

Response to Gil Bohrer

We thank the reviewer for his comments. The comments have led us to examine our measurements in more detail. We reply to each comment in the following.

RC1.1 The manuscript provides a very technical assessment of the effects of a drier and a compactor on removing the spectral cross contamination of water vapor in CO₂ flux measurements. It is relevant, and reports interesting findings with direct implications to observation techniques of ocean CO₂ fluxes.

RC1.2 Given the topic, I found the narrative diverging to describing other unrelated findings (turbulence, gap filling, and roughness length). These sections should be removed, or, the direct relevance of these findings to understanding the differences between the measurement setups should be described.

In addition to the analysis of H₂O interference effects on the CO₂ fluxes, a main aim of this paper is to introduce a new eddy covariance site and study its overall feasibility for sea-air flux measurements. In the revised version, we clarify the aims of the paper in the end of the introduction:

In this paper, we introduce a newly established and currently operating eddy covariance measurement site, located on the Utö Island in the Baltic Sea. This paper has two objectives: 1) Study the characteristics of the new site and measurement setup and 2) Analyze empirically the effect of water vapor on the CO₂ sea-air fluxes.

Integral turbulence characteristics and roughness length within the footprint were analyzed in order to address the quality of the fluxes measured at the new site. These sections are important for the overall quality assurance of the new setup, so we did not remove this material from the paper. However, to clarify the paper, we moved them to the appendix.

The brief discussion of gap filling was moved to the conclusions to highlight the fact that gaps are evident in sea-air CO₂ flux measurements and that auxiliary measurements (notably dissolved CO₂) are required for the gap filling for CO₂ budgets, which is one of the primary goals of these measurements.

RC1.3 Otherwise, I only have a few minor comments: p3L15-20, I think sea breeze is worth mentioning here. Also, you should mention specifically that sea-land gradient is almost always present and violates the horizontal homogeneity assumption. Please reference Rey Sanchez et al 2017 <https://www.tandfonline.com/doi/abs/10.1080/20964129.2017.1392830> which evaluated the relative effect of horizontal affection.

The presence of sea-land gradient and its effect on horizontal homogeneity are now mentioned in the introduction:

Horizontal CO₂ gradients develop easily in the vicinity of sea-land boundary, violating the assumptions of horizontal homogeneity and negligible advection (Rey-Sánchez et al., 2017).

As Utö is a small island (0.81 km²) and its distance to the mainland is more than 50 km, the influence of sea breeze alone is small.

RC1.4 Fig 1- please say explicitly where is the ec flux station. I assume it is A, but a bit confused about what B is.

The caption of Fig. 1 was clarified:

The research installations on the island consist of the Utö Atmospheric and Marine Research Station and its flux tower (A), the inlet of the flow-through pumping system (B), the Atmospheric ICOS station (C), and a weather and air quality station (D).

RC1.5 The location of the tower at the edge of a cliff is problematic. The sharp change of roughness and the physical disturbance to the flow probably generate increased turbulence and a vertical ejection flow that violate a few of the ec assumptions (0 mean vertical flow, ergodicity of turbulence). There are many papers discussing the effects of forward facing step on vertical flow. See for example our paper <https://link.springer.com/article/10.1007%2Fs10546-014-9923-5> and references within. Roughness and surface heat flux transition create circulations patterns that are particularly problematic for edge-of-shore flux measurements. See Higgins et al 2013 <https://journals.ametsoc.org/doi/full/10.1175/JHM-D-12-0166.1> and Kenny et al 2017 <https://link.springer.com/article/10.1007/s10546-017-0268-8>. These will be a problem even when the footprint is all water. Please at least discuss this issue, around where you discuss other difficulties of measuring carbon flux in the ocean.

The authors are also concerned about this problem. However, the observed vertical wind speed indicates that this is unlikely to constitute a serious problem; please see the following reply. A discussion about the possible secondary circulation due to the cliff was added to the revised version:

Because an obstacle in a flow field generates an uplift zone on the windward side of an obstacle (Chatziefstratiou et al., 2014), there should not be steep elevation changes near the flux tower in order to avoid non-zero vertical wind speed. Also the roughness and flux discontinuities on a sea-land boundary generate secondary circulation that drives advection and causes challenges for coordinate rotation (Kenny et al., 2017).

RC1.6 P7L15 in the same issue of vertical flow - how did you rotate your wind coordinates? Most rotations assume 0 vertical wind. That will affect your momentum flux. In your case with the cliff facing the wind, you should filter out cases where the unrotated mean w was large.

A double coordination rotation was used to ensure a zero mean vertical velocity for each 30-min averaging period. During the whole measurement period, the unrotated vertical velocity varied within 0-1 m/s with a mean of 0.39 m/s and standard deviation of 0.21 m/s. The vertical rotation angle within the sea sector varied within 0-5° with a mean of 3.1° and a standard deviation of 1.4°, indicating that the flow divergence due to the cliff is limited.

RC1.7 P7L26 you cannot remove more than half of the observations based on a subjective eyeball analysis for "distortion". Please provide an objective definition for which observations should be removed and remove only and all of those that fit these criteria.

We should note first that this screening only refers to the data used for spectral analysis; it was not used as a quality criterion for flux data. The spectral analysis was carried out mainly to estimate the high-frequency attenuation in terms of the transfer function specified. For the revised version of the manuscript, we adopted objective criteria for removing poorly structured cospectra:

Observations with an appropriate wind direction (180–260 °) and stationary conditions ($RN_{wc} < 0.3$) were accepted for spectral analysis. 607 half-hour periods met this criterion. Next, we discarded small fluxes ($< 0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$), after which we had 381 half-hour periods. Furthermore, a cospectrum was discarded if its peak was not within a predefined frequency range (0.01–0.5Hz). 283 cospectra passed

this frequency range criterion. Also, a cospectrum was discarded if its normalized peak size ($Co_{wCO_2} / w'CO_2'$) was not within predefined range (0.1–1.0). Thus, 238 observations from a 4 month period were used for the spectral analysis.

RC1.8 P12L5 The stationarity is an environmental property and should not vary between instruments. I do not understand why you have different stationary cases for each of your setups which are at the same location. That can only be the outcome of different observation errors in each of the setups. I suggest adopting a common criterion, when both sensors observe stationary conditions.

Yes, the difference in measured CO₂ flux relative non-stationarity values originates from observation errors. We agree that it is more logical to adopt a common criterion and thus we now require that stationarity is observed by both setups. This had only a minor effect on the results.

A sentence was added to the Materials and methods chapter (page 6 line 11):

Here, a 30 min period is regarded as stationary if both of the CO₂ flux measurements fulfil the condition $RN_{wc} < 0.3$.

RC1.9 P13L19 “co2 flux station” seems odd. Maybe “co2 flux exchange at the station”. This paper is not about carbon budgets. I suggest removing this section. If you insist to keep it, please provide more information on the gap filling approach you used, how you estimated uncertainty, and the resulting co2 flux budget.

Changed the sentence to:

Thus, continuous measurements of surface seawater and atmospheric CO₂ concentration at the Utö station provide useful additional data for the calculation of sea-air CO₂ flux exchange.

The gap filling text was moved to the conclusions. Please see the reply for RC1.2.

Response to Brian Butterworth

We thank the reviewer for his thorough comments. These comments forced us to investigate our measurement installation even further and revealed important insights. We reply to each comment in the following.

General Comments

RC2.1 The work laid out in this methods paper is thorough and up-to-date, with the current best practices in the field. The researchers designed and clearly described what appears to be a functional eddy covariance tower for measuring CO₂ fluxes in a marine environment. Which is not an easy task. With regard to scientific quality, I believe the authors have done an excellent job.

RC2.2 There are several areas that the paper could be improved. Broadly, the paper needs to stay more focused on CO₂ flux measurements. Several analyses seemed unnecessary (e.g., roughness length and similarity theory), veering away from the overriding goal. These could be replaced by a more in-depth assessment of the performance of the system with regard to CO₂ flux (e.g., gas transfer velocity or bulk flux comparisons).

While these analyses may seem obsolete, we should note that the paper has several aims, one of which is an overall assessment of the feasibility of the new marine flux station. Integral turbulence characteristics and roughness length analyses were carried out to test the fulfillment of theoretical assumptions of eddy covariance method at this particular location. For this aim, these sections provide useful information that we wish to keep in the paper, however moving them to an appendix.

In the revised version, we clarify the aims of the paper in the end of the introduction:

In this paper, we introduce a newly established and currently operating eddy covariance measurement site, located on the Utö Island in the Baltic Sea. This paper has two objectives: 1) Study the characteristics of the new site and measurement setup and 2) Analyze empirically the effect of water vapor on the CO₂ sea-air fluxes.

To improve the focus of the paper, the sections dealing with turbulence and horizontal homogeneity were removed from the main text and presented as appendices. The following sentences were added to the beginning of the Stationarity section:

In order to evaluate the quality of our measurements, several theoretical assumptions of the eddy covariance method were analyzed. The flux footprint area was found to be horizontally homogeneous (Appendix B), and turbulence was well-developed as integral turbulence characteristics could be expressed as functions of stability parameter (Appendix C). In this section, we analyze the fulfillment of the stationarity assumption and determine the effect of CO₂ flux nonstationarity on the CO₂ fluxes.

RC2.3 Also, because the method (i.e., dried closed-path IRGA) has been presented in previous papers, this paper would improve its contribution by delving a little deeper into the challenges facing the system (e.g., distorted spectra). Doing so could enable those deploying similar systems in the future to address those challenges and improve data retention.

We figured out the source of distortion. Please, see the response for RC2.13.

RC2.4 This is a good paper. The work is thorough, the methods are sound. I recommend it for publication and look forward to seeing the science papers that follow.

Specific comments

RC2.5 The paper should attempt some way to corroborate the magnitude of the measured fluxes with previous results. While we have no reason to doubt that the fluxes are good, we also have no evidence that they are good. Accomplishing this should be straightforward given the fact that waterside pCO₂ was measured. This could be done by presenting gas transfer velocity. Or it could be done by comparing against bulk CO₂ flux calculated using an existing parameterization for gas transfer velocity.

Typically, eddy covariance measurements are used for developing parametrizations, not vice versa. However, we compared the k-U relationship determined from our data to the traditional quadratic equation of Wanninkhof (1992):

*As no previous measurement data are available for comparison, we validated the magnitude of the measured air-sea CO₂ fluxes roughly by calculating the gas transfer velocity ($k_{660} = F/K_0 \Delta pCO_2 (Sc/660)^{1/2}$) from our data and compared it with the universal parametrization proposed by Wanninkhof (1992). Schmidt number (*Sc*) and solubility (*K₀*) of CO₂ were calculated according to Wanninkhof (1992) and Weiss (1974), respectively. For this comparison, we only included cases in which the absolute partial pressure difference (ΔpCO_2) between the sea and atmosphere was larger than 3Pa. The gas transfer velocities derived from our measurements were in good accordance with predictions (Fig. 7), which lends credence to our flux measurements.*

RC2.6 The percentages of data lost due to non-stationarity (63%) and wind direction (51%) are reported separately. It's worth reporting somewhere in the paper the combined loss / total percentage of data that made it to the final analysis.

We agree that this is important information for the general representativeness of the station. The total percentage of lost data is added to the text:

Overall, 91% of data were discarded due to unsuitable wind direction, nonstationarity or a positive momentum flux.

RC2.7 Page 3 – line 13 –The closed-path design does not automatically mean increased sensitivity to motion. Miller et al. (2010) found that the LI6262 and LI7000 were more sensitive to motion. This doesn't apply to all closed-path IRGAs on the market (e.g., the LI7200 [closed-path], which has the same internal design as a LI7500 [open-path], doesn't show the same degree of motion sensitivity as those named by Miller et al. [2010])

The motion sensitivity problem was clarified:

However, this does not apply to all closed-path analyzers, since some of them have internal design resembling open-path instruments (LI-COR, 2016).

Before ending up with the current measurement system, we tested several years (since October 2012) different instrument set-ups including LI-7500 and LI-7200. After several test installations (and broken instruments due to sea spray, strong winds and wintertime icing) we finally ended up with the current setup.

RC2.8 Page 5 – I like the photograph (Figure 2). It makes the case that the virtual impactor is necessary. But it seems like a photograph that is a little closer to the tower, and that shows the instrumentation a little better,

would be more helpful here (where you're describing the physical design of the system) and that this one could potentially be moved to the Appendix. Just a thought.

The following figure shows the tower instrumentation slightly better. The anemometer is seen on the left side of the boom, and the orange sample line and its inlet are seen at the middle of the boom. Also, the previously used LI-7500 is at the top of the mast.

Before the current inlet location, we tested placing the inlet in more ideal position, but could not get it function due to the sea spray. We are still investigating a technical construction which would tolerate the environmental conditions with minimal flow disturbances.

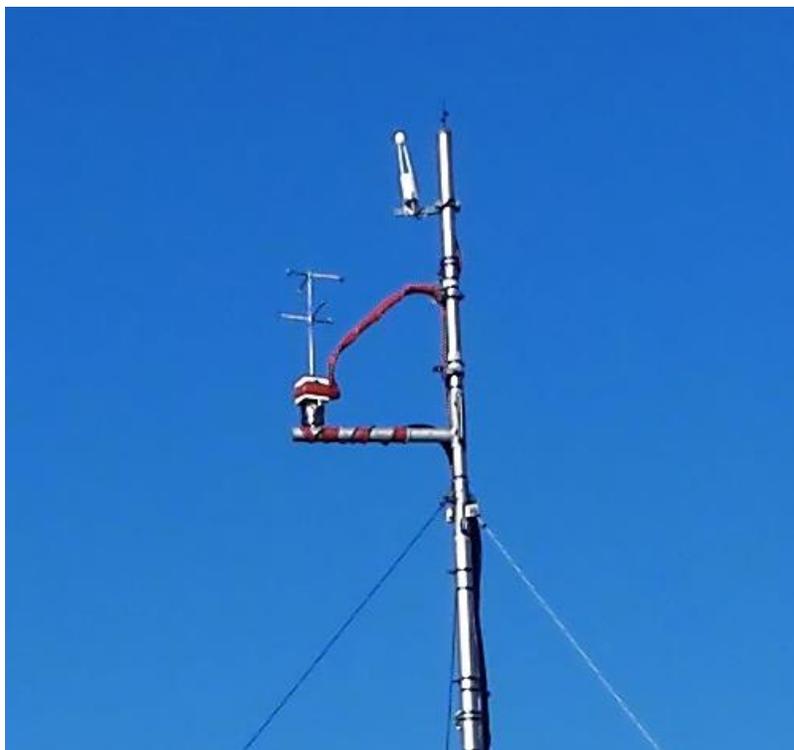


Fig R1. Top of the flux tower.

RC2.9 Page 6 – How do you generate your purge air for the nafion? And zero gas for the LI7000?

The same sample air coming from the gas analyzer is directed to the outer cell of the drier. Thus, the total pressure difference drives the water vapor removal. This indeed does not remove all water vapour but effectively attenuates the fluctuations, as shown by the H₂O variances. Please see the figure below.

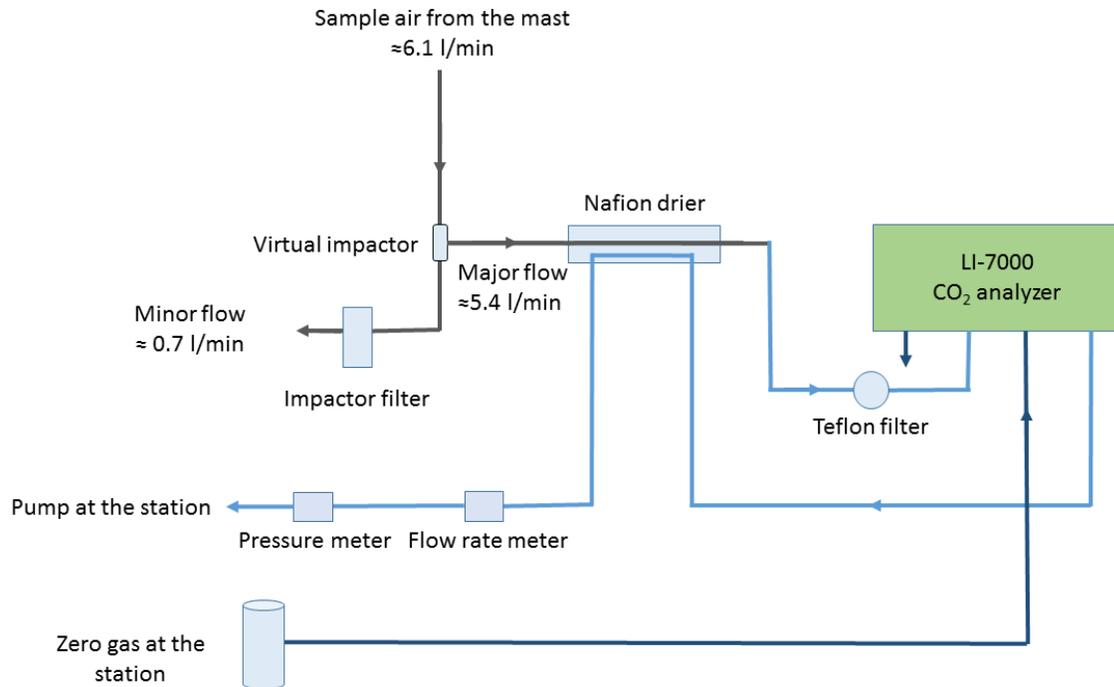


Fig R2. Schematics of the test setup. Dark lines represent steel pipes and light blue lines are Bev-A-line-tubings.

Sentences were added to the page 6 line 9:

The sample air leaving the gas analyzer of the test setup is directed to the purge cell of the drier. Thus, the total pressure difference drives the attenuation of water vapor fluctuations.

Sentences were added to the page 6 line 17:

The same zero gas flows through both analyzers. The actual zero gas bottle (40 l) is located at the station, and a small stream of zero gas flows continuously to the gas analyzers in the instrument hut.

RC2.10 Page 7 – line 14 – Suggest removing the “flow” in “stationary flow conditions”. It’s not purely flow that is involved ($w'c'$).

“Stationary flow conditions” was changed to “stationary conditions”. In addition to the page 7, line 14, this affects also page 1, line 14 and page 7, line 23.

RC2.11 Page 7 – Section 2.3.1. Spectral analysis: Here you’ve applied a limit of $|z/L| < 0.05$. But later, in Figure 8, it appears that about half of the data fall outside of this range. Why did you apply this more stringent criteria? Was there something wrong with the spectra outside this range? Or was it just so the peaks of your spectra lined up more cleanly?

The stringent stratification criterion was chosen so that the peaks of the cospectra would be located at the same frequency range. The spectral analysis procedures were updated:

Observations with an appropriate wind direction (180–260 °) and stationary conditions ($RN_{wc} < 0.3$) were accepted for spectral analysis. 607 half-hour periods met this criterion. Next, we discarded small fluxes ($< 0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$), after which we had 381 half-hour periods. Furthermore, a cospectrum was discarded if its peak was not within a predefined frequency 30 range (0.01–0.5Hz). 283 cospectra passed this frequency range criterion. Also, a cospectrum was discarded if its normalized peak size ($Co_{wCO_2} / w'CO_2'$) was not within predefined range (0.1–1.0). Thus, 238 observations from a 4 month period were used for the spectral analysis.

RC2.12 Within the more limited selection of 612 observations, over half are discarded because they are 'distorted.' I assume this is so you can use the 'good' spectra to get a reasonable/ workable transfer function. That makes sense. But then are you applying that transfer function to correct all observations that pass the stationarity and wind direction criteria, even the ones with distorted spectra? The transfer function should not be expected to fix the fluxes for these other intervals.

The spectral analysis was carried out to determine the performance of the measurement system for estimating and correcting for the flux losses due to attenuation of high-frequency fluctuations. This attenuation is specific to the measurement setup and was described by means of the transfer function shown in Eq. 4. For this function, we estimated the half-power frequency, f_0 , which characterizes the overall performance of the measurement system. As the reviewer agrees, it is reasonable to use the best-quality data for this. The distorted spectras obviously cannot be corrected this way and this is not what we try to do. Rather, we use the specified transfer function with the estimated f_0 and convolute this with the generic cospectra of Kaimal et al., which depend on wind speed and stability, to obtain an estimate of the flux loss that needs to be compensated for.

RC2.13 I think this is an area of the paper that can be developed. If the quality control for CO₂ fluxes (shown in Figures 6 and 9) consists only of the wind direction and stationarity criteria, then the distortion of spectra mentioned in this section needs to be addressed. What is causing the 365 of 612 intervals that satisfy $|z/L| < 0.05$ (and presumably some percentage of intervals with z/L outside this range) to have distorted spectra? Is the distortion in the spectra from low or high frequencies? Or a consistent spike? Does it happen under specific environmental conditions? Is there some way to measure and account for the error such distortions likely introduce into the measured flux? The shape of the spectra, especially if they're consistent, will be useful for indicating what problems may be affecting the tower. Maybe it's low frequency contribution coming from the residual water vapor, maybe the tower is swaying, maybe there is high frequency noise from the IRGAs. If you can give the readers more information here it will help those who plan to deploy similar systems to address those challenges.

We calculated $u'w'$ cospectra and $u'u'$ and $w'w'$ power spectra and found that these followed expected shapes. This implies that the mast does not disturb the flow. However, the position of our gas inlet close to the base of the anemometer was found to be non-ideal for some wind directions. This placement was chosen to minimize the accumulation of sea spray in the tubings (please also see the answer to comment RC2.8 above). Because of this, the $w'c'$ -cospectra of the northernmost wind directions showed a disturbance in high frequencies that grew with increasing wind speed. Thus, we decided to use only southwestern wind directions in this paper. This is now stated in the beginning of Instrumentation chapter:

In this paper, we utilize data from the open sea sector towards the Baltic Proper (180—260 °). The fetch in the sector 260—340 ° may be limited and, as the anemometer base potentially disturbs the flow, the data from this sector were not included in this study.

RC2.14 Page 9 – Figure 3 – When printed the dashed cyan line on subplots d and e is not visible when it overlaps with the blue line. Might want to consider some way to increase the contrast.

The cyan color was changed to yellow in Fig. 3.

RC2.15 Page 10 – Section 3.1.2 – With respect to z_0 , no one was going to complain that an extended open water surface does not satisfy horizontal homogeneity conditions for EC measurements. Yes, the figure does show that you've successfully selected the right wind direction window. But that seemed obvious just from your map. And you could always just include one sentence that says it was confirmed because z_0 was consistently below 1 mm in that window. There isn't anything wrong with this section, but it is not particularly necessary.

Yes, the result is trivial – this calculation was part of our overall QA/QC and site analysis. The Horizontal homogeneity section was moved to the appendices.

RC2.16 Page 7 – line 3 – Here you've handled the tube delays by taking the maximum covariance. I know this is a common practice. But my experience has been that it often results in the selection of fluxes which have large contributions from frequencies outside the expected range. Have you calculated the expected tube delays based on your known tube lengths, tube diameters, and flow rate? How well do the maximum covariance lags match the expected lag based on this calculation? If you base the tube delay on this calculation do you see improvement in the percentage of spectra that are distorted (page 7 – line 26)? I don't think this necessarily needs to be reported on in the final paper, but it's worth checking.

The maximum absolute covariance is calculated within a predefined lag range, which is selected on the basis of the expected delay. If no maximum is found within this lag window, a default value is used. As the reviewer points out, this is a common practice. However, the default value is derived from the statistics of the calculated lags rather than tube geometry and flow rate.

The setups are complex, especially the one with a drier and a virtual impactor, and the effective tubing volume cannot be evaluated accurately. Using the dimensions of the outer and inner tubings and the measured flow rate, the lag would be 2.6 s, whereas the maximum covariance is found using the lag of 3.0 s on average. The cospectra become clearly disturbed if a non-optimal lag is adopted.

We have checked the cases where the $w'c'$ cospectrum is distorted and tested a wide range of different lags. The distortion is seen with all lags. Assuming the 'expected' lag does not improve the cospectra; it only affects the frequency at which the deviation from the ideal cospectrum appears.

RC2.17 Page 11 – line 2 – What is the average high-frequency correction?

The sentence was changed to:

The average high-frequency correction of the CO₂ flux during the measurement period was 17 % for the test setup and 13 % for the standard setup.

RC2.18 Page 11 – line 15 – How do you handle the range of f_0 (e.g., 0.04 to 0.22) in correcting the attenuation of latent heat flux? Did you calculate the different transfer functions for different relative humidities based on

their f_0 ? Your assertion that the flux attenuation (for RH=80%) is 44% of the real flux would be strengthened by a comparison of your result to an empirically-based model (e.g., COARE [Fairall et al. 2003]).

We plotted f_0 values as a function of RH, and fitted a power law curve on it.

The H₂O flux attenuation is mainly produced by absorption and desorption of water vapor on the surface of the tubings. Tube aging plays a role in the size of this attenuation (Mammarella et al., 2009). In our case, this aging is likely caused by the accumulation of sea salt in the tubings. Thus, this attenuation is setup-specific.

C2.19 Not critical, but since you are using these latent heat fluxes to interpret your CO₂ fluxes it wouldn't hurt to show the CowH₂O cospectra of the undried system.

Yes, this would give a better expression of the size of the H₂O flux attenuation in the tubing in marine environment. We added a median of w'H₂O' cospectra in the Fig. 4.

RC2.20 Page 12 – line 8 – So the reader doesn't have to flip back several pages to Figure 3 it would be helpful here to place a reminder that all the CO₂ fluxes in July were expected to be negative. Maybe insert something like “(all of which were expected to be negative)” after “July 2017”.

Added the suggested sentence to page 12 line 8:

all of which were expected to be negative

RC2.21 Page 14 – Section 3.1.5 Turbulence: I think this section is unnecessary. It distracts from the main purpose of the paper (CO₂ fluxes). In reading it felt like a distinct transition to a new subject. One which required more effort than the payoff was worth. I think this section would be better left to its own paper, when the authors have developed it further and have the space to discuss the implications. For this paper, there was no practical application. If there is a reason that this relates to the CO₂ fluxes that you've shown then that reason should be made more clear.

We feel that this section is important for the overall quality assurance of our new measurement setup but to clarify the text, we moved it to the appendix C.

Technical Corrections

RC2.22 Page 3 – line 26 – Word choice on “effortless”. Might want to go with something like more feasible, practical, or straightforward (or conversely ‘not as logistically challenging’).

Agreed, these measurements indeed are not completely effortless. The word was changed to “more feasible”.

RC2.23 Page 3 – line 31 – Grammar: “and the drying of sample is straightforward to implement” to “and allows for straightforward implementation of sample air drying” (or similar)

Changed the sentence to:

and allows straightforward implementation of sample air drying

RC2.24 Page 5 – Citations at the ends of each paragraph should be moved inside the period.

The citations regarded the whole paragraphs.

RC2.25 Page 5 – line 17 – Change “A : : tower is placed” to “A : : : tower was placed”

The grammatical tense was fixed.

RC2.26 Page 7 – line 6 – “was considered” to “were considered”

Done.

RC2.27 Page 7 – line 23 – “based on the criterion that $RN_w'c' < 0.3$ ” would read better if it were enclosed in parentheses rather than commas. This would match the way you’ve presented the wind direction criterion.

True. Changed the sentence to:

Observations with an appropriate wind direction (180–340°) and stationary conditions ($RN_w'c' < 0.3$) were accepted for spectral analysis.

RC2.28 Page 8 – line 3 – Consider reorganizing the sentence that begins with “To correct for: : :”. It is difficult to read.

The sentences were modified:

To correct for the high-frequency attenuation of fluxes, the universal Co_{wT} equations reformulated by Horst (1997) from those originally presented by Kaimal et al. (1972) and Kaimal and Finnigan (1994) were used as a reference. As the shape of this universal cospectrum depends on stability and wind speed, the attenuation for each 30 min flux was calculated as a function of these meteorological parameters.

RC2.29 Page 8 – line 26 – “seasons of carbon cycle” to “seasons of the carbon cycle”

Done.

RC2.30 Page 10 – line 13 – “Especially, a large swell : : :” is an incomplete sentence.

The sentence was removed.

RC2.31 Page 14 – Figure 8 – “f” in the xlabel of subplot b should be “fc” for consistency with how it’s written in the text.

Done.

RC2.32 Page 16 – line 25 – “the difference between the dried and undried sea-air CO₂ flux measurements were very similar” needs to either become “the difference between the dried and undried sea-air CO₂ flux measurements was small” or “the difference between the dried and undried sea-air CO₂ flux measurements were very similar.”

Page 16 line 25 was changed to:

the difference between the dried and undried sea-air CO₂ flux measurements was very small

RC2.33 Also, the second part of this sentence doesn’t work as it’s written because the subject of the sentence changes.

The sentence was broken down to two sentences:

This also proves that a Nafion drier (in our case combined with a virtual impactor) does not disturb the CO₂ flux measurements.

RC2.34 Page 18 – Figure 11 caption – move “(standard setup – test setup)” to immediately after “CO₂ flux difference”

Done.

References:

Mammarella, I., S. Launiainen, T. Gronholm, P. Keronen, J. Pumpanen, Ü. Rannik and T. Vesala. Relative humidity effect on high-frequency attenuation of water vapor flux measured by closed-path eddy covariance system. *Journal Of Atmospheric And Oceanic Technology* 26:1856-1866. 2009.

Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97(C5), 7373–7382, doi: 10.1029/92JC00188.

Measuring turbulent CO₂ fluxes with a closed-path gas analyzer in marine environment

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Abstract. ~~Sea-air~~ In this study, we introduce new observations of sea-air fluxes of carbon dioxide (CO₂) ~~were measured~~ using the eddy covariance method ~~at a new station established.~~ The observations took place at Utö Atmospheric and Marine Research Station on the Utö ~~island~~ Island in the Baltic Sea. The flux measurement system is based on a closed-path infrared gas analyzer (LI-7000, LI-COR) requiring only occasional maintenance, so the station is capable of continuous monitoring. However, such

5 infrared gas analyzers are prone to significant water vapor interference in a marine environment, where CO₂ fluxes are small.

In July–October 2017, two LI-7000 analyzers were run in parallel to test the effect of a sample air drier which dampens water vapor fluctuations, and a virtual impactor, included to remove liquid sea spray, both of which were attached to the sample air tubing of one of the analyzers. The systems showed closely similar ($R^2 = 0.99$) sea-air CO₂ fluxes when the latent heat flux was low, which proved that neither the drier nor the virtual impactor perturbed the CO₂ flux measurement. However, the

10 undried measurement had a positive bias that increased with increasing latent heat flux, suggesting water vapor interference.

For both systems, cospectral densities between vertical wind speed and CO₂ were distributed within the expected frequency range, with a moderate attenuation of high-frequency fluctuations. While the setup equipped with a drier and a virtual impactor generated a slightly higher flux loss, we opt for this alternative for its reduced water vapor cross-sensitivity and better protection against sea spray. The integral turbulence characteristics were found to agree with the universal stability dependence observed

15 over land. Non-stationary ~~flow~~ conditions caused unphysical results, which resulted in a high percentage (~~up to 63~~ 65%) of discarded measurements. After removing the non-stationary cases, the direction of the sea-air CO₂ fluxes was in good accordance with the measured CO₂ partial pressure difference between the sea and the atmosphere. Atmospheric CO₂ concentration changes larger than 2 ppm during a 30 min averaging period were found to be associated with the non-stationarity of CO₂ fluxes.

20 ~~The Utö Atmospheric and Marine Research Station continues to monitor the regional CO₂ exchange between the sea and the atmosphere, utilizing the results of this work.~~

1 Introduction

Anthropogenic actions, such as combustion of fossil fuels and land use changes, have perturbed the global carbon cycle, resulting in climatic changes (e.g. Solomon et al., 2009). A quarter of the anthropogenic carbon dioxide (CO₂) emissions to the atmosphere are bound by the oceans (Heinze et al., 2015), causing ocean acidification (Feely et al., 2009). To better understand the global carbon cycle, measurements of the CO₂ exchange between the atmosphere and marine ecosystems are required. These measurements are also useful for developing parameterizations of gas exchange intensity, such as the gas transfer velocity, used in global carbon models (e.g. Takahashi et al., 2002). In the case of coastal seas, sea-air CO₂ flux measurements provide information about the feedbacks between the aquatic carbonate system and marine ecosystems, since the direction and magnitude of these fluxes depend on the photosynthetic carbon assimilation in surface seawater. Although the continental margin seas cover only a small portion of the oceans, up to 15 % of the total ocean primary production takes place in these seas, which are responsible for over 40 % of the total oceanic carbon sequestration (Muller-Karger et al., 2005).

With the development of fast-response infrared CO₂ analyzers, it has become possible to apply the eddy covariance method for directly measuring the sea-air CO₂ fluxes (Jones and Smith, 1977). Early on, however, Webb et al. (1980) showed that the CO₂ flux measurements made with this technique need to be corrected for the effects of temperature and water vapor (H₂O) fluctuations. This correction can be significant in aquatic environment, even of the same order as the measured CO₂ flux (Sahlée et al., 2011). More recently, it has been recognized that CO₂ gas analyzers suffer from water vapor cross-sensitivity (Kohsiek, 2000). Blomquist et al. (2014) concluded that this is the most significant error source in sea-air CO₂ flux measurements, because the CO₂ fluxes in marine environment are typically small, as compared to terrestrial ecosystems. A solution to the cross-sensitivity problem is to dry the sample air before the measurement (e.g. Miller et al., 2010). Also, efforts have been made to correct for the cross-sensitivity problem in the data post-processing phase (e.g. Prytherch et al., 2010; Edson et al., 2011). However, these corrections may be inadequate and thus do not obviate the use of a drier (Landwehr et al., 2014).

The cross-sensitivity results from the overlap of the infrared radiation frequency bands of CO₂ and H₂O, because of which the H₂O molecules present will increase the apparent CO₂ concentration. If the optical filter, used for the selection of the transmitted frequency band, leaks out-of-band radiation, a substance with a different absorption frequency band can interfere the measurement. This effect is referred to as the direct absorption cross-sensitivity. In addition, the collisions with different molecules cause the frequency bands to broaden (so-called pressure broadening). By testing some commercial infrared gas analyzers, Kondo et al. (2014) found out that the factory-calibrated correction for the direct absorption interference may not be optimized and that the pressure broadening effect caused an overestimation of the CO₂ flux, which increased with increasing water vapor flux.

Infrared gas analyzers are classified according to the type of the optical path: the open-path analyzers measure the absorption of the infrared signal in ambient air, whereas the closed-path gas analyzers have an enclosed measurement chamber. Both types suffer from H₂O cross-sensitivity but otherwise have differing pros and cons; for instance, the closed-path instruments are known to act as low-pass filters, which generates a loss in the measured flux (Leuning and King, 1992). On the other hand, a long sample line attenuates temperature fluctuations, thus eliminating the need for correcting for sample air expan-

sion/contraction (Rannik et al., 1997). For a closed-path analyzer, the dilution due to water vapor (Webb et al., 1980) can be corrected accurately as a point-by-point operation on the high frequency data, which is not possible with open-path analyzers (Ibrom et al., 2007).

As direct sea-air gas exchange measurements are performed in the surface boundary layer, in a close proximity to the water surface, liquid sea spray may block the optical path of open-path sensors and clog the inlet of closed-path analyzers. In addition, high relative humidity can produce H₂O condensation on the lenses of an open-path system. In a closed-path system, the accumulation of sea salt on the optical lenses is minimized as the inlet is typically protected by a Teflon filter. Efforts have been made to solve the sea-spray contamination problem of open-path sensors by cleaning the optics regularly (Kondo and Tsukamoto, 2007). However, this may be technically challenging, because sea salt films can be formed on the windows of an open-path analyzer in a matter of hours (Miller et al., 2010).

Open-path gas analyzers have been mostly applied for sea-air CO₂ flux measurements due to their low power consumption, small high frequency attenuation and ease of data synchronization with wind measurements (Blomquist et al., 2014). Additionally, Miller et al. (2010) found out that closed-path sensors are more sensitive to (ship) motion than the open-path sensors. However, this does not apply to all closed-path analyzers, since some of them have internal design resembling open-path instruments (LI-COR, 2016).

While the eddy covariance method is widely used for directly measuring the surface-atmosphere exchange of energy and matter, it is based on several theoretical assumptions. These include the horizontal homogeneity of terrain and the stationarity of transport processes, and that turbulence is fully developed and there exists no other transport mechanisms than vertical turbulence (e.g. Dabberdt et al., 1993). Foken and Wichura (1996) noted that flow non-stationarity is one of the most serious problems affecting the surface exchange measurements, as in such conditions the observed turbulent flux does not equal the flux at the surface. The stationarity assumption can be violated owing to diurnal forcings and varying weather patterns, for example. Horizontal CO₂ gradients develop easily in the vicinity of sea-land boundary, violating the assumptions of horizontal homogeneity and negligible advection (Rey-Sánchez et al., 2017). Because an obstacle in a flow field generates an uplift zone on the windward side of an obstacle (Chatziefstratiou et al., 2014), there should not be steep elevation changes near the flux tower in order to avoid non-zero vertical wind speed. Also the roughness and flux discontinuities on a sea-land boundary generate secondary circulation that drives advection and causes challenges for coordinate rotation (Kenny et al., 2017).

The Baltic Sea forms a large and diverse biogeochemical system, providing a great potential for studying interactions between the marine ecosystem and the aquatic carbonate system. However, only a few fixed measurement sites measuring sea-air CO₂ fluxes are located in the Baltic Sea (Rutgersson et al., 2008; Lammert-Stockschaeder and Ament, 2015). A micrometeorological tower placed on the shore of an island offers a cost-effective alternative to ship measurements, as maintenance and installations are more effortlessfeasible. Moreover, a motion correction, required with ship measurements, is not needed and the flow distortion can be minimized with a suitable positioning of the flux tower.

In this paper, we introduce a newly established and currently operating eddy covariance measurement site, located on the Utö ~~island~~ Island in the Baltic Sea, ~~and analyze~~. This paper has two objectives: 1) Study the characteristics of the new site and measurement setup and 2) Analyze empirically the effect of water vapor on the CO₂ sea-air fluxes. After experimenting with

an open-path and a semi-open-path gas analyzer, we opted for a closed-path sensor, which can be protected against sea spray contamination, and ~~the drying allows straightforward implementation~~ of sample air ~~is straightforward to implement~~drying. We compare measurements made with two identical closed-path analyzers, one of which is equipped with a drier and a virtual impactor. We also address the quality of these measurements by analyzing the stationarity and integral turbulence characteristics of the flow and the homogeneity of flux footprints.

2 Materials and methods

2.1 Site description

The measurement site is located on the island of Utö in the southern edge of the Archipelago Sea in the Baltic Sea (59°46'55" N, 21°21'27" E) (Fig. 1). The Archipelago Sea is a small sea area between the southwest coast of Finland and the sea of Åland and is characterized by thousands of small islands. The island of Utö is a treeless cliff with small shrubs, with an area of 0.81 km².

~~Location of the Utö island in the Archipelago Sea. The research installations on the island consist of the Utö Atmospheric and Marine Research Station (A), a flow-through pumping system (inlet at B), the Atmospheric ICOS station (C), and a weather and air quality station (D). The red dashed lines indicate the wind sector suitable for sea-air flux measurements (180–340).~~

Since 2012, the Finnish Meteorological Institute has been building up the new Utö Atmospheric and Marine Research Station in collaboration with the Finnish Environment Institute (Laakso et al., 2018). The choice of this island was due to its easy access, well-developed technical infrastructure, permanent inhabitation and the long-term meteorological and marine measurements. ~~Finnish Meteorological Institute's meteorological measurements date back to 1881, and the seawater temperature and salinity measurements were initiated in 1900 (Laakso et al., 2018). Also, the Integrated Carbon Observation System (ICOS) research infrastructure has an atmospheric station on the island.~~

~~The Utö Atmospheric and~~

The Marine Research Station and its flux tower are located on the western side of the island. To the west of the shore, the water depth quickly deepens to 80 m. The closest shoal, Tratten, is located 1.4 km to the southwest and has an area of 0.6 hectares.

The mean annual wind speed at Utö is 7.1 m s⁻¹. On average, the minimum monthly wind speed occurs in July (5.6 m s⁻¹) and the maximum in December (8.9 m s⁻¹). The wind blows approximately 60 % of the time from the sector between south and northwest (Fig. 1), providing a good temporal coverage for the sea-air flux measurements. (Pirinen et al., 2012)

The mean annual air temperature in Utö is 6.6 °C, whereas the mean annual surface seawater temperature at the depth of 5 m is 8.1 °C. In deep water (at 50 m depth), the mean annual seawater temperature is 4.4 °C. The maximum monthly mean air temperature (16.7 °C) is observed in July, whereas the seawater at 5 m depth reaches its maximum temperature (16.1 °C) in August. The minimum temperature of air (-2.1 °C) occurs in February, while the temperature of the surface seawater is at its minimum (1.0 °C) in March. On average, there exists ice around Utö for every few years with a typical ice cover duration ranging from one to three months. (Laakso et al., 2018)



Figure 1. Location of the Utö island in the Archipelago Sea. The research installations on the island consist of the Utö Atmospheric and Marine Research Station and its flux tower (A), the inlet of the flow-through pumping system (B), the Atmospheric ICOS station (C), and a weather and air quality station (D). The red dashed solid lines indicate the wind sector used for sea-air flux measurements (180–260°) used in this paper and the dashed line indicates the possible region used in future.

Unlike the oceans, the carbon cycle in the Baltic sea is heavily influenced by biological activity. During summer, the partial pressure of CO₂ (pCO₂) in surface water declines to approximately ~~15~~10 Pa (100 μatm) as a result of primary production. pCO₂ in surface water has its maximum ~~60~~ Pa (600 μatm) during winter, when biological activity is diminished, mineralization prevails and mixing processes transport CO₂-rich seawater to the surface. Due to the annual cycle of primary production, the Baltic Sea is a source of CO₂ to the atmosphere in winter and a sink in summer. Upwelling and diurnal biological cycle generate short-term variations in the surface water pCO₂. (Wesslander, 2011)

2.2 Instrumentation

A 9 m tall micrometeorological tower ~~is was~~ placed on the western shore of the island (Figs. 1, 2). The tower is mounted on a cliff that has no vegetation. The base of the tower is approximately 3 m above the sea level and the horizontal distance between the tower and the sea is approximately 4 m. ~~When measuring sea-air exchange, only the fluxes related to the westerly winds (180–340) are used. In this paper, we utilize data from the open sea sector towards the Baltic Proper (180–260°). The fetch in the sector 260–340° may be limited and, as the anemometer base potentially disturbs the flow, the data from this sector are not included in this study.~~

Air velocity components together with air temperature, T , were measured with an acoustic anemometer/thermometer (uSonic-3, Metek) attached to the top of the tower (11.5 m a.s.l.). CO₂ and H₂O molar fractions were measured by using two closed-path differential non-dispersive infrared gas analyzers (LI-7000, LI-COR) that were placed in a 1.5 m tall instrument hut close to the



Figure 2. The flux tower on the shore of the Utö island during a high-western-swell-wintertime westerly storm (photo by Ismo Willström).

tower (Fig. 2). The inlets of both sample flows are protected with a grate and are located directly beneath the anemometer; the distance between the inlets and the lower anemometer transducers is 30 cm. The outside parts of the tubes are approximately 10 m long and are made of Teflon (inner diameter of 3.175 mm) and steel (inner diameter of 4.0 mm). The steel-tube sample line is equipped with a virtual impactor (see Appendix A), to protect the instrument from possible exposure to liquid water, and a 30 cm long PD-100T-12-MKA drier (Perma-Pure) to attenuate water vapor fluctuations. The drier is based on the partial pressure difference that drives water vapor from the sample air to the purge stream through a Nafion membrane. The sample air leaving the gas analyzer of the test setup is directed to the purge cell of the drier. Thus, the total pressure difference drives the attenuation of water vapor fluctuations. Nafion driers are found to have only a small permeability to CO₂ (Welp et al., 2013).

Inside the instrument hut, the flow continues in 1 m long Bev-A-Line tubes, which are protected by Teflon filters and connected to the analyzers. Data are logged at a 10 Hz frequency and transmitted through the Internet to a server. The hut temperature is regulated using a fan and a radiator, since large temperature changes influence the performance of the CO₂ analyzers.

An external pump is used for producing a sample flow at a rate of approximately 6 l min⁻¹ for both setups. We operate the LI-7000 gas analyzers in the absolute mode, which means that a small stream of zero gas (0 ppm CO₂) is constantly flowing through the reference cell of both analyzers. The gas analyzers same zero gas flows through both analyzers. The actual zero gas bottle (40 l) is located at the station, and a small stream of zero gas flows continuously to the gas analyzers in the instrument hut. The gas analyzers are calibrated with zero and span (364.4 ppm CO₂) gases every three months. After calibration, the Teflon filters are renewed and the virtual impactor is cleaned. The outside tubes are washed with an isopropyl alcohol-water mixture annually. At the same time, the Bev-A-Line tubes and the internal chemicals of the gas analyzers are renewed and the optical paths are cleaned.

The setup with the Nafion drier and the virtual impactor is referred here to as the 'test setup' and the other setup as the 'standard setup'. The standard setup represents a typical closed-path gas analyzer-based eddy covariance setup commonly

applied on terrestrial ecosystems (e.g. Aurela et al., 2015). The test setup is an improved version of this configuration, designed especially for a marine environment where water vapor and sea spray are likely to give rise to problems.

2.3 ~~Methods used in flux calculations~~ Data processing

2.3.1 Flux calculation

- 5 As the LI-7000 gas analyzer does not directly provide molar fractions with respect to dry air, we first calculated the dilution corrected CO₂ molar fraction as:

$$c = \frac{c_w}{1 - q}, \quad (1)$$

where c_w is the uncorrected molar fraction of CO₂ and q is the molar fraction of H₂O.

- 10 It is assumed that the long pipe lines, both Teflon and steel, strongly attenuate the temperature fluctuations and thus there is no need for correcting for expansion/contraction effects in the sample air (Rannik et al., 1997). The eddy covariance mass flux was calculated from the fluctuations of molar fractions of an atmospheric quantity, χ , and vertical wind speed, w :

$$F = \rho_d \overline{w' \chi'}, \quad (2)$$

- 15 where ρ_d is the dry air density. The primes denote the 10 Hz fluctuations with respect to a time average and the overbar denotes arithmetic averaging. An averaging period of 30 min was adopted. For each period, the time delay between the acoustic anemometer and gas analyzer data flows was determined by maximizing the (absolute) covariance in Eq. 2 within a predefined time window, and a double coordinate rotation was applied to ensure zero vertical wind speed.

- Obvious outliers were discarded by including only those CO₂ fluxes that are within three standard deviations from the mean. The fulfillment of several theoretical requirements for the eddy covariance measurements ~~was~~ were considered. The non-stationarity of the flux measurements was analyzed by comparing the average of the CO₂ fluxes calculated for 5 min subperiods ($\frac{1}{6} \sum_{i=1}^6 \overline{w' c'}_{5 \text{ min}, i}$, where i is the index of the subperiod) with the 30 min flux ($\overline{w' c'}_{30 \text{ min}}$) (Foken and Wichura, 1996). The relative non-stationarity, RN , for a given variable, ζ , was defined as:

$$RN_{\zeta} = \left| \frac{\frac{1}{6} \sum_{i=1}^6 \zeta_{5 \text{ min}, i} - \zeta_{30 \text{ min}}}{\zeta_{30 \text{ min}}} \right|. \quad (3)$$

- 25 In the case of CO₂ flux, $\zeta = \overline{w' c'}$. Here, 30 min period is regarded as stationary if both of the CO₂ flux measurements fulfil the condition $RN_{\overline{w' c'}} < 0.3$. To test the development of turbulence, integral turbulent characteristics of temperature and vertical velocity were compared to universal surface-layer functions (Thomas and Foken, 2002). It is assumed that turbulent transport of all scalars (T , CO₂ and H₂O) are similar, and thus only the characteristics of T are examined here. For this examination, only stationary ~~flow conditions~~ ($RN_{\overline{w' c'}} < 0.3$) conditions within the sea sector are included. An observation is also discarded if a positive momentum flux is measured, as these can be considered a sign of flow non-stationarity (Yang et al., 2016).

2.3.2 Spectral analysis

Spectral analysis was carried out in order to evaluate the high frequency attenuation of the fluxes. High frequency attenuation was examined by calculating the cospectra between w and c ($C_{o_wCO_2}$) and q ($C_{o_wH_2O}$) and comparing these with the corresponding cospectra between w and T (C_{o_wT}). For this purpose, it is assumed that the high frequency end of C_{o_wT} is unattenuated and the atmospheric turbulent transport of heat, water vapor and CO_2 are similar.

5 Before calculating the half-hourly cospectra using the discrete Fourier transform, the 10 Hz data were linearly detrended and the Hamming window was applied. The cospectra were normalized with the corresponding covariances and interpolated into 64 logarithmically equally spaced bins.

Observations with an appropriate wind direction (~~180–340~~180–260^o) and stationary ~~flow conditions~~, ~~based on the criterion that conditions~~ ($RN_{w'c'} < 0.3$), were accepted for spectral analysis. ~~Observations during slightly unstable to slightly stable hydrostatic stability conditions ($|z/L| < 0.05$) were examined, where z is the measurement height and L is the Obukhov length. In total, 612 observations met these criteria. Furthermore, every cospectrum was visually inspected and the clearly distorted ones (365) were discarded~~ 607 half-hour periods met this criterion. Next, we discarded small fluxes ($< 0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$), after which we had 381 half-hour periods. Furthermore, a cospectrum was discarded if its peak was not within a predefined frequency range (0.01–0.5 Hz). 283 cospectra passed this frequency range criterion. Also, a cospectrum was discarded if its
 15 normalized peak size ($C_{o_wCO_2}/w'CO_2'$) was not within predefined range (0.1–1.0). Thus, ~~247~~238 observations from a 4 month period were used for the spectral analysis.

~~To describe the~~ The spectral attenuation of the flux as a function of frequency, f , ~~a~~ was described by an exponential transfer function, Γ , ~~was determined.~~

$$\Gamma(f) = \exp\left[-\log(2)\left(\frac{f}{f_0}\right)^2\right], \quad (4)$$

20 where f_0 is the half-power frequency at which the ratio of spectral densities is 0.5. For fitting the transfer function, the cospectra were normalized so that their peaks were leveled. Also, the outermost points were discarded. Using a non-linear least squares fit, an exponential transfer function was fitted to the ratio of $C_{o_wCO_2}$ or $C_{o_wH_2O}$ to C_{o_wT} :

$$\Gamma(f) = \exp\left[-\log(2)\left(\frac{f}{f_0}\right)^2\right],$$

~~where f_0 is the half-power frequency at which the ratio of spectral densities is 0.5.~~ In the case of H_2O fluxes, a power-law relationship between f_0 and relative humidity (RH) was additionally derived similarly to Mammarella et al. (2009).

To correct for the high-frequency attenuation of fluxes, ~~which depends on stability and wind speed,~~ the universal C_{o_wT} equations reformulated by Horst (1997) from those originally presented by Kaimal et al. (1972) and Kaimal and Finnigan (1994) were used as a reference. As the shape of this universal cospectrum depends on stability and wind speed, the attenuation for each 30 min flux was calculated as a function of these meteorological parameters.

30 2.4 Auxiliary data

In addition to the flux measurements, we present here data of the dissolved CO_2 concentration in surface seawater, which is ~~monitored~~ measured using a Super CO_2 system (Sunburst Sensors) connected to a flow-through pumping system. The

SuperCO₂ instrument consists of a shower-head equilibration chamber and an infrared gas analyzer (840A, LI-COR). To account for sensor drift, the flows of four reference gases are directed into the instrument every four hours, and a linear correction is calculated from these calibration measurements. The system automatically cleans the equilibration chamber with hydrogen peroxide periodically. The inlet for seawater intake is located 250 m west of the station (Fig. 1) and ~~it is kept at~~
5 ~~5~~ is kept 4.5 m depth by below the mean sea level using floats. The water depth at this location is 23 m. Since sample water exchanges heat with the pipe and its surroundings, a correction for this temperature effect was applied according to Takahashi et al. (1993):

$$p\text{CO}_{2\text{in}} = p\text{CO}_{2\text{eq}} \exp[0.0423(T_{\text{in}} - T_{\text{eq}})], \quad (5)$$

where $p\text{CO}_{2\text{in}}$ is the temperature-corrected partial pressure of CO₂, $p\text{CO}_{2\text{eq}}$ is the observed partial pressure of CO₂, T_{in} is
10 seawater temperature measured close to the inlet, and T_{eq} is the temperature measured in the tubing right before the equilibration chamber. This correction is, however, applied only since the beginning of August 2017, after the installation of the inlet thermometer measuring T_{in} . Additionally, sea bottom temperature below the inlet is ~~monitored using another thermometer~~
measured by an internal thermometer inside an Acoustic Doppler Current Profiler (ADCP).

The atmospheric concentration of CO₂ at the height of 57 m was measured at the ICOS station (C in Fig. 1). At this station,
15 the dry molar fraction of CO₂ is measured by using a very stable cavity ring-down spectroscopy technique (G2401, Picarro). For more information on the atmospheric ICOS measurements at Utö, the reader is referred to Kilkki et al. (2015).

3 Results and discussion

3.1 Suitability of the site for eddy covariance measurements

3.1.1 Environmental conditions

20 The measurement period (1 July – 1 November 2017) represents the late summer and autumn seasons of the carbon cycle, when biological activity diminishes and the sea-air $p\text{CO}_2$ difference shifts from negative to positive (Fig. 3e). At the beginning of this period, from July to mid-August, the atmospheric $p\text{CO}_2$ exceeded that in the sea, and the sea acted as a sink of atmospheric CO₂. The average sea-air $p\text{CO}_2$ difference from July to mid-August was 8.0 Pa. During the latter part of August, the sea turned to a source as a result of diminished primary production. The efflux was enhanced when thermal stratification broke down and
25 CO₂-rich water surfaced at the beginning of September, resulting in increased surface $p\text{CO}_2$. After this event, the partial pressure difference stayed predominantly within 10–20 Pa for the rest of the measurement period, showing only occasional deviations from this range.

The values reported for the sea surface $p\text{CO}_2$ represent conditions at the depth of 5 m at a single point 250 m away from the flux tower, in the middle of the flux measurement sector. In some cases, this location may not represent the carbonate conditions
30 of the whole sea sector area. Especially during the beginning of the measurement period, it is possible that there is horizontal differences in the surface $p\text{CO}_2$ due to variations in biological activity (Rutgersson et al., 2008). During other periods, the

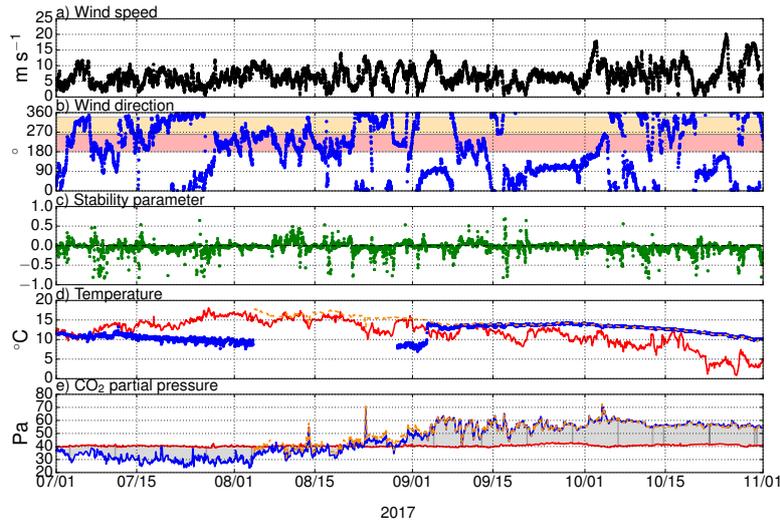


Figure 3. Environmental conditions at Utö in July–November 2017: (a) wind speed, (b) wind direction (red band indicates the directions suitable used for sea-air flux measurements in this study and yellow band indicates additional directions that will be considered in the future), (c) stability (z/L), (d) air temperature (red) and sea temperature at 5 m depth (cyan/orange) and at the sea bottom (blue), and (e) CO₂ partial pressure in air (red), and temperature-corrected (cyan) and uncorrected (blue) CO₂ partial pressure in seawater at 5 m depth. Wind speed, wind direction, stability and air temperature were measured in the flux station (A in Fig. 1). Seawater temperatures and pCO₂ were measured at the inlet (B in Fig. 1). The pCO₂ in air was measured in the ICOS station (C in Fig 1).

horizontal differences are likely to be small in the open sea areas and the surface sea layer is likely to be well-mixed at least to the depth of 5 m. Thus, we assume that our pCO₂ observations represent the surface conditions.

During our study period, the wind blew from the sea sector (180–340/180–260°) for 49/28 % of the time (Fig. 3). This caused gaps in the sea-air flux time series; for instance during the last two weeks of September, the wind directions were unsuitable for sea-air exchange measurements. The average wind speed within the marine wind sector was 6.9 m s⁻¹. Stability was mostly near-neutral. A small part (3.7 %) of the momentum fluxes measured in the marine sector were positive, and thus the corresponding CO₂ flux data were discarded.

In July, air temperature was still gradually increasing and it reached 18 °C by the end of the month. From the beginning of August, both air and sea surface temperature decreased approximately linearly. During the last three months, surface sea water cooled by 7 °C and air by 10 °C.

3.1.2 Horizontal homogeneity

Horizontal homogeneity within the sea sector (180–340) was examined in terms of the surface roughness length (z_0), which was calculated from the logarithmic wind profile law using data collected during neutral conditions, $|z/L| < 0.01$ (Fig. B1).

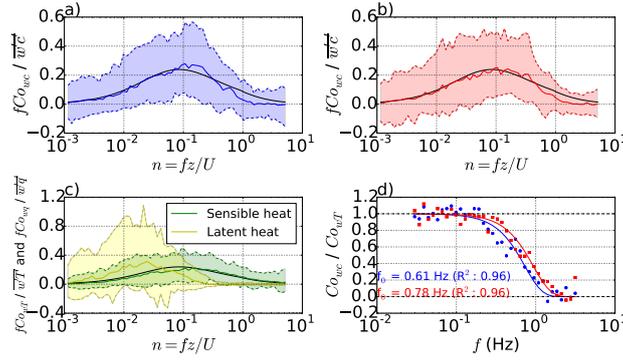


Figure 4. Cospectral Normalized cospectral densities $C_{O_wCO_2}$ of (a) the test setup and (b) the standard setup, and (c) C_{O_wT} (green) and C_{O_wQ} (yellow). The solid lines represent the mean-median cospectra and the dashed lines represent the 10th and 90th percentiles. The black line is the model C_{O_wT} (Horst, 1997). (d) Ratios of cospectral densities (dots) and the fitted exponential transfer functions (solid lines), where the red color indicates the standard setup and the blue color indicates the test setup.

Surface roughness length as a function of wind direction. The red band indicates the directions considered the open sea sector:

The sea sector is clearly visible in a range of $180-340^\circ$, where z_0 is mainly lower than 1. Outside this sector, z_0 is clearly higher, up to 1 in northeastern wind directions. The sea sector indicated by z_0 coincides well with the sector deduced from the geographical map (Fig. 1).

While the sea sector can be considered sufficiently homogeneous, there is scatter in z_0 reflecting the fact that it depends on the sea state. Taylor and Yelland (2001) found that over a sea surface z_0 depends on the significant wave height and the slope of the wave. Since the measurement site is located on the coast, both the fetch and swell can depend on wind direction. Especially, a large swell can originate from the south, i.e. from the open waters of the Baltic Proper.

3.1.2 Spectral characteristics

The cospectra $C_{O_wCO_2}$ of both measurement setups agreed well with the modeled cospectrum (Horst, 1997) in all frequencies (Fig. 4). The low frequency ends of the measured cospectra approach zero in a similar way to the modeled cospectrum.

The attenuation of the highest frequencies was slightly higher in the more complex tubing: $C_{O_wCO_2}$ of the test setup (with a drier and a virtual impactor) diverged from the modeled C_{O_wT} at a slightly lower frequency than that of the standard setup.

The half-power frequency for the standard and test system was 0.770.78 Hz and 0.590.61 Hz, respectively. These values were used to correct the CO_2 fluxes according to the model cospectrum. The average high-frequency correction of the CO_2 flux during the typical meteorological conditions ($U = 6.9 \text{ ms}^{-1}$ and $z/L = -0.05$) is 15 measurement period was 16 % for the test setup and 1112 % for the standard setup.

The drier and virtual impactor added approximately 1 m to the length of tubing, which only has a minor effect on the attenuation of turbulent fluctuations. However, the virtual impactor forms a 90° angle to the tubing, which can stabilize the

flow making it laminar at a higher Reynolds number, Re , than in a straight tube (Lenschow and Raupach, 1991). It would be ideal to have turbulent conditions in the tubes, because scalar fluctuations dampen less in a turbulent pipe flow due to the more uniform velocity profile (Lenschow and Raupach, 1991). At low temperatures ($0\text{ }^{\circ}\text{C}$), Re of the standard setup was calculated to be 2980, whereas in the test setup it was 2380. By using the tube attenuation equations of turbulent flow presented by Massman and Ibrom (2008), the half-power frequencies were 13.7 and 7.2 Hz for the standard and test setup, respectively. Thus, at low temperatures, fluctuation attenuation due to transport in the tubes is not likely to affect the measurements. However, at higher temperatures ($20\text{ }^{\circ}\text{C}$), the Reynolds number of the test setup (2100) falls into the laminar flow region, because kinematic viscosity increases with increasing temperature. By using the tube attenuation equations for laminar flow by Lenschow and Raupach (1991), the half-power frequency of the test setup at $20\text{ }^{\circ}\text{C}$ was only 1.4 Hz, which is still higher than the empirically determined f_0 .

The high frequency attenuation of H_2O signals of the standard setup was corrected in order to accurately compare the CO_2 flux measurements with different setups as a function of latent heat flux. The high frequency attenuation of H_2O flux of the standard setup was marked: f_0 ranged between 0.04 and 0.22 Hz, decreasing with increasing RH , which varied within 48–100 %. This attenuation is caused by sorption and desorption of water vapor at the walls of the tubes (Massman and Ibrom, 2008). During typical humidity conditions ($RH = 80\%$), the flux attenuation is 44 % of the real H_2O flux. The $C_{O_{wH_2O}}$ of the test setup was found to be distorted in all frequencies.

3.1.3 Stationarity

~~About~~ In order to evaluate the quality of our measurements, several theoretical assumptions of the eddy covariance method were analyzed. The flux footprint area was found to be horizontally homogeneous (Appendix B), and turbulence was well-developed as integral turbulence characteristics could be expressed as functions of stability parameter (Appendix C). In this section, we analyze the fulfillment of the stationarity assumption and determine the effect of CO_2 flux nonstationarity on the CO_2 fluxes.

Over half of the flow conditions for which the CO_2 flux was determined, ~~55.65 % for the standard setup and 63 % for the test setup~~, were found to be non-stationary, i.e. the difference between the 30 min flux and the mean of the corresponding 5 min fluxes exceeded 30%. Overall, 91 % of data were discarded due to unsuitable wind direction, nonstationarity or a positive momentum flux.

We found that this stationarity criterion removed unphysical values effectively (Fig. 5). During July, the partial pressure difference was negative (-9.3 Pa on average), and thus downward (negative) fluxes were expected. Relaxing the stationary limit from 30 % to 60 % had only a small effect on data filtering. If no stationarity limit was applied, 20 % and 25 % of CO_2 sea-air fluxes measured during July 2017 ~~all of which were expected to be negative~~ by the test and standard setup, respectively, were positive. By using the 60 % stationarity limit, only 5 % (test) and 6 % (standard) of the measured CO_2 fluxes were positive. With the 30 % stationarity limit, these numbers were only slightly lower, 3 % and 4 %, respectively.

Similarly high rejection rates have been obtained in previous studies. Miller et al. (2010) reported that 65 % of the sea-air CO_2 flux measurements failed a stationarity test in which the 13.7 min fluxes were compared with the averages of 3.4 min fluxes, and assumed that CO_2 concentration heterogeneity could be a reason for the high rejection rate. Likewise, Blomquist

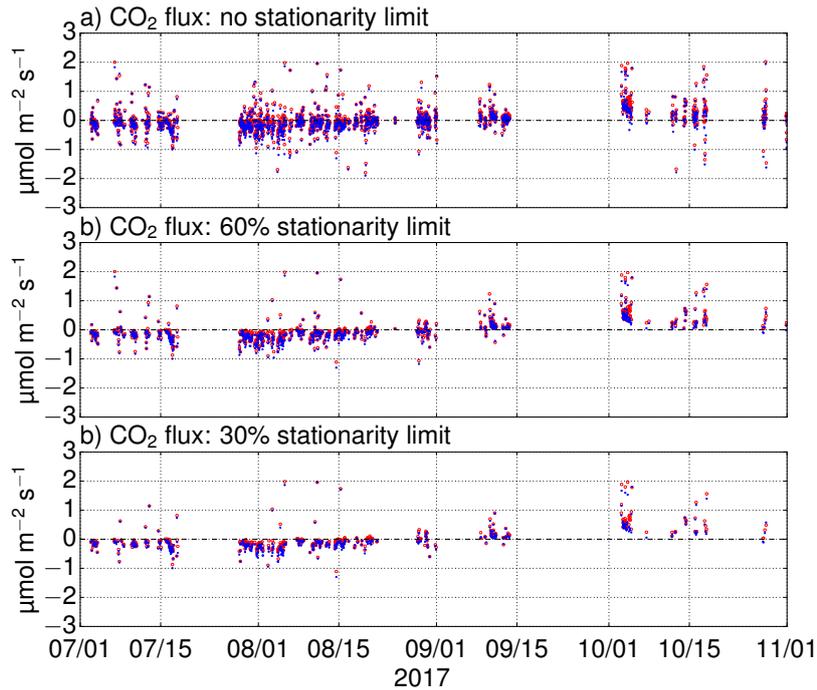


Figure 5. The effect of removal of non-stationarity cases on the CO₂ flux data: (a) no stationarity limit, (b) $RN_{w'c'} < 0.6$ and (c) $RN_{w'c'} < 0.3$. Red circle refers to the standard setup and blue dot to the test setup.

et al. (2014) concluded that horizontal CO₂ concentration gradients caused by continental pollution sources can reduce the number of stationary situations. At Utö, concentration gradients may be produced by the horizontal heterogeneity due to the land-sea interface and the variations in marine primary production.

We examined how the absolute change in CO₂ concentration during the averaging period of 30 min relates to non-stationarity of CO₂ fluxes (Fig. 6b). The change in CO₂ concentration was calculated as a difference in the mean CO₂ molar fraction of the last 30 s and the first 30 s. Typically, a change larger than 1 ppm was associated with rejection of the measurement due to the non-stationarity of CO₂ flux. Only 14 % and 18 % of the sea-air CO₂ fluxes for the test and standard setup, respectively, passed the stationarity test with the 30 % limit, for the cases with a CO₂ concentration change larger than 1 ppm. For the cases where CO₂ concentration changed more than 2 ppm during the averaging period, only 54 % and 6 % of sea-air CO₂ fluxes passed this stationarity test.

If the time scale of the processes generating non-stationarity was less than the averaging time, it would be possible to reduce the amount of discarded non-stationary data by shortening the averaging time. To test for non-stationarity with shorter averaging periods, we calculated CO₂ fluxes for 15 min periods, which were compared with the average of 2.5 min CO₂ fluxes.

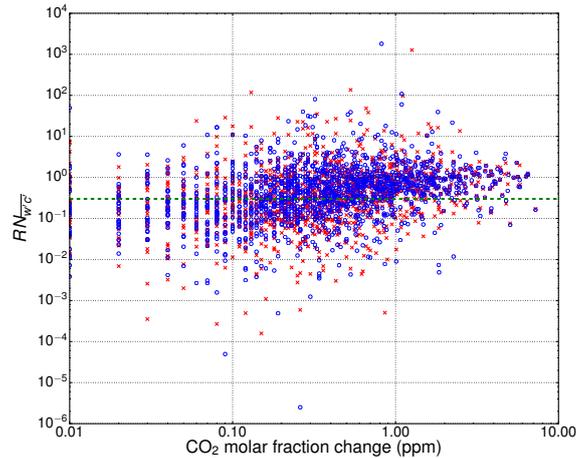


Figure 6. Relative non-stationarity of CO₂ flux as a function of the absolute change in CO₂ concentration during the averaging period: standard (red cross) and test (blue circle) setups. The green dashed line indicates the limit of $RN_{w'c'} = 0.3$.

It was found that this increased the number of accepted data only a little: by 6.1 % for the standard setup and 1.9 % for the test setup.

Even though a large number of the measurements did not meet the stationarity criterion ($RN_{w'c'} < 0.3$), the occurrence of non-stationary conditions was temporally random, whereas unsuitable wind directions produced long continuous gaps in the measurement time series. For the calculation of a CO₂ budget, these gaps must be filled, for instance by using the measured pCO₂ difference and a gas transfer velocity parameterized as function of wind speed. Thus, continuous measurements of surface seawater and atmospheric CO₂ concentration provide useful additional data for a sea-air CO₂ flux station.

3.1.4 Turbulence

The Monin-Obukhov similarity theory predicts that statistical turbulence variables within the atmospheric surface layer are unique functions of the stability parameter (z/L), which combines information about the height above ground, surface shear stress, surface heat flux and buoyant processes. These so-called integral turbulence characteristics have been found to have the same stability dependence over the sea as on land (e.g. Smith and Anderson, 1984) and can be used to examine the development of turbulence.

Integral turbulence characteristics. (a) σ_w/u_* as a function of stability parameter z/L , (b) σ_w/u_* as a function of $z f_c/u_*$ and (c) σ_T/T_* as a function of z/L during unstable stability and (d) σ_T/T_* as a function of z/L during stable stability.

Our data are in accordance with the results of Panofsky et al. (1977), who determined the relationship between the normalized standard deviation of vertical velocity and stability parameter:-

$$\frac{\sigma_w}{u_*} = \alpha \cdot (1 - \beta \cdot z/L)^{1/3}$$

where u_* is friction velocity, $\alpha = 1.3$ and $\beta = 3.0$. With large z/L values, the power law of 1/3 fits well to our observations, and the observed $\frac{\sigma_w}{u_*}$ approaches a constant of 1.3 in the neutral range similarly to Eq. C1. Most of the observations fall into the stability range between -0.1 and -0.01. Within this range, the observed $\frac{\sigma_w}{u_*}$ is mainly scattered between values 1.0 and 1.5.

However, Monin-Obukhov similarity theory does not consider all the necessary information for describing turbulence characteristics in all conditions; e.g. the effect of Coriolis and pressure gradient forces are excluded. Högström (1990) showed that during neutral stratification $\frac{\sigma_w}{u_*}$ can be described with z , u_* and Coriolis parameter, f_c . Smedman (1990) found that this relationship is valid at widely differing sites, including both terrestrial and marine surfaces. Thus we tested our data with neutral stratification, $|z/L| < 0.1$, against the function proposed by Högström (1990):-

$$\frac{\sigma_w}{u_*} = \gamma \cdot \log(z f_c / u_*) + \delta,$$

where $\gamma = 0.11$ and $\delta = 1.93$. This function provides a reasonable fit to our data and a better description of $\frac{\sigma_w}{u_*}$ in the stability range between -0.1 and -0.01 than Eq. C1 (Fig. C1).

For temperature, we compared the observations to the model of Foken et al. (1991):-

$$\frac{\sigma_T}{T_*} = \begin{cases} 1.0 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/3} & , \quad \frac{z}{L} \leq -1 \\ 1.0 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/4} & , \quad -1 \leq \frac{z}{L} \leq -0.0625 \\ 0.5 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/2} & , \quad -0.0625 \leq \frac{z}{L} \leq 0.02 \\ 1.4 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/4} & , \quad \frac{z}{L} \geq 0.02 \end{cases}$$

Our observations were in accordance with the shape of this relationship, except for the near-neutral stability range, where the observations differ greatly from the model (Fig. C1c-d). As these cases have a very small sensible heat flux, $\frac{\sigma_T}{T_*}$ could be biased by division by a small number. However, this is not observed as the slope is well-organized and the spread is small. Our data suggest a steeper relationship should be used in this near-neutral stability range ($|z/L| < 0.02$):-

$$\frac{\sigma_T}{T_*} = 0.1 \cdot \left(\left|\frac{z}{L}\right|\right)^{-0.94}$$

In the logarithmic scale, the slope (-0.94) in our fit is almost twice as steep as the corresponding slope determined by Foken et al. (1991), i.e. -0.5.

Overall, our observations were well organized as a function of stability parameter, or friction velocity in the neutral case, and thus we did not discard any of data based on the integral turbulence characteristics.-

3.2 Setup comparison

The observed direction of the sea-air CO₂ fluxes was mainly consistent with the pCO₂ difference between the sea and the atmosphere, and both setups showed similar fluxes most of the time (Fig. 8). The standard setup tended to show slightly more positive fluxes than the test setup. In July, the pCO₂ difference was negative, and the mean sea-air CO₂ flux measured with the standard and test setup was ~~-0.158 and -0.231~~ -0.163 and -0.226 μmol m⁻² s⁻¹, respectively. During the latter part of August (15–31 August), when the pCO₂ difference was shifting from negative to positive, the mean flux measured with the standard system (~~0.003–0.050~~ 0.003–0.050 μmol m⁻² s⁻¹) was close to zero, while the test system still showed clearly negative fluxes (mean ~~-0.082–0.122~~ -0.082–0.122 μmol m⁻² s⁻¹). During ~~this period~~ August, the highest latent heat fluxes of the measurement period were measured, peaking at ~~274~~ 120 W m⁻². During September, low latent heat fluxes (~~163.3~~ 163.3 W m⁻² on average) were observed and both measurements showed ~~the same mean closely similar~~ monthly sea-air CO₂ flux: ~~0.1800, 188~~ 0.1800, 188 μmol m⁻² s⁻¹ (~~test~~ test) and ~~0.158~~ 0.158 μmol m⁻² s⁻¹ (~~standard~~ standard). The highest absolute monthly CO₂ fluxes were measured in October, when pCO₂ difference was continuously high (16.6 Pa on average) and wind speed peaked occasionally, resulting in monthly sea-air CO₂ flux averages of ~~0.364 and 0.301~~ 0.524 and 0.434 μmol m⁻² s⁻¹ by the standard and test setup, respectively.

~~There is limited amount of direct CO₂ flux measurements from this part of the Baltic Sea. The As no previous measurement data are available for comparison, we validated the magnitude of the measured monthly sea-air air-sea CO₂ fluxes was of the same order as the modeled sea-air roughly by calculating the gas transfer velocity ($k_{660} = \frac{F}{K_0 \Delta p_{CO_2}} \sqrt{\frac{Sc}{660}}$) from our data and compared it with the universal parametrization proposed by Wanninkhof (1992). Schmidt number (Sc) and solubility (K_0) of CO₂ fluxes in the Eastern Gotland basin (?). The modeled sink strength during the summer months was -0.1 were calculated according to Wanninkhof (1992) and Weiss (1974), respectively. For this comparison, we only included cases in which the absolute partial pressure difference (Δp_{CO_2}) between the sea and atmosphere was larger than 3 Pa, whereas the measured flux was approximately twice as high in Utö in July. The shift from the negative to positive pCO₂ difference in Utö occurred two months before the corresponding shift in the model run. The gas transfer velocities derived from our measurements were in good accordance with predictions (Fig. 7), which lends credence to our flux measurements.~~

The Nafion drier eliminated the water vapor fluctuations effectively. The latent heat flux (measured with the standard system) was mostly positive, ranging within ~~-31–297–28–122~~ 53–27 W m⁻², with an average of ~~53–27~~ 53–27 W m⁻². The H₂O variance measured with the standard setup was ~~0.042–0.021~~ 0.042–0.021 mmol² mol⁻² on average, whereas the test setup measured the mean H₂O variance of 0.001 mmol² mol⁻². Even though the Nafion drier in our setup did not remove water vapor completely, it attenuated the fluctuations at all frequencies, in the same way as the tubing of a closed-path system attenuates temperature fluctuations. Water vapor molar fraction measured by the test setup varied within ~~2.42–9~~ 2.42–9–8.8 mmol mol⁻¹, whereas the standard setup showed water vapor values of ~~3.85–7–15–6.7~~ 3.85–7–15–6.7 mmol mol⁻¹. Thus, a total removal of water vapor from the sample air is not required to eliminate the water vapor fluctuations.

A high correlation was found between the two measurement setups (Fig. 9). The Pearson product-moment correlation coefficient between the sea-air CO₂ fluxes measured by the setups was ~~0.96–0.97~~ 0.96–0.97. During low latent heat fluxes (< 30 W m⁻²), the correlation coefficient increased to 0.99. As latent heat flux increases, the standard setup shows more positive CO₂ fluxes than

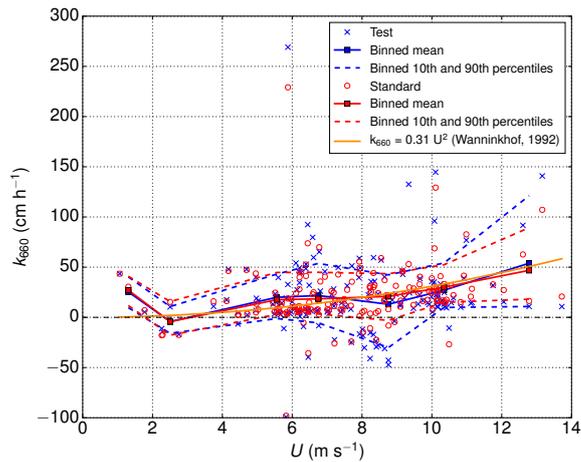


Figure 7. Measured gas transfer velocities as a function of wind speed. The orange line is the parametrization by Wanninkhof (1992).

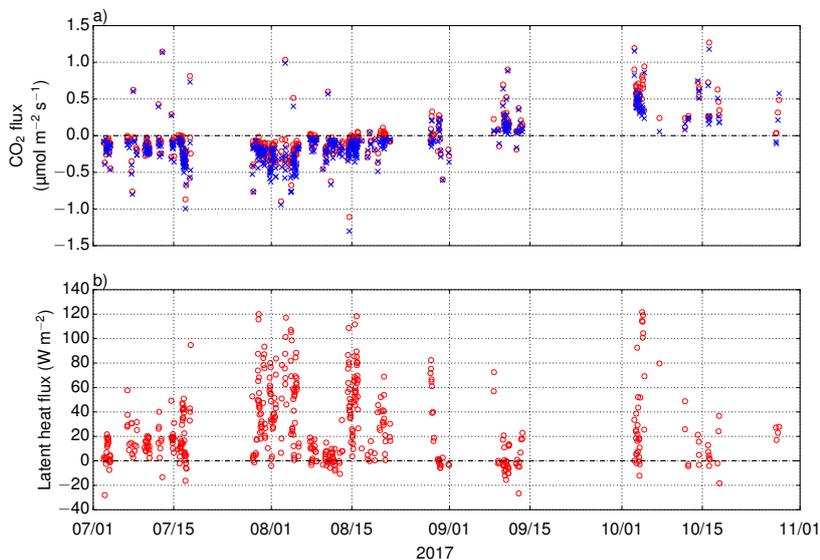


Figure 8. Sea-air fluxes of (a) CO₂ and (b) water vapor: standard setup (red circles) and test setup (blue crosses). Only the fluxes originating from the south-western open sea sector (Fig. 1) are shown.

the test setup (Fig. 10). These results are in agreement with the conclusions of Landwehr et al. (2014), who found that during low latent heat fluxes the difference between the dried and undried sea-air CO₂ flux measurements ~~were very similar, also proving was very small.~~ This also proves that a Nafion drier (in our case combined with a virtual impactor) does not disturb the CO₂ flux measurements.

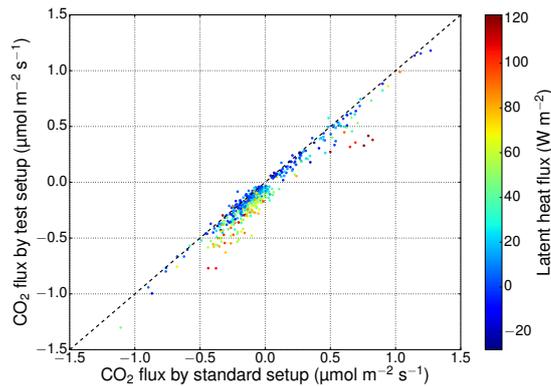


Figure 9. The sea-air CO₂ flux measured with the standard setup vs. the test setup (equipped with a drier and a virtual impactor). The marker color indicates the concurrent latent heat flux, and the dashed line represents the 1:1 relationship.

A comparison of the CO₂ flux difference as a function of latent heat flux shows that the error is negligible for very small latent heat fluxes ($< 10 \text{ W m}^{-2}$). With ~~high~~ higher latent heat fluxes (~ 100 ~~40~~ 125 W m^{-2}), the mean difference is approximately ~~0.150~~ 0.125 $\mu\text{mol m}^{-2} \text{ s}^{-1}$. Since the sea-air fluxes of CO₂ are typically small, the effect of water vapor on CO₂ flux measurement can cause a change in its sign, as observed during the latter part of August. However, as the mean difference increases, also the scatter increases. There are only few data points with negative latent heat fluxes, so no conclusions can be drawn concerning the effect of negative water vapor fluxes on CO₂ fluxes.

We showed that the use of the combination of a virtual impactor and a Nafion drier did not disturb the measurement of CO₂ fluxes. Closed-path instruments are typically protected by one or two Teflon filters (one close to the inlet and another next to the instrument), which should prevent any liquid water from reaching the instrument. However, the use of a Teflon filter close to the inlet may be unpractical, as a regular change of this filter may prove laborious. In such a case, we suggest a virtual impactor as an option for the protection of the instrument and the tubing from water and sea salt.

4 Conclusions

In this paper, we presented new sea-air CO₂ flux measurements, comparing two closed-path gas analyzer setups installed on a shore of an island in the Baltic Sea. One of the setups was equipped with a drier and a virtual impactor. By inspecting several theoretical assumptions of the eddy covariance method, we showed that this land-based flux site is capable of effectively monitoring CO₂ fluxes between the atmosphere and the sea. The w -CO₂ cospectral densities calculated from our data showed an expected behavior with a moderate high frequency loss. Turbulence was well-developed, and the integral turbulence characteristics followed unique functions of stability and friction velocity.

We found that the two closed-path infrared gas analyzer setups showed similar CO₂ fluxes when latent heat fluxes were small. Correlation coefficient increased from ~~0.96~~ 0.97 to 0.99 when only the CO₂ fluxes during small latent heat fluxes ($<$

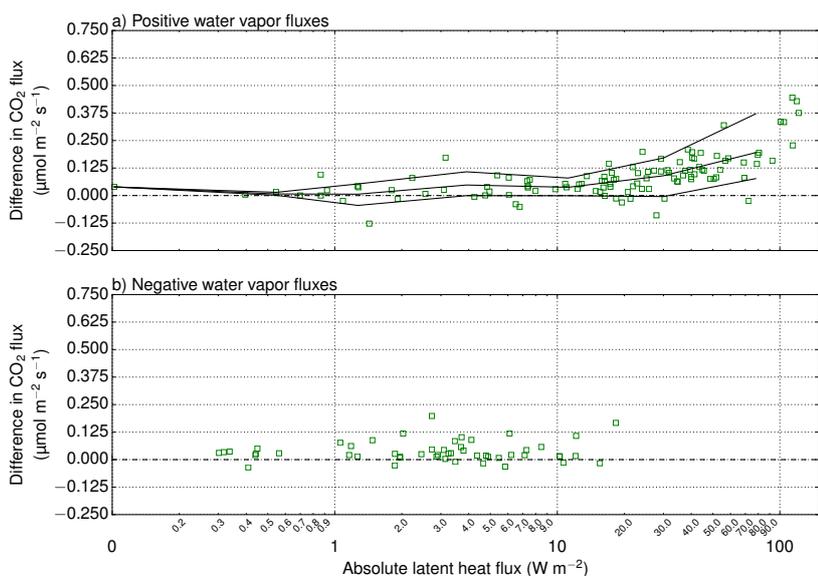


Figure 10. CO₂ flux difference ~~as a function of latent heat flux~~ (standard setup – test setup) as a function of latent heat flux for (a) positive and (b) negative water vapor fluxes. The lines show a fitted mean together with the 10th and 90th percentiles for eight logarithmically equally spaced bins.

30 W m⁻²) were included. A higher latent heat flux resulted in a positive bias to the undried measurement. During high latent heat fluxes (~10040 W m⁻²), the difference between the CO₂ flux measurements was 0.150.125 μmol m⁻² s⁻¹ on average, which is comparable to the monthly mean sea-air CO₂ flux. In July, the CO₂ partial pressure in the atmosphere exceeded that in the surface seawater, resulting in negative sea-air CO₂ fluxes, with monthly averages of -0.16 and -0.23 μmol m⁻² s⁻¹ for the standard and test (drier) setup, respectively. In October, when the surface seawater had a higher CO₂ partial pressure than the atmosphere, the average sea-air CO₂ fluxes were 0.36 and 0.30.0.52 and 0.43 μmol m⁻² s⁻¹ for the standard setup and test setup, respectively.

~~Even though producing a high percentage of discarded observations (55–63%), for high quality~~ Our analysis indicated that, to obtain high-quality sea-air CO₂ flux ~~measurements it is essential to reject non-stationary observations data, a large~~ proportion (65%) of the original observations had to be discarded for non-stationarity. If the non-stationary cases were not discarded, 20–25 % of the sea-air CO₂ fluxes in July had a wrong sign, whereas only 3–4 % of the measured fluxes had an unphysical direction if the non-stationary cases were rejected. This non-stationarity was found to be linked to the changes in atmospheric CO₂ concentration during the averaging period. A change larger than 2 ppm was associated with in the rejection rate of 94–95 % due to non-stationarity. The occurrence of non-stationary conditions was random in time, whereas unsuitable wind directions produced long continuous gaps in the measurement time series. For the calculation of a CO₂ budget, these gaps must be filled, for instance by using the measured pCO₂ difference and a gas transfer velocity parameterized as function of

wind speed. Thus, continuous measurements of surface seawater and atmospheric CO₂ concentration at the Utö station provide useful additional data for the calculation of sea-air CO₂ flux exchange.

We showed that the use of the combination of a virtual impactor and a Nafion drier did not disturb the CO₂ flux measurement. While this configuration generated a slightly higher flux loss, we opt for this alternative for its reduced water vapour cross-
5 sensitivity and better protection against sea spray.

Appendix A: Virtual impactor

The virtual impactor is based on two perpendicular air streams, which provides a means to separate particles by size (Fig. A1). The sample air stream is divided into minor and major flows : smaller particles are diverted to the major flow and large particles with higher inertia, in this case water droplets, continue to the minor flow. The 50 % cut-point of our virtual impactor
10 was calculated to be 1.2–1.3 µm, i.e. a particle of this size has a 50 % probability of removal, while smaller particles are more likely to enter the major flow.

Appendix B: Horizontal homogeneity

Horizontal homogeneity within the sea sector (180–340°) was examined in terms of the surface roughness length (z_0), which was calculated from the logarithmic wind profile law using data collected during neutral conditions, $|z/L| < 0.01$ (Fig. B1).

15 The sea sector is clearly visible in the expected range of 180–340°, where z_0 is mainly lower than 1 mm. Outside this sector, z_0 is clearly higher, up to 1 m in northeastern wind directions. The sea sector indicated by z_0 coincides well with the sector deduced from the geographical map (Fig. 1).

While the sea sector can be considered sufficiently homogeneous, there is scatter in z_0 reflecting the fact that it depends on the sea state. Taylor and Yelland (2001) found that over a sea surface z_0 depends on the significant wave height and the slope
20 of the wave. Since the measurement site is located on the coast, both the fetch and swell can depend on wind direction.

Appendix C: Turbulence

The Monin-Obukhov similarity theory predicts that statistical turbulence variables within the atmospheric surface layer are unique functions of the stability parameter (z/L), which combines information about the height above ground, surface shear stress, surface heat flux and buoyant processes. These so-called integral turbulence characteristics have been found to have the
25 same stability dependence over the sea as on land (e.g. Smith and Anderson, 1984) and can be used to examine the development of turbulence.

Our data are in accordance with the results of Panofsky et al. (1977), who determined the relationship between the normalized standard deviation of vertical velocity and stability parameter:

$$\frac{\sigma_w}{u_*} = \alpha \cdot (1 - \beta \cdot z/L)^{1/3} \tag{C1}$$

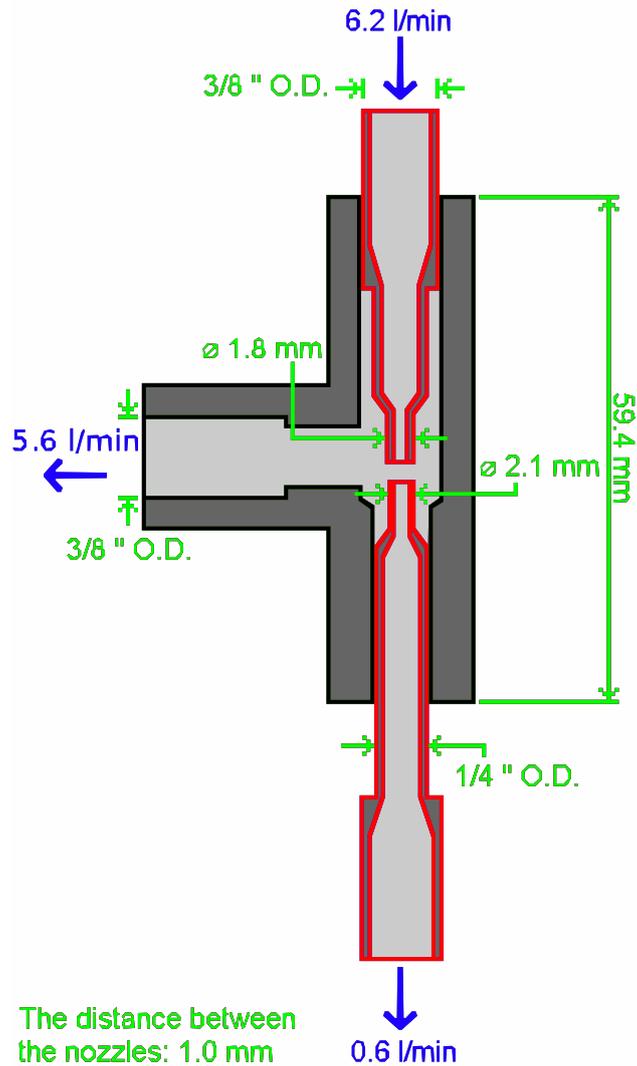


Figure A1. Schematics of the virtual impactor attached to the test setup. O.D. stands for outside diameter. The red pipes are enclosed by the black outer case. A more detailed figure is available on request.

where u_* is friction velocity, $\alpha = 1.3$ and $\beta = 3.0$. With large $-z/L$ values, the power law of 1/3 fits well to our observations, and the observed $\frac{\sigma_w}{u_*}$ approaches a constant of 1.3 in the neutral range similarly to Eq. C1. Most of the observations fall into the stability range between -0.1 and -0.01. Within this range, the observed $\frac{\sigma_w}{u_*}$ is mainly scattered between values 1.0 and 1.5.

5 However, Monin-Obukhov similarity theory does not consider all the necessary information for describing turbulence characteristics in all conditions; e.g. the effect of Coriolis and pressure-gradient forces are excluded. Högström (1990) showed that during neutral stratification $\frac{\sigma_w}{u_*}$ can be described with z , u_* and Coriolis parameter, f_c . Smedman (1990) found that this relationship is valid at widely differing sites, including both terrestrial and marine surfaces. Thus we tested our data with neutral

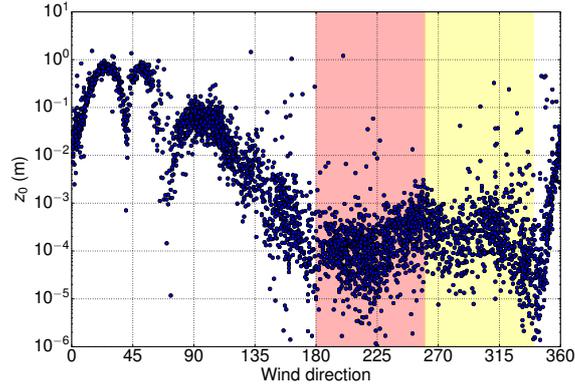


Figure B1. Surface roughness length as a function of wind direction. The red band indicates the directions considered the open sea sector used in this paper and the yellow band indicates a wind sector that potentially provides useful data but is not considered in the present study.

stratification, $|z/L| < 0.1$, against the function proposed by Högström (1990):

$$\frac{\sigma_w}{u_*} = \gamma \cdot \log(zf_c/u_*) + \delta, \quad (\text{C2})$$

where $\gamma = 0.11$ and $\delta = 1.93$. This function provides a reasonable fit to our data and a better description of $\frac{\sigma_w}{u_*}$ in the stability range between -0.1 and -0.01 than Eq. C1 (Fig. C1).

5 For temperature, we compared the observations to the model of Foken et al. (1991):

$$\frac{\sigma_T}{T_*} = \begin{cases} 1.0 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/3}, & \frac{z}{L} \leq -1 \\ 1.0 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/4}, & -1 \leq \frac{z}{L} \leq -0.0625 \\ 0.5 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/2}, & -0.0625 \leq \frac{z}{L} \leq 0.02 \\ 1.4 \cdot \left(\left|\frac{z}{L}\right|\right)^{-1/4}, & \frac{z}{L} \geq 0.02 \end{cases} \quad (\text{C3})$$

Our observations were in accordance with the shape of this relationship, except for the near-neutral stability range, where the observations differ greatly from the model (Fig. C1c-d). As these cases have a very small sensible heat flux, $\frac{\sigma_T}{T_*}$ could be biased by division by a small number. However, this is not observed as the slope is well-organized and the spread is small. Our data suggest a steeper relationship should be used in this near-neutral stability range ($|z/L| < 0.02$):

$$\frac{\sigma_T}{T_*} = 0.1 \cdot \left(\left|\frac{z}{L}\right|\right)^{-0.94} \quad (\text{C4})$$

In the logarithmic scale, the slope (-0.94) in our fit is almost twice as steep as the corresponding slope determined by Foken et al. (1991), i.e. -0.5.

Overall, our observations were well organized as a function of stability parameter, or friction velocity in the neutral case, and thus we did not discard any of data based on the integral turbulence characteristics.

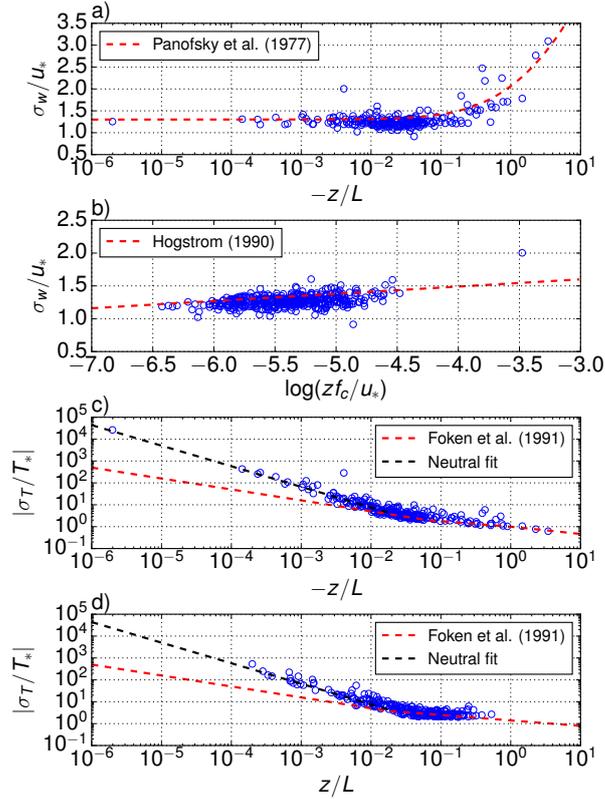


Figure C1. Integral turbulence characteristics. (a) σ_w/u_* as a function of stability parameter z/L , (b) σ_w/u_* as a function of zf_c/u_* and (c) σ_T/T_* as a function of z/L during unstable stability and (d) σ_T/T_* as a function of z/L during stable stability.

Competing interests. The authors declare that they have no conflict of interest.

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References

- Aurela, M., Lohila, A., Tuovinen, J.-P., Hatakka, J., Penttilä, T. and Laurila, T. Carbon dioxide and energy flux measurements in four northern-boreal ecosystems at Pallas. *Boreal Environment Research* 20:455–473. 2015.
- Blomquist, B. W., B. J. Huebert, C. W. Fairall, L. Bariteau, J. B. Edson, J. E. Hare and W. R. McGillis. Advances in Air–Sea CO₂ Flux Measurement by Eddy Correlation. *Boundary-Layer Meteorology* 152:245–276. 2014.
- [Chatziefstratiou, E. K., V. Velissariou and G. Bohrer. Resolving the Effects of Aperture and Volume Restriction of the Flow by Semi-Porous Barriers Using Large-Eddy Simulations. *Boundary-Layer Meteorology* 152:329–348. 2014.](#)
- Dabbert, W. F., D. H. Lenschow, T. W. Horst, P. R. Zimmerman, S. P. Oncley and A. C. Delany. Atmosphere-surface exchange measurements. *Science* 260. 1993.
- Edson, J.B., C. W. Fairall, L. Bariteau, C. J. Zappa, A. Cifuentes-Lorenzen, W. R. McGillis, S. Pezoa, J. E. Hare and D. Helmig. Direct covariance measurement of CO₂ gas transfer velocity during the 2008 Southern Ocean gas exchange experiment: wind speed dependency. *Journal Of Geophysical Research* 116. 2011.
- Feely, R., S. Doney and S. Cooley. Ocean Acidification: Present Conditions and Future Changes in a High-CO₂ World. *Oceanography* 22(4):36–47. 2009.
- Foken, T., G. Skeib and S. H. Richter. Dependence of the integral turbulence characteristics on the stability of stratification and their use for doppler-sodar measurements. *Meteorologische Zeitschrift* 41(4):311–315. 1991.
- Foken, T. and B. Wichura. Tools for quality assessment of surface-based flux measurements. *Agricultural and Forest Meteorology* 78(1-2):83–105. 1996.
- Heinze, C., S. Meyer, N. Goris, L. Anderson, R. R. Steinfeldt, N. Chang, C. Le Quere, and D. Bakker. The ocean carbon sink impacts, vulnerabilities and challenges. *Earth System Dynamics* 6:327-358. 2015.
- Horst, T. W. A simple formula for attenuation of eddy fluxes measured with first-order response scalar sensors. *Boundary-Layer Meteorology* 82:219–233. 1997.
- Högström, U. Analysis of turbulence structure in the surface layer with a modified similarity formulation for near neutral conditions. *Journal Of the Atmospheric Sciences* 47(16). 1990.
- Ibrom, A., E. Dellwik, S. E. Larsen and K. Pilegaard. On the use of the Webb-Pearman-Leuning theory for closed-path eddy correlation measurements. *Tellus Series B: Chemical and Physical Meteorology* 59(5):937–946. 2007.
- Jones, E. P. and S. D. Smith. A first measurement of sea-air CO₂ flux by eddy correlation. *Journal Of Geophysical Research* 82(37). 1977.
- Kaimal, J. C., J. C. Wyngaard, Y. Izumi and O.R. Cote. Spectral characteristics of surface-layer turbulence. *Quarterly Journal of the Royal Meteorological Society* 98(417):563–589. 1972.
- Kaimal, J. C. and J. J. Finnigan. *Boundary layer flows - their structure and measurement*. Oxford University Press. 1994.
- [Kenny, W. T., G. Bohrer, T. H. Morin, C. S. Vogel, A. M. Matheny and A. R. Desai. A Numerical Case Study of the Implications of Secondary Circulations to the Interpretation of Eddy-Covariance Measurements Over Small Lakes. *Boundary-Layer Meteorology* 165:311–332. 2017.](#)
- Kilkkki, J., T. Aalto, J. Hatakka, H. Portin and T. Laurila. Atmospheric CO₂ observations at Finnish urban and rural sites. *Boreal Environmental Research* 20:227–242. 2015.
- Kohsiek, W. Water vapor cross-sensitivity of open path H₂O/CO₂ sensors. *Journal of Atmospheric and Oceanic Technology* 17(3):299–311. 2000.

- Kondo, F. and O. Tsukamoto. Air-sea CO₂ flux by eddy covariance technique in the Equatorial Indian Ocean. *Journal Of Oceanography* 63:449–456. 2007.
- Kondo, F., K. Ono, M. Mano, A. Miyata and O. Tsukamoto. Experimental evaluation of water vapour cross-sensitivity for accurate eddy covariance measurement of CO₂ flux using open-path CO₂/H₂O gas analysers. *Tellus Series B: Chemical and Physical Meteorology* 5 66(1). 2014.
- Laakso, L., ~~Mikkonen, S., S. Mikkonen, A.~~ Drebs, A., ~~Karjalainen, A., Pirinen, P., and Alenius, P. : One hundred Karjalainen, P. Pirinen and P. Alenius. 100~~ years of atmospheric and marine observations at [the Finnish Utö Island](#), ~~in the Baltic Sea, Ocean Sci. Discuss.,~~ <https://doi.org/10.5194/os-2017-105, in review>, *Ocean Science* 14:617-632. 2018.
- Lammert-Stockschlaeder, A. and F. Ament. CO₂-flux measurements above the Baltic Sea at two heights: flux gradients in the surface layer. *Earth System Science Data* 7:311–317. 2015.
- Landwehr, S., S. D. Miller, M. J. Smith, E. S. Saltzman and B. Ward. Analysis of the PKT correction for direct CO₂ flux measurements over the ocean. *Atmospheric Chemistry And Physics* 14:3361–3372. 2014.
- Lenschow, D. H. and M. R. Raupach. The attenuation of fluctuations in scalar concentrations through sampling tubes. *Journal Of Geophysical Research*. 96(D8):15259–15268. 1991.
- 15 Leuning, R. and K. M. King. Comparison of eddy-covariance measurements of CO₂ fluxes by open- and closed-path CO₂ analysers. *Boundary-Layer Meteorology* 59(3):297–311. 1992.
- [LI-COR, Inc. LI-7200RS Enclosed CO₂/H₂O Gas Analyzer Instruction manual. 2016.](#)
- Mammarella, I., S. Launiainen, T. Gronholm, P. Keronen, J. Pumpanen, Ü. Rannik and T. Vesala. Relative humidity effect on high-frequency attenuation of water vapor flux measured by closed-path eddy covariance system. *Journal Of Atmospheric And Oceanic Technology* 20 26:1856-1866. 2009.
- Massman W. J. and A. Ibrom. Attenuation of concentration fluctuations of water vapor and other trace gases in turbulent tube flow. *Atmospheric Chemistry and Physics* 8:6245–6259. 2008.
- Miller, S. C., C. Marandino and E. S. Saltzman. Ship-based measurement of air-sea CO₂ exchange by eddy covariance. *Journal Of Geophysical Research* 115(D2). 2010.
- 25 Muller-Karger, F. E., R. Varela, R. Thunell, R. Luerssen, C. Hu and J. J. Walsh. The importance of continental margins in the global carbon cycle. *Geophysical Research Letters* 32(1). 2005.
- ~~Norman, M., A. Rutgersson and E. Sahlée. Impact of improved air-sea gas transfer velocity on fluxes and water chemistry in a Baltic Sea model. *Journal of Marine Systems* 111:175–188. 2013.~~
- Panofsky, H. A., H. Tennekes, D. H. Lenschow and J. C. Wyngaard. The characteristics of turbulent velocity components in the surface layer 30 under convective conditions. *Boundary-Layer Meteorology* 11:355–361. 1977.
- Pirinen, P., H. Simola, J. Aalto, J.-P. Kaukoranta, P. Karlsson and R. Ruuhela. Tilastoja Suomen ilmastosta 1981–2010. 2012.
- Prytherch, J., M. J. Yelland, R. W. Pascal, B. I. Moat, I. Skjelvan and C. C. Neill. Direct measurements of the CO₂ flux over the ocean: Development of a novel method. *Geophysical Research Letters* 37(3). 2010.
- Rannik, Ü., T. Vesala and R. Keskinen. On the damping of temperature fluctuations in a circular tube relevant to the eddy covariance 35 measurement technique. *Journal Of Geophysical Research* 102(D11):12789—12794. 1997.
- [Rey-Sánchez, A. C., G. Bohrer, T. H. Morin, D. Shlomo, G. Mirfenderesgi, H. Gildor and A. Genin. Evaporation and CO₂ fluxes in a coastal reef: an eddy covariance approach. *Ecosystem Health and Sustainability* 3\(10\). 2017.](#)

- Rutgersson, A., M. Norman, B. Schneider and H. Pettersson. The annual cycle of carbon dioxide and parameters influencing the air-sea carbon exchange in the Baltic Proper. *Journal Of Marine Systems* 74(1–2):381–394. 2008.
- Sahlée, E., K. Kahma, H. Pettersson and W. Drennan. Damping of humidity fluctuations in a closed-path system. In *Gas Transfer at Water Surfaces 6* (Eds. Komori S., McGillis W. and Kurose R.), Kyoto University Press, Kyoto, Japan, 516–523. 2011.
- 5 Smedman, A.-F. Some turbulence characteristics in stable atmospheric boundary layer flow. *Journal Of The Atmospheric Sciences* 48(6):856–868. 1990.
- Smith, S. D. and R. J. Anderson. Spectra of humidity, temperature and wind over the sea at Sable Island, Nova Scotia. *Journal Of Geophysical Research* 89(C2):2029–2040. 1984.
- Solomon, S., G.-K. Plattner, R. Knutti ja P. Friedlingstein. Irreversible climate change due to carbon dioxide emissions. *Proceedings of the National Academy of Sciences of the United States of America* 106(6): 1704–1709. 2009.
- 10 Takahashi, T., J. Olafsson, J. G. Goddard, D. W. Chipman and S. C. Sutherland. Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study. *Global Biogeochemical Cycles* 7(4):843–878. 1993.
- Takahashi, T., S. C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tilbrook, N. Bates, R. Wanninkhof, R. A. Feely, C. Sabine, J. Olafsson and Y. Nojiri. Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects. *Deep Sea Research II* 49(2002):1601–1622. 2002.
- 15 Taylor, P. K. and M. J. Yelland. The dependence of sea surface roughness on the height and steepness of the waves. *Journal Of Physical Oceanography* 31. 2001.
- Thomas, C. and T. Foken. Re-evaluation of Integral Turbulence Characteristics and their Parameterisations. In: 15th conference on turbulence and boundary layers, Wageningen, NL, 15–19 July 2002, American Meteorological Society, City, 129–132. 2002.
- 20 [Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97\(C5\):7373–7382. 1992.](#)
- Webb, E. K., G. I. Pearman, and R. Leuning. Correction of flux measurements for density effects due to heat and water vapour transfer. *Quarterly Journal of the Royal Meteorological Society* 106(447):85–100. 1980.
- [Weiss, R. F. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* 2\(3\):203–215. 1974.](#)
- 25 Welp, L. R., R. F. Keeling, R. F. Weiss, W. Paplawsky and S. Heckman. Design and performance of a Nafion dryer for continuous operation at CO₂ and CH₄ air monitoring sites. *Atmopsheric Measurement Techniques* 6:1217–1226. 2013.
- Wesslander, K. The carbon dioxide system in the Baltic Sea surface waters. Doctoral thesis. University of Gothenburg. 2011.
- Yang, M., T. G. Bell, F. E. Hopkins, V. Kitidis, P. W. Cazenave, P. D. Nightingale, M. J. Yelland, R. W. Pascal, J. Prytherch, I. M. Brooks and T. J. Smyth. Air-sea fluxes of CO₂ and CH₄ from the Penlee Point Atmospheric Observatory on the south-west coast of the UK. *Atmopsheric Chemistry and Physics* 16:5745–5761. 2016.
- 30