmosphere, and thus its effect on the biological component should be positive. If this process is not taken into account, we might end up with an underestimated biological component, i.e. low slopes in Fig 10. In winter, vice versa would happen."

We dove little deeper in the model analysis than is shown in the manuscript. For instance, we learnt that the effect of the oxygen flux on the biological component is most important during the winter months: the change of oxygen generated by the air-sea exchange is large compared to the oxygen change. During winter months, the oxygen flux is positive and we also observe too strong modeled pCO2 component. When the oxygen flux is negative and the effect of the oxygen flux on the biological component is small in summer, we observe too low modeled pCO2 change.

The 4.2.5 chapter was slightly reorganized due to the addition of these new paragraphs. Also, the paragraph dealing with R2 values was removed as a redundant. The R2 values are still visible in the figure.

4 Results and discussion

Section 4.2: why did you choose two days one after the other as an example? You could present two days from two different seasons or where the weight of the diverse pCO2 components is different. Otherwise you can show only one day of pCO2 data and add a picture with the daily variability of the other variables (temperature, oxygen,: ::).

Two consecutive days were selected in order to show that the variability can be large within just two days. However, the referee's suggestion is convincing as it reflects the seasonality of pCO2 diurnal cycle. We therefore now selected days from late summer (3 September) and winter (12 December). The late summer day is the same one that was in the original manuscript.

The following text was added on P11R10:

"The pCO2 on December 20, 2018, was decreasing, almost linearly (Fig. 3b). This example was chosen in order to show that the biological variation in winter is low, and the oxygen is primarily altered by mixing and air-sea exchange of oxygen. Both the air-sea exchange of carbon and cooling of water strive to decrease the pCO2."



P13: Add a description of the daily variability of temperature to improve the discussion and to allow a better comparison of your results with other areas

We gladly followed this advice. For this reason, we calculated monthly averages of daily temperature ranges (daily maximum temperature – daily minimum temperature).

This text was added in P13R7:

"The daily variation in seawater temperature follows the cycle of solar irradiation. The highest monthly average of daily temperature ranges (daily maximum temperature – daily minimum temperature) was in July with 1.6 degC and the lowest in February with 0.2 degC."

Both in figure 6 and 7 the data reported at h 00:00 are often markedly different from that reported at h24:00: they should be the same number or a very close one. Could you please explain better the data reported in your figures or double check your calculation?

The time windows are not completely identical. We added the following explanation in P10R14:

"In all of the following figures, the pCO2 difference between times, t2 and t1, is plotted in the middle of t1 and t2. The first point at 00:00 represents the pCO2 difference between 00:00 and 01:00 UTC, and the last point represents the difference between 23:00 and 24:00."

Figures

Figure 1: It contains a lot of information but I found it hard to read. Please, increase the size along the "y" axis. Fig 1 (a): it's hard to see the red crosses and the black line. Is this temperature from monthly CTD casts in the nearby station? You should mention it in the caption. You could also present just the top of the CTD casts, down to the depth of the seafloor at the inlet position, and highlight the depth of the inlet to the flow-through system. Please add the conversion to local time in the caption as well.

The size of the y axis, the red crosses and the black line were increased. The top graph shows the temperature from the CTD casts; a mention of this was added. The time zone was included in the caption.

Originally the figure 1 had five subplots and the figure 2 had only three subplots. The subplots in figure 1 were too tightly packed. For this reason, the oxygen plot was moved from figure 1 to figure 2.



Figure 2: Please, increase the size of the figure and of the symbols in the captions within the figures, especially that of figure 2 (b).

The size of the symbols in the legend of flux subplot in Fig 2 was increased. Note also that the oxygen plot was moved here, and we added the saturation concentration of the oxygen. The color coding of



the fluxes was modified in order to avoid confusion with (a) and (d) plots.

Appendix D

The gas transfer velocity for seawater normalized at 20_C (k660) is always a positive value. The direction of the flux is given by air-sea pCO2 difference: it is directed from the sea to the atmosphere (positive) if pCO2 sea> pCO2 atm and vice-versa. When k660 is estimated from direct FCO2 measurements gathered by the eddy covariance method, the absolute value should be used. Making this correction to figure D1 the agreement between the experimental results and the theoretical model will greatly improve.

Thank you for pointing this out. Now, the k value is given as an absolute value, which slightly increased the R^2 value of the fit.



The text was modified to take into account the absolute value of k in P23R3: "The applicability of this parametrization for the western marine region of Utö was assessed by calculating the absolute value of k660 -"

The text was also modified to take into account new values in P23R11:

"The best quadratic fit (0.37U10²) is somewhat larger than the parametrization proposed by Wanninkhof et al., 2014, which might indicate enhanced gas transfer due to the coastal characteristics of the study site. However, for best comparability and consistency, we stick with the common parametrization by Wanninkhof et al., 2014."

Technical corrections

Methods:

P.5 L3.: which instruments log data every 15 sec? The ones mentioned at the end of the page?

We added the sampling frequency in the description of each observation. Please see the reply for the second next question for an example.

We removed the P5R3 sentence: "Most of the instruments that analyze seawater logged data every 15 s."

P5 L12: Is the gas calibration traceable to international CO2 standards (e.g. WMO, NOAA, ..)? If yes, please, add this information.

The reference gases are not traceable to WMO or other international standards.

A mention was added in P5R12:

"FMI buys the reference gases from a Finnish branch of Linde-Gas (previously AGA). The gas concentrations are checked with instruments using cavity ring-down spectroscopy in FMI's laboratory prior to measurements. These instruments are calibrated using gases that are verified by the National Oceanic and Atmospheric Administration (USA). Aluminum gas containers have been used in order to minimize the concentration drift."

P5 L15-27: There is a mix of "calculated values" with measured ones, please, describe here only measured ones. Improve the description of temperature and salinity measurements: frequency, accuracy, frequency of calibration, etc. Describe the thermistor chain when you present the marine station. Add briefly the methods for TA measurements.

The paragraph dealing with the temperature correction of pCO2 was moved to the section of calculated data. The chapter of alkalinity-salinity relationship was removed as it was now redundant. The figure of TA-S relationship was moved to the methods section.

The following text about the thermosalinograph was added in the section dealing with the other flowthrough measurements:

"The equilibrator temperature (together with salinity) was measured using a thermosalinograph (SBE45 MicroTSG, Sea-bird Scientific) that was next to the SuperCO2 instrument. The thermosalinograph is cleaned 1-2 times a year. The accuracies for temperature and salinity given by the manufacturer are respectively 0.002 °C and 0.005. The temperature drift is less than a few thousandths of a degree a year, whereas the stability of conductivity measurement depends mostly on the cleanliness of the measurement cell. The thermosalinograph logged data every 15 s."

Accuracy for the thermistors were included:

"Pt-100 thermistors were calibrated prior to the deployment in FMI's laboratory, and the maximum error in temperature was found to be less than 0.015 °C. Thermistors logged data every 30 s."

The text about total alkalinity was moved to its own chapter:

"The total alkalinity used here is calculated using a local alkalinity-salinity relationship, which is based on the samples gathered from the flow-through system at Utö in summer 2017 (Lehto, 2019). Total alkalinity was determined from these samples by using the potentiometric titration method (Metrohm Titrino 716). The samples were conserved with mercury chloride before the analysis in Finnish Environment Institute's research laboratory in Helsinki. The titrant and the rinsing water had the salinity of 7. Alkalinity was calculated from the titration curve based on the least squares method."

P5L 28: Even if in Kilkki et al., 2015 there is a detailed description of the methods, please, add the most important details: instrument model, accuracy, sampling frequency, reference to international standards.

We added more details on the ICOS measurement P5R28:

"The atmospheric xCO2 was measured at the Atmospheric ICOS site (Kilkki et al., 2015). The sample air was drawn from the tower (56 m) to the ground level where it was analyzed using using cavity ringdown spectroscopy (Picarro G2401). The data was logged as one minute average values. Three standard gases made by FMI were used for the reference measurement. Differences between the target and measured values of these gases were within -0.20 and 0.20 ppm. (Kilkki et al., 2015)."

P5 L30-34: Please, add detail on instrument accuracy, frequency of calibration etc..

More information on these sensors was added in P5R30:

"Oxygen was measured with an oxygen optode (Aanderaa 4330) with multipoint calibration. The optode has a preburned foil providing long term stability. The accuracy of the optode is 2 uM according to the manufacturer. In this paper we are mostly interested in hourly changes of oxygen, and thus the drift of absolute value is of minor concern. Chlorophyll a was measured with a Wetlabs FLNTU fluorometer, as a qualitative proxy of chlorophyll concentration, using factory calibration."

P6 L1-12: it is not clear which data are reported in Figure 1.

A mention of CTD was added in the caption of Fig. 1:

"Temperature of the seawater (Tw) assessed by the CTD casts - "

P6 L8-22: move to the section of calculated parameters

The estimation of the mixed layer depth (P6R8-22) was moved to new subsection "The determination of mixed layer depth" under the section of calculated data.

P6 L22: delete "be"

The excessive 'be' was removed:

"This implies that the mixed layer depths were well reproduced using the CTD castings unless the thermocline was located close to the bottom of the inlet location."

P6 L23 Please, define "Fas" when it is used for the first time. I suggest to delete the division in two subsections or modify the titles. As they are it seems that "the flux parametrization" is related to the eddy covariance method, not a different method to calculate fluxes.

The definition of Fas is found in P2R3.

P7 L20 – 28: first describe how TA is calculated from salinity and the robustness of the choice done, then describe the calculations of the derived carbon chemistry parameters.

The TA chapter was moved before introducing the CO2SYS calculations.

P7 L29 – P8 L3: Please, rephrase and explain better.

P7R29-P8R3 was modified:

"First, the carbon chemistry is calculated in CO2SYS for each hour based on the measured partial pressure of CO2 and the parameterized total alkalinity. This way, we derive the DIC at every hour.

In the case of the hourly temperature-related pCO2 change, we assume that DIC and TA do not change over that time frame. Using the temperature of the next hour together with the previously known DIC and TA, we calculate the new pCO2 in CO2SYS that is governed solely by the temperature change."

P8 L4-6: Please, describe step by step, it is quite confusing

P8R4-6 was modified to:

"In the case of air-sea exchange and biological transformations, we calculated how much DIC changed over one hour by these processes separately and added this DIC change, dDIC, to the original DIC content. Then, we calculated the carbon system using this new DIC and the unaltered total alkalinity in order to get the new pCO2."

P8 L22: Please rephrase, it is not clear what do you mean with ": : : each day at a time".

P8R22 was rephrased to:

"For each day, the cumulative sums of the hourly pCO2 changes generated by a specific process (temperature, biological transformations or air-sea exchange of CO2) were calculated for 00:00 – 24:00, in order to know how the specific process alters the pCO2 during a day. Finally, the mean of the cumulative sum was removed from these values, because we are interested in the daily changes, not the absolute values."

P8 L22-26: it is not clear, what pCO'2,i is

A definition was added in P8R24: "pCO'2,i is the cumulative pCO2 change between the i:th and the first hour."

P8 L28-30: please, explain better, this point is not clear.

P8R28-30 was modified:

"This is calculated using the DIC that is altered by both the air-sea exchange of CO2 and biological transformation, and additionally taking into account the temperature change."

Results and discussion

P9 L5: A more appropriate title would be "Environmental conditions and seasonal pCO2 variability".

The title in P9R5 was changed to: "The environmental conditions and seasonal pCO2 variability".

Conclusions

P18 L30-32: All the parametrizations for gas transfer velocity contain a cubic o quadratic component function.

The text was changed in P18R30-32 to:

"The most popular parametrizations for gas transfer velocity are either quadratic or cubic functions of the wind speed..."