MS No.: bg-2022-82
Authors: Lucía Gutiérrez-Loza et al.
https://doi.org/10.5194/bg-2022-82

Authors' reply to Bernd Jähne

Dear Bernd Jähne,

We would like to thank you for taking the time to comment on this manuscript. Please find below our replies to your comments, which we have tried to address in the best way possible.

The response to each comment is written in blue italics, while the changes made in the revised manuscript are in red.

1. Empirical correlation instead of analysis of mechanisms

> The authors claim in their paper to analyze the physical mechanisms controlling air-sea gas transfer beyond wind speed using a nine year record of continuous eddy covariance measurements taken at the Östergarnsholm tower. Such a long time series is, of course, a treasure, but the title of the paper is misleading in my view. The paper does just list possible other mechanisms than wind (or more precisely wind stress at the ocean surface) as the main driving force, but does not discuss at all any possible conceptual model to be checked by the data. All they do are empirical correlations with some other parameters. In addition, even an observed correlation does not mean that another driving force is found, because the investigated parameter might be correlated to another, which is the real driving force.
>
> Therefore a more appropriate title would be "Empirical correlations of the gas transfer velocity with other parameters than wind speed" or a similar wording.

In the revise manuscript, a different approach was used (brief discussion comes as a reply to the comments below). This approach allowed us to identify conditions at which the gas transfer velocity showed higher values than those predicted by the k_660-wind relationship found in the current study, as well as by other wind-based parametrizations used as reference (W14 and Mc01). By identifying these conditions, it was possible to explain part of the variability observed at high and low wind speed conditions. We, therefore, considered that a more suitable title for the manuscript is "On physical mechanisms enhancing air-sea CO2 fluxes".

*The **title** of the manuscript was modified to "**On physical mechanisms enhancing air-sea CO2 exchange**".*

2. The statistical analysis is not convincing

- The authors use a multistep scheme to select only reliable measurements. But they do not specify which fraction is remaining. It is important to know to which extent specific conditions are excluded from the analysis. If the exclusion were large, this may severely bias any averaging and correlations.

The authors agree with this comment. The data selection process implied that a very large percentage of the data was discarded from the final data set used in the analysis. Additional information was included in the manuscript to clarify this fact (see below).

The final data set consisted of 18.7% of the initial FCO2 data and 15% of the k660 data, with respect to the total amount of data available for the open-sea sector.

Furthermore, we would like to point out that, even if the exclusion of data was indeed large, the distribution of the data shows similar patterns between the initial data set (before quality control) and the final data set (after quality control). Indicating that the statistical representation of the data is adequate and only small biases are expected. Some figures are included here as an example:

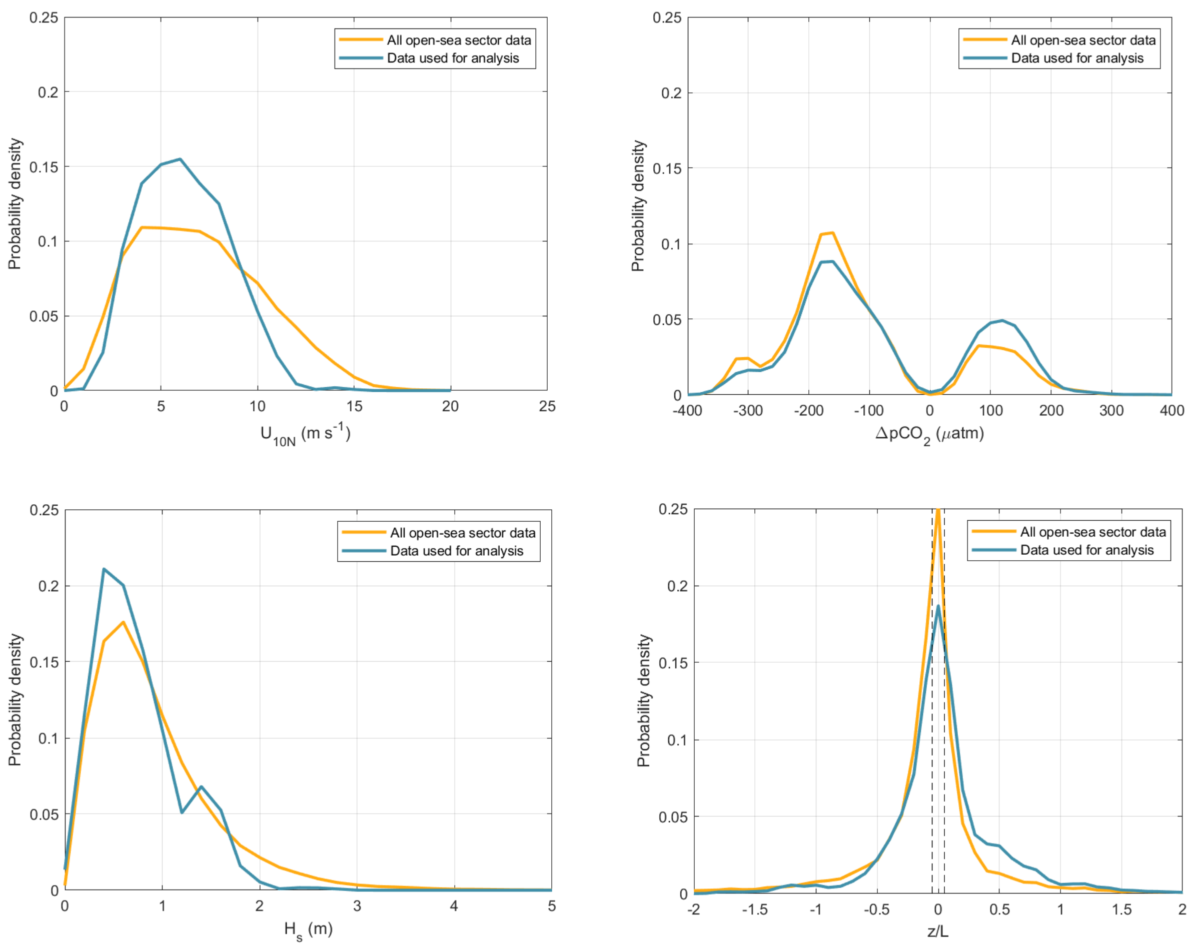

Figure CC1.1. Probability density function of U10N (upper left), ΔpCO2 (upper right), Hs (lower left), and stability (z/L, lower right) for all data available for the open sea sector (yellow line) and for the processed (quality controlled) data used in the analysis (blue line).

A paragraph including some general numbers indicating the size of the initial data set (for the open-sea sector) and the remaining amount of data after quality control was included at the end of the ***Data Processing*** *section (**2.2**).*

Appendix B *was included. In this section, a more detailed description of the relative importance of every QC criterion (i.e. the effect of each criterion on the total amount of data) was included (**Table B1**).*

- For the averages shown in Fig. 5 all, also negative gas transfer velocities have been used, but not in the following more detailed analysis. This is inconsistent. Either you rely data or not at all.

We agree with this comment, removing the negative k values was inconsistent. We have initially thought that these negative k values would introduce some unrealistic results as we could not find a feasible explanation for them, even if they had fulfilled all quality control steps. However, we have reconsidered this decision and have included the negative k values in the revised version as part of the analysis. Thus, avoiding biases in the data and the subsequent analysis.

All data fulfilling the quality control procedures were considered in the analysis, including the negative k_660 values. The corresponding modifications were made throughout the manuscript. In particular, modification were made to the data processing ***section 2.2*** *and in the results from* ***section 3.2*** *and onwards.*

- The concept of the residual gas transfer velocity and the correlation with a single other parameter seems not to be a good choice. A theoretically more sound approach would be to use a multi-parameter space approach with all possible parameters and then perform a principal component analysis or similar approach, as it is standard in pattern recognition and classification. Then it would be possible to identify the most important parameters and the degree of correlation between the parameters quantitatively and whether the results are statistically relevant. The approach of the authors is just qualitatively.

Based on this, and other comments from the reviewers, we have reconsidered the use of the residual gas transfer velocity (k_r). Instead, a different approach using a normalized gas transfer velocity was used. Such normalized gas transfer velocity defined as k_660/k_wind, where k_wind was obtained as the cubic (best) fit to the bin-averaged k_660 data of the current study. This approach allowed us to quantify the difference between k_660 from the expected wind-speed relationship. Based on these values, conditions leading to significant deviations of k_660 from k_wind, were identified and further analyzed. We consider this method to be, statistically, more robust than the previous approach which, as suggested, was based on *qualitative relations. A description of the changes made (including figures) can be found in the response to the comments from Reviewer 1 and 2.*

***Data processing section (2.2)**. Information regarding k_r was removed and a short paragraph describing the calculations of the normalized gas transfer velocity was included.*

*Corresponding changes in the **Results** section**,** from **sub-section 3.2** and onwards, as well as in the **Discussion.***

Furthermore, a preliminary attempt of using a multivariate approach (Partial Least Squares, (PLS) analysis) was considered to analyze the data, as suggested. We considered this method, similar to PCA, to be suitable for this particular application as it can handle data that are non-normally distributed, as well as accounting for the effect of cross-correlated predictor variables. The results of the PLS analysis suggest that, for high-wind speed conditions, it is possible to explain up to 90% of the variability in k_660 by using five components (up from 65.2% using only one component). At low wind speed conditions, on the contrary, increasing the number of components in the analysis only improves the model by 11.3% (from 61.6% with one component to 73.2% with five components). In both, high and low wind-speed conditions, the model with five components was considered to be the best base on the RMSEP and explained variability. These results, suggest that even if a strong correlation existed between predictor variables (e.g. wind speed and significant wave height) the additional contribution of parameters, other than wind speed, to the explained variability is relevant. In particular, under high wind speed conditions. Accounting for the effect of additional control mechanisms, seems therefore relevant to further explain the variability of k_660.

Even when PLS (or other statistical models) can provide insights about the relationship between k_660 and other parameters, the characteristics of the data set such as the presence of large gaps in the data, non-normal behavior, cross-correlation of predictor variables, etc. make it hard to interpret the obtained results. For this reason, such statistical analysis was not included in the revised manuscript.

3. Claimed effect of sea spray in enhancing air-sea CO2 fluxes questionable

The authors claim that "sea spray can enhance the transport of CO2 across the interface, as it does with heat and moisture". This is an oversimplification, because the transport of heat and water vapor is air-side controlled, while the transport of CO2 is water-side controlled. Therefore a much more detailed analysis is required. Droplets may partly be a dead surface for gas transfer in the same way as those bubbles, which come in a much shorter time scale into equilibrium with the surrounding water than their life time. However, the influence of solubility is inverse. Droplets are efficient for highly soluble tracers.

Yes, we suggest that sea spray can enhance the transport of CO_2, but only under particular conditions. Here, we are not challenging the well-stablished theory about the water-side controlled transport of CO2. However, we acknowledge (as other studies have) that atmospheric processes might also be relevant for air-sea CO_2 gas exchange under particular conditions (e.g. effect of atmospheric stability). We offered, based on the analysis presented here, a plausible explanation for the higher transport observed under such conditions suggesting the potential effect of sea spray on FCO_2. This is not to say that sea spray does not occur under *other conditions but, as expected from the water-side controlled transport perspective, it is not expected to affect FCO_2.*

The approach used in the revised manuscript allowed us to identify (in a clearer way) these conditions, and to show that such conditions were consistently linked with higher values of k_{660} than those predicted by wind-speed relationships (Fig. 7 of the revised manuscript). However, we recognize that further investigation is necessary to understand this transport mechanism, and to quantify its impact on the regional and global fluxes.

Further investigation of the sea spray as a control mechanisms of air-sea CO_2 exchange is suggested in the ***Discussion*** *and* ***Conclusions.***