Response to Anonymous referee #2

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. 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 by Honkanen et al. presents measured pCO2 data over a year from July 2018 to June 2019 from a marine site off the island Utö in the Baltic Sea. A variety of additional data is provided from the marine site, from two additional coastal sites and from the flux tower at the Utö island. The authors have examined the different drivers for the observed changes in pCO2, and they address the importance of high frequency data when precise air-sea CO2 fluxes are to be calculated. Data from coastal sites like this is highly valuable and the manuscript is very welcomed. However, the manuscript is poorly written and needs improvement both regarding English language and the structure. In the current version, the reader needs to jump back and forth to get a grip on the story, and it is not always clear what the authors want to communicate.

We followed the reviewer's comment and restructured the manuscript including specific suggestions by both reviewers. We also carefully addressed the English language and grammar. Additionally, as we have no native English speakers amongst the authors, the manuscript underwent a professional English proofreading.

Specific comments

Abstract: phrases like "monthly median diurnal pCO2 peak-to-peak amplitude" is difficult to understand. Please change to e.g. "monthly median of diurnal : : :" throughout the manuscript

All the occurrences of "monthly median diurnal pCO2 peak-to-peak amplitude" were changed to "monthly median of diurnal pCO2 variability."

This applied to P1R7, P1R11 and P2R16.

Chapter 1: The dataset are from 2018-2019, why not use a more updated reference for the global carbo cycle (e.g. the years 2009-2018: Friedlingstein et al., 2019, Earth Syst. Sci. Data, 11, 1783–1838, 2019, https://doi.org/10.5194/essd-11-1783-2019).

The reference was changed to:

Friedlingstein, P., Jones, M., O'Sullivan, M., Andrew, R., Hauck, J., Peters, G., Peters, W., Pongratz, J., Sitch, S., Le Quéré, C., Bakker, D., Canadell, J., Ciais, P., Jackson, R., Anthoni, P., Barbero, L., Bastos, A., Bastrikov, V., Becker, M., and Zaehle, S..: Global Carbon Budget 2019, Earth System Science Data, 11, 1783--1838. 10.5194/essd-11-1783-2019, 2019.

This naturally caused modifications in the values in the manuscript:

“During 2009–2018, 9.5 gigatonnes of anthropogenic carbon was released annually into the atmosphere in the form of carbon dioxide (CO2) mainly through fossil fuel and land use and cement production; approximately a half of these emissions was bound by the terrestrial biosphere, 3.2 GtCy−1, and the oceans, 2.5 GtCy−1, together (Friedlingstein et al. 2019).”

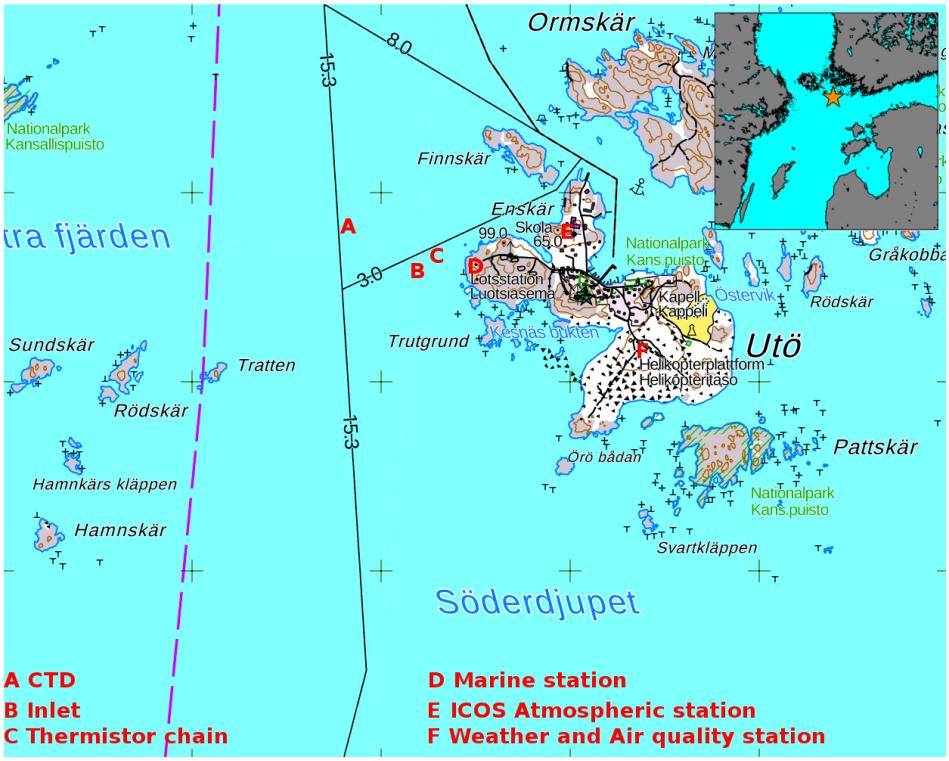
Chapter 2: Please note that Appendix A is not mentioned in the text.

We added a mention of the Appendix A (P2R8):

”The partial pressure of surface seawater CO2 and the direction of the air--sea CO2 flux (Fas, See Appendix A)

Chapter 3 Materials and methods: This chapter needs improvement. It would be helpful if a map was included where the position of the Utö station, its water intake, thermistor chain position as well as the position of the ctd casts were marked.

A map was added in the beginning of the Materials and methods section.



“Figure 1. 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 marine stations were shortly introduced:
“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).”

We added a link to the full list of the up-to-date measurements:
“For the complete list of observations, visit Finnish Meteorological Institute's web site (https://en.ilmatieteenlaitos.fi/uto-observations).”

Also, more information on the biogeochemical and physical setup of the study were added:
““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).
“

We updated rigorously the methods section. For the sake of clarity, we divided it into the sections of flow-through measurements, other measurements and calculated data. More information of different measurements, including accuracies, was added.

You should clarify the difference between the marine station and station, maybe it is better to use “laboratory” for the on-shore facility?

The name of Utö Atmospheric and Marine Research Station is used for covering all of the measurements on the island. Mostly, in this paper we only use the marine station on the western edge of the island.

P4L26 was modified to:

“The marine station, located on the western shore of the island, is equipped with a flow-through system. A submersible pump located 250m from the shore transports seawater to the marine station, where seawater is analyzed automatically and manually on demand (see Fig. 1 for site map).”

”

LI-COR 840 measures CO2 and H2O, but are the gas dried prior to the detection (if so, please include information). Are you using the H2O measurements to calculate dry xCO2, or are you calculating pH2O from T and S?

There is a water trap on the gas line prior to the analyzer.

The following information was added in P5R10:

"Since the water trap attached to the sample gas line may slightly affect the water vapor content, the following calculation is used: the dry CO2 molar fraction is calculated using the H2O measured using the analyzer. The real water vapor content in the equilibrium chambers is calculated using the temperature and salinity data assuming the full saturation. This real water vapor content is used when calculating the partial pressure of CO2."

The pCO2 is corrected for temperature difference between water intake and equilibrator, and this should be done according to Takahashi et al. (1993). Why are you including TA in this recalculation?

The temperature conversion factor of 0.0423 proposed by Takahashi et al.(1993) is based on measurements performed on ocean water samples, i.e. it is applicable under fully marine conditions. At the study site, salinity is below 7 and likewise all CO2 system parameters reflect brackish waters conditions. Under those conditions, the actual dependence of pCO2 on seawater temperature can differ significantly from the Takahashi value (See for example chapter 2 in Schneider and Müller (2018)). A temperature conversion that reflects the actual conditions at site was achieved by using standard software for CO2 system calculation and TA as an additional input parameter. This is now shortly explained in the text:

"The typical temperature correction of pCO2 suggested by Takahashi et al. (1993) is not applicable in the brackish conditions of the Baltic Sea."

Please include accuracy and precision of Optode and Clorophyll A.

The following information was added in P5R31:

"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 not concern. Chlorophyll A was measured with Wetlabs FLNTU fluorometer, as a proxy of chlorophyll concentration, using factory calibration."

The value of the one month of thermistor chain data is not properly explained.

The chain was deployed in July 2018 and was used through the entire measuring period (July 2018-June 2019).

A clarification of the data use was added in P6R7:
"The thermistor profiles were used to verify the applicability of the CTD casts carried out at slightly different location. The 3 m thermistor measurement was used for correcting the pCO2 for the temperature change that occurs during the sampling procedure."

Please include reference for CO2SYS program used.

A reference for the MATLAB version was added:

"van Heuven, S., Pierrot, D., Rae, J., Lewis, E., Wallace, D.W.R.: CO2SYS v 1.1, MATLAB program developed for CO2 system calculations, ORNL/CDIAC-105b, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. DoE, Oak Ridge, TN, 2011."

The citation was added when first time mentioning the CO2SYS in P5R16:

"Since the sample water temperature can change during the transport, we took the effect of the temperature change on pCO2 into account by using the CO2SYS matlab program (van Heuven et al., 2011)."

There are some repetition of information that is fund in Appendix, please decide where to present it.

The salinity-alkalinity chapter was removed from the Appendix as redundant.

Flux of oxygen is most commonly presented as a function of (measured O2 concentration minus saturation O2 concentration). Why not use this here?

We are indeed using the concentration difference (measured O2 and calculated saturated O2 concentrations) together with wind speed dependent gas transfer velocity in order to calculate the oxygen flux.

This is now clarified in P8R18:

"This flux, FO2, is calculated similarly to the carbon dioxide flux (Eq. A1) by using the gas transfer velocity and the oxygen solubility, the measured oxygen concentration in seawater and the oxygen concentration calculated for hypothetical equilibrium with the atmosphere."

Technical corrections:

P2 L25: Replace "voluntary" with "Voluntary".

P2L25 voluntary was changed to Voluntary

P3 L10: Please rewrite sentence and include more explanation.

P3L10 and P3L14 were repetition from chapter 2.4 and thus were removed.

P4 L26: Please rewrite this line to clearly differentiate between marine station and station. E.g. "Water from the marine station, which is situated 250 m from shore, is pumped to an onshore laboratory, where analyses are performed".

The location of the different components of the infrastructure are shown in the map added, together with a clarifying text.

P4L26 was modified to:

"The marine station, located on the western shore of the island, is equipped with a flow-through system. A submersible pump located 250m from the shore transports seawater to the marine station, where seawater is analyzed automatically and manually on demand (see Fig. 1 for site map)."

P5 L15: Rewrite the paragraph starting on line 15. The temperature difference between inlet and equilibrator can be corrected for by using Takahashi et al. (1993). Why introducing the salinity-alkalinity relationship here?

P5L15 was modified:

"Since the sample water temperature can change during the transport, we took the effect of the temperature change on pCO2 into account by using the CO2SYS matlab program (van Heuven et al., 2011)."

The correction given by Takahashi et al.(1993) is based on measurements on the ocean. The Baltic Sea is a brackish sea, and for this reason we relied on using two carbon variables on the carbon system program. The salinity and alkalinity are strongly connected due to the fact that both are affected by conservative mixing.

P5 L26: Delete "between the".

P5L26 a duplicate “between the” was removed:

“ -- the root mean square difference between the sea inlet and the --”

P5 L27: Rewrite the last sentence.

The sentence was rewritten:

“Because the pCO2 difference between the inlet and station is small, we conclude that the pCO2 analysis carried out at the station represents the inlet conditions.”

P6 Ch 3.4: The chapter needs improvement/restructure.

The chapter was divided into smaller subsections, also addressing comments of reviewer 1: first one introduces the measurement, the second describes the mixed layer depth assessment and derivation of variables.

P6R3 was simplified:

“The thermistor chain was deployed 150 m northeast from the seawater inlet in July 2018; --”

P6 L3: Capitalize the first letter of “temperature” and “depth”.

P6R3 All letters in CTD were capitalized:

“The vertical temperature profiles were measured with temperature chains, supported with regular interval profiles of Conductivity-Temperature-Depth instrument (CTD).”

P6 L5: The depth closest to the surface was selected for what?

We clarified the use of the thermistor measurement at 3 m depth:

“The 3 m thermistor measurement was used for correcting the pCO2 for the temperature change that occurs in the sampling.”

Also P6R5 was modified to:

“**I**n order to avoid instrument damages during the rough weather conditions, there was no thermistors closer than 3 m to the surface.”

Further, the temperature chain was deployed for only one month in 2018. Is this representative for the whole year?

The chain was deployed in July 2018 and was used thorough the whole measuring period (July 2018-June 2019).

P6 L8: Replace “temperature vertical profiles” with “vertical temperature profiles”.

P6L8 was modified accordingly:

“The mixed layer depth (zmix) was determined from the vertical temperature profiles --”

P6 L9: I suggest moving the name Ismo Willström to the Acknowledgements.

Ismo’s name was moved to the acknowledgments:

"CTD profiles were taken by using a small boat, --"

P6 L24: Replace "1) on the the" with "1) an".

P6R24 the repetition was removed:

"The estimation of the air-sea exchange of CO2 between the sea and atmosphere is based on two methods: (1) the eddy covariance method –"

P6 L26: Replace "2) on the" with "2) a".

P6R26 the repetition was removed:

"-- and (2) the wind speed-based flux parametrization."

P7 L20: Please include reference for CO2SYS.

The reference for CO2SYS was added

"van Heuven, S., Pierrot, D., Rae, J., Lewis, E., Wallace, D.W.R.: CO2SYS v 1.1, MATLAB program developed for CO2 system calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. DoE, Oak Ridge, TN, 2011."

And citation in P7R20:

"Calculations of the carbon system were performed using the CO2SYS matlab program (van Heuven et al., 2011).

P7 L21: Explain why you use constants from Millero (2010), as Lueker et al (2000) is recommended in open sea.

Millero (2010) is developed for estuary (brackish) waters. The salinity at Utö varies between 6 and 8.

P7 L26: The TA-salininty relationship is presented in Appendix C, there is no need for repetition, please chose where to include it.

The alkalinity-salinity chapter in Appendix was removed.

P8 L18: Remove parenthesis. The flux of oxygen is usually presented as a function of (measured O2 concentration minus saturation concentration of O2).

The parenthesis around the oxygen words were removed as they were redundant in P8R18:

"This flux, FO2, is calculated similarly to the carbon dioxide flux (Eq. A1) by using the gas transfer velocity and the oxygen solubility, the measured oxygen concentration in seawater and the oxygen concentration calculated for hypothetical equilibrium with the atmosphere."

P9 Figure 1 text: Please clarify in figure text from where the different data are from, e.g. in panel a) the T structure is based upon ctd station data, etc.

A mention of CTD was added in the caption of Fig. 1:
"Temperature of the seawater (Tw) assessed by the CTD casts – "

P9 L1: You write that r is used to describe the diurnal pCO2 variability, but in Figure 8, r is used as root mean square.

The r in Fig. 8 was changed to R^2.

P9 L8: Replace “ca month“ with either “a month” or “one month”.

P9R8 “ca month” was changed to “a month”:

“- --for **a** month (Fig. 2a).”

P10 L5: Do you mean remineralization?

Mineralization was changed to remineralization thorough the paper to be consistent.

P10 L11: The assumption of fresh water lenses is not introduces anywhere else, please explain more.

A clarification was added in the chapter 2.1 (P3R10):

“The processes controlling the freshwater balance evaporation, precipitation and the formation and melting of sea ice. Precipitated water or melted sea ice may produce a layer of low saline water at the sea surface, but is likely eroded easily by turbulence except under very calm conditions.”

P12 Figure 4 text: Please replace “monthly diurnal variability” with “monthly median of diurnal variability” (as used in Chapter 5 Conclusion).

Fig4 caption was modified to be:

“Observed monthly medians of pCO2 diurnal variability --”

P13 L19: Rewrite the last sentence.

P13R19 was rewritten:

“The exchange of CO2 between the sea and atmosphere is driven by the CO2 partial pressure difference between them: CO2 is transported from higher partial pressure to lower. As the atmospheric partial pressure of CO2 is relatively stable compared to the one in sea, the direction is mainly given by the pCO2 in the sea. The diurnal pattern of pCO2 generated by air-sea exchange represents the accumulation of carbon in the sea in summer when the pCO2 is smaller in the sea than in the atmosphere and vice versa in winter.”

P14 L7: Replace “observed one during” with “observed during”.

The redundant “one” was removed in P14R7:

“-- as large as the one observed during the spring bloom.”

P15 L5: Replace “is an increasing trend” with “seems to be increasing throughout the day”.

P15R5 was modified accordingly:

“-- the diurnal pCO2 pattern generated by the biological processes seems to be increasing throughout the day, --”

P16 L5: The correlation coefficient (R2) is called “r” in the panels of Figure 8. Please be consistent.

Fig. 8 was updated, now with R2.

P16 L10: Please explain the sensitivity evaluation better.

P16R10 was rewritten:

“For each month, we divided the RMSE value with the average absolute change in hourly pCO2 to find out this sensitivity – “

We also did rigorous testing on the model applied. We added discussion on the possible sources of the discrepancies (air-sea exchange of oxygen, mixing, mixed layer depth) in the results.

P16 L11 and P17 L1: This sentence needs rewriting and more thorough explanation.

P16R11 was rewritten:

“Thus, the error introduced by the model during these winter months, though comparatively small in its absolute value, is large compared to the observed variability, which suggests that the estimates of the biological component during the winter time should be treated with caution.”

P18 L9: Replace “02” with “O2”.

The “02” was replaced with “O2”:

“Wesslander et al. (2011) determined the CO2-02 ratio –“

P18 L22: Remove “to the”.

The “to the” was removed:

“The atmospheric CO2 partial pressure is approximately constant when compared with the variability in the surface water.”

P18 L27: Replace “and smallest afternoon” with “and smallest in the afternoon”.

P18R27 was updated to:

“ -- the largest difference is before noon and the smallest is in the afternoon.

P20 L22: Replace “solubility constant” with “solubility”. Solubility is not a constant but rather dependent on T and S.

The “solubility constant” was replaced with “solubility”.

P21 L8: Hydrogen carbonate dissociate into carbonate AND hydrogen ion.

P21R8 was corrected:

“-- which further dissociates to carbonate (CO_3^{2-}) and hydrogen ions."

P21 L18: DIC does vary with temperature.

We added the following text in P3R3 to clarify the issue:

"In contrast to pCO2, DIC and TA behave conservatively with respect to temperature changes and mixing of water masses, when expressed in concentration units of µmol per kg of seawater."

P22 L10: TA is highly dependent on salinity (and to a minor degree on temperature) and thus not a conservative variable.

We added the following text in P3R3 to clarify the issue:

"In contrast to pCO2, DIC and TA behave conservative with respect to temperature changes and mixing of water masses, when expressed in concentration units of µmol per kg of seawater."

P22 L19: ": : :which was based on the direct total alkalinity and salinity measurements carried out: : :.".

The alkalinity-salinity chapter in the Appendix was removed.

P22 L25: You claim that salinity has no units, why introduce PSU?

The alkalinity-salinity chapter in Appendix was removed, and with that, any use of PSU

P23: I suggest merging Appendix A: Air-sea gas exchange of CO2 and D: Gas transfer velocity, as these paragraphs discuss similar things.

The gas transfer velocity parametrization was merged in Appendix A as a subchapter.

P23 L9: Insert "than" between "less" and "30%".

P23R9 was corrected:

" -- fluxes can deviate less than 30% from --"

P23 L10: Insert "a" between "purely" and "theoretical".

P23R10 was corrected:

"The fully stationary condition is purely a theoretical concept, --"

P23 L11: You used you own CO2 flux measurements and calculated "The best quadric fit (0.31U2: : :.)", right? Or are you referring to Wanninkhof (1992), who presented exactly the same number? Moreover, on line 12, what is the "common parameterisation"; is it Wanninkhof (1992); 0.31U2: : :, or Wanninkhof (2014); 0.25U2: : :?

Yes, the best quadratic fit was based on our own measurements. The common parametrization means the Wanninkhof (2014), as it is the updated version. A clarification was added:

"-- we stick with the common parametrization by Wanninkhof et al. (2014)."

P25 L5: Please include "(ICOS)" after "Integrated Carbon Observation System".

The abbreviation was added:

"Also, thanks are due to the Integrated Carbon Observation System (ICOS) for providing the atmospheric CO2 data at Utö"

P26 L15: The doi of this paper is placed in the middle of the word “methods”. I would also recommend using the updated reference: Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp.

Thank you for pointing out up-to-date material. The reference was updated.