Author Comment with regard to:

"Insights from year-long measurements of air-water CH4 and CO2 exchange in a coastal environment"

by Yang et al.

Many thanks for the detailed *comments and suggestions from Anonymous Referee #1*. We are very glad to hear that the referee found our contribution timely and interesting. Below are our replies to the referee's comments, which are in *italic*.

Anonymous Referee #1

General comments: this manuscript by Yang et al deals with CH4 and CO2 fluxes in a coastal environment. Assessing CO2 and CH4 air-water exchanges is an important exercise to determine the impact of given ecosystems on the atmospheric CO2 and CH4 burden. It is particularly the case for aquatic ecosystems such as estuarine and coastal ones which are of relative influence compared to the area they are covering at the global scale. Most of the previous studies dealing with the subject have been based on indirect estimate through air-sea concentration difference and gas transfer velocity, the so-called Boundary-Layer method. The work by Yang et al presents an interesting and rather rare time series of EC measurement performed over one year. The authors have done a good job in data collecting and study design at the Penlee Point Atmospheric Observatory (PPAO), on a nearby buoy (L4), and from different research Vessels. Data base includes CO2 and CH4 exchange fluxes as well as a description of meteorological data and some of the water quality parameters (Chla for example). This MS is generally well written, is timely and interesting to understand the parameters of influence on CO2 and CH4 exchanges in coastal environments. Several parameters of influence on transfer velocities have been checked, all of them are relevant. Though, curiously, the effect of precipitation rate on fluxes have not been investigated. Impact of drops on the water surface can enhance significantly (several tens of percent) the gas transfer velocity. Were the precipitation periods withdrawn from the date as part of the EC quality control process? In all cases, the influence of precipitation of the data set (whether on the EC data quality or on the transfer velocity) should be discussed.

This is an interesting question. Rain can add substantial noise to the measurement of wind velocities by sonic anemometers, especially at high frequencies, thereby increasing the uncertainty in the EC fluxes. In our case, the Gill R3 anemometer (used for the second half of the 1-yr campaign) is much less affected by rain than the Windmaster Pro anemometer (used for the first half of the 1-yr campaign) for CO2 flux. We have not filtered our CO2 flux by a threshold rain rate (e.g. a commonly used value would be 1 mm/hr), but our quality control filtering that includes the noise level of the vertical wind velocity has removed most of the fluxes during rainy periods for the first half of the 1-yr campaign. The second half of the 1-yr campaign (when the R3 anemometer was used) retains more rainy periods.

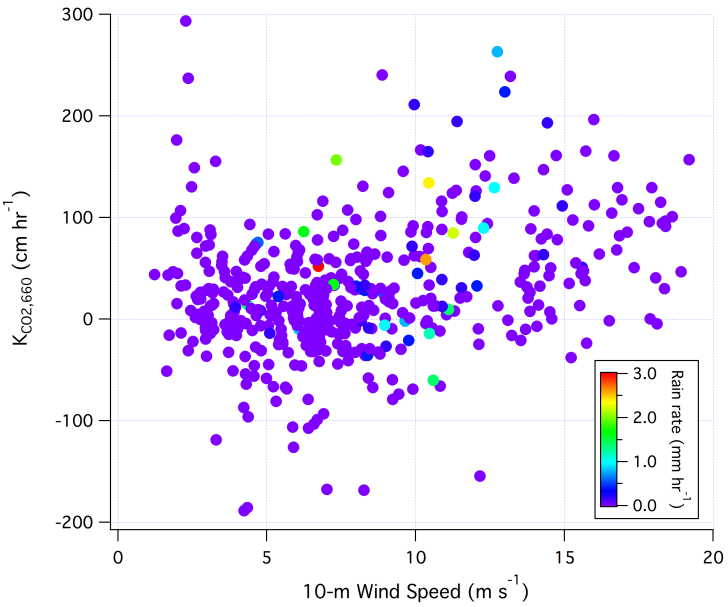
Would our annual mean CO2 flux be significantly biased by excluding most of the rainy periods? Over the entire year, hourly rain rate exceeded 1 mm/hr 7% of the time at PPAO when winds were from southwest. The average wind speed was about 50% higher during these rainy periods than during non-rainy periods. The Nightingale et al. (2000) wind speed relation predicts that the average K (and so flux magnitude) should be about 120% higher during rainy periods than during non-rainy periods. Thus excluding fluxes during these rainy periods could result in an underestimation of the mean annual flux by approximately 8.4% (=0.07*1.2).

Mechanistically, rain could affect direct air-sea CO2 flux through at least three mechanisms. First, lab studies show that the falling raindrops increase the near-surface turbulence, thereby increasing total K (e.g. Ho et al., 1997; Zappa et al., 2009). This effect is relatively more important at low wind speeds (e.g. Harrison et al., 2012). Secondly, rainwater could reduce the near-surface pCO2 via changes in the carbonate chemistry and gas solubility (e.g. dilution effect, Turk et al. 2010), and so result in more negative (or less positive) CO2 fluxes. Lastly, dissolved CO2 in rain droplets are taken up by the sea, which is often

termed the wet deposition flux (e.g. Ashton et al. 2016). We examine each of these three mechanisms below:

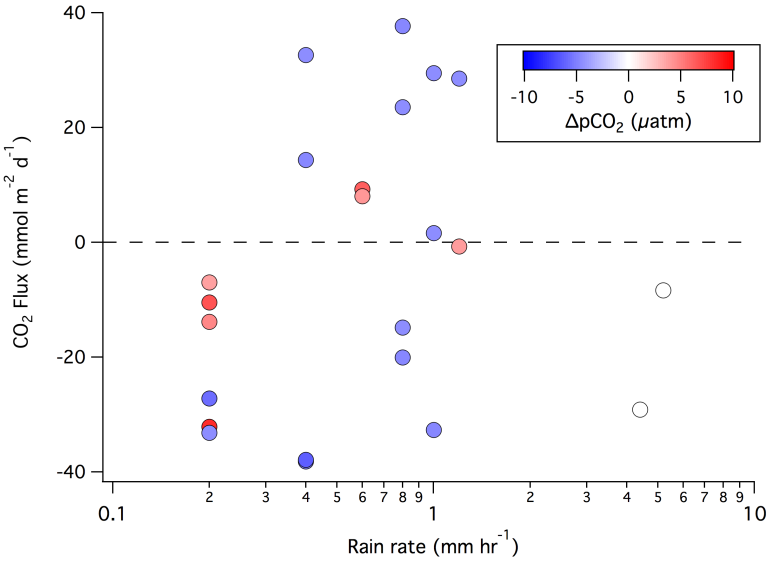
1. Effect of rain on K

The plot below shows the hourly kCO2,660 vs wind speed for the open water sector, color-coded by rain rate (data filtered by a |dpCO2|≥20 uatm threshold). We use the noisier hourly KCO2,660 data here because rainfall is highly episodic. It is not obvious that at a given wind speed, rain enhances K. This could be in part because compared to lab studies or parts of the tropics where rain rates are often on the order of tens of mm/hr, the typical rain rates at PPAO are roughly an order of magnitude lower. A caveat here is that the pCO2 measurements were made approximately once a week from ~3 m depth. Thus they do not fully describe short-term changes in pCO2 at the air-sea interface as a result of rain. This could in turn influence the K estimate.



2. Dilution effect (changes in near-surface pCO2)

To tease out the effect of rain on CO2 flux via the dilution effect (and not on K), we focus on periods where we do not ordinarily expect to see much flux (i.e. when the expected |dpCO2| is approximately zero). The plot below shows hourly CO2 flux vs. rain rate for the open water wind sector. Here we have only retained data where the expected |dpCO2| is ≤10 uatm. Within our limited dataset and given the measurement uncertainties, it is not obvious that rain makes CO2 flux more negative (or less positive) via the dilution effect at PPAO. For the open water sector with |dpCO2| ≤10 uatm, the mean CO2 flux during rainy periods was -5.3 (SE of 5.1) mmol/m2/d. During non-rainy periods, the mean CO2 flux was -2.1 (SE of 2.1) mmol/m2/d. The two estimates are not statistically different from each other as well from zero.



3. Wet deposition flux

The wet deposition flux of CO2 is estimated on an hourly basis as - sol_{CO2} * $CO_{2,a}$ * rain_rate. Here it is assumed that the falling rain droplets are in equilibrium with the atmosphere in terms of CO2. The mean wet deposition flux over the entire year (including rainy and non-rainy periods) was computed to be about -0.1 mmol/m2/d, which is orders of magnitude smaller than the air-sea gas flux (e.g. Figure 4). During rainy periods only, the mean wet deposition flux was -0.4 mmol/m2/d. Overall, we see that the impact of rain on air-sea CO_2 exchange is fairly limited at PPAO, largely as a result of the modest rain rate.

We will add the discussion above to a newly created section 6 and to the supplementary materials of the manuscript.

As pointed out by Nilsson and colleagues, statement by Yang and colleagues on the performance of open-path sensor should be revised. Sentences should be reworded to include a more tempered statement on potential interferences of open-path analyzer over water bodies. Effect of salinity on these spectral interferences should be discussed as suggested by Nilsson.

Per suggestion by Nilsson et al., we have agreed to remove the sentence about the performance of the open path sensors from our manuscript.

- Specific comments: here are some specific comments that should strengthen the MS.
P5, l 133: Can you quantify more precisely the effect of stability on the Xmax and X90 distances? This would help for the discussion on CO2 fluxes on p8

The effect of stability on the footprint for this site was discussed in Yang et al. 2016a. In the Kljun et al. 2004 model, stability is simply accounted for by adjusting the ratio between the standard deviation in w (σw) and the friction velocity u_*. We represented the strongly unstable, neutral, and strongly stable cases with σw: u_* ratios of 1.75, 1.3, and 0.9, respectively. Compared to a neutral atmosphere, Xmax (as well as X90) is about 20% closer to PPAO under the unstable case and 35% further away from PPAO under the stable case above. We will refer to our 2016 paper in the BGD manuscript. Note that the strongly unstable and stable conditions above correspond to air-sea sensible heat fluxes > ~200 W/m2 and <~ -100 W/m2, respectively. Sensible heat flux measured at Penlee Point had typical magnitudes of tens of W/m2 (see line 173) and thus the atmosphere was generally quite close to neutral.

P7, l 185-195: Not clear, mean flux should be the same whatever the way it is calcu- lated.
P7, l 192: not clear, but 6h fluxes should be the reference fluxes when compared to annual fluxes, how could they be skewed?

The number of valid flux measurements, largely depending on the wind direction, varied from month to month. In some months there were valid flux measurements for the open water sector ~40% of the time (i.e. ~12 days), and in other months only ~10% of the time (~3 days). Thus annual averages computed directly from the 6h fluxes are more heavily weighted by the periods with high proportion of valid flux measurements. In contrast, annual averages computed from the monthly means give more equal weighting to all the months.

P8, l 212: give details on how the total CH4 flux was calculated

This is computed as follows: 0.047 mmol/m2/d * 1400 m * 12429000 m *365 d/yr / 1000 * 16 g/mol = 4.8e9 g/yr. We will specify in the revised ms that we are extrapolating the annual mean from the open water sector (0.047 mmol/m2/d).

P8, l 216: give details to the reader on how the random instrument noise is calculated. Is the instrumental noise mentioned on line 219 the same noise?

Yes we are referring to flux uncertainty due to random instrumental noise on both of these occasions. As explained by Yang et al. 2016b, the random uncertainty in the fluxes can be estimated either theoretically (based on instrument's band-limited noise) or using experimental data (by offsetting w and gas mixing ratio, or by choosing a period of zero flux). We will refer interested readers to the detailed analyses in Yang et al. 2016b rather than repeating something similar here.

P8, l 229: only daytime measurements of pCO2 are mentioned, no night time measurements performed, right?

Correct.

P8, l 231: Not clear which data were interpolated, and how they were interpolated

We will state that pCO2 was measured on the 7th and 12th of July and these data were linearly interpolated to the times of the flux measurements.

P8, l 235: see comment on page 5. How far further upwind?

The Kljun et al. (2004) model predicts that the Xmax under these conditions will be greater compared to the neutral condition by a few tens of percent or less.

P9, l 248-29: again, not clear why mean calculated from monthly mean and from 6h mean are (so) different

See earlier response.

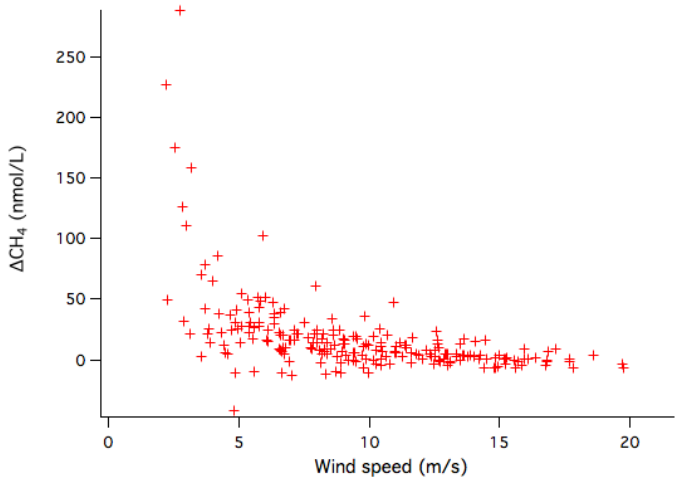
P9, l 259: there are many speed-dependant transfer velocity relationships. Choice of the only one from Nightingale et al 2000 paper should be justified. On which basis this choice was made.

There are obviously numerous gas transfer parameterizations (K) in the literature. We use Nightingale et al. (2000) here not necessarily because it is 'right', but because it is commonly used and lies between the very strong and the very weak wind speed dependent relationships. In section 5 we compute the actual gas transfer velocity from the fluxes and dpCO2, which is then compared against Nightingale et al. (2000) and a few other K parameterizations.

P9, l 261: wind speed threshold above 5 ms-1 seems quite high. Any justification of that wind speed value?

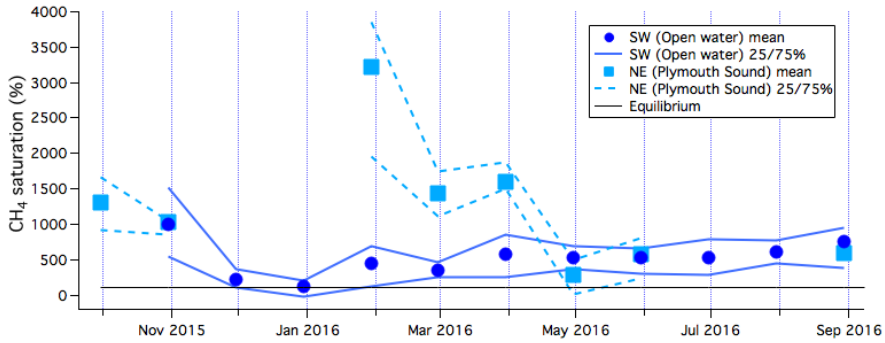
A threshold of 5 m/s is used here in the calculation of deltaC = flux / K because at low wind speeds, both the flux and K trend towards zero. Dividing one by the other then obviously leads to large uncertainties.

This is shown in the figure below of the implied CH4 air-sea concentration difference. A 5 m/s wind speed cutoff appears to remove the most obvious ouliers.



P9 l 264-268: saturation level relative to atmospheric saturation are defined but not used on figure 6. This could be done for the reader to better follow the discussion

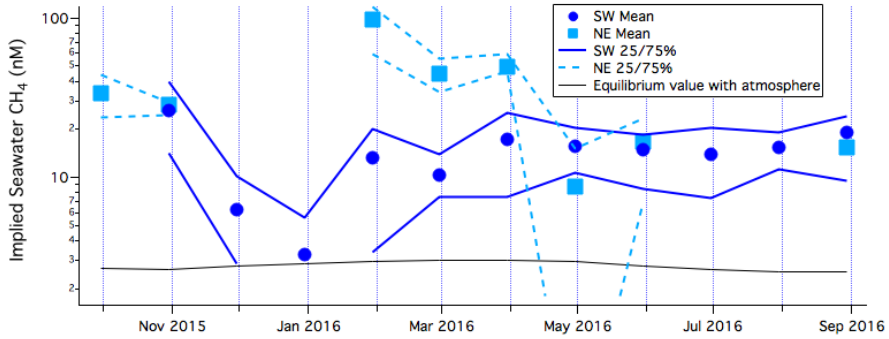
Atmospheric CH4 mixing ratio varies by approximately 10% on a seasonal basis, while CH4 solubility varies by about 14%. As a result of this fairly weak seasonality, a plot of saturation (=Cw/(Ca*H)) looks very similar to a plot of Cw, just with different scales.



We can add a figure of the implied CH4 saturation level in the supplementary material.

P9, l 268: Is the effect of salinity and temperature accounted for in the 14% variation of CH4 solubility? Not evident on figure 6.

Yes temperature and salinity are accounted for in the CH4 solubility and equilibrium value calculation. You can see the latter a bit more clearly in the log scale version of figure 6 below.



P10, l 277: which time series is commented here, 6h or 1h mean data?

We assume that the reviewer is asking about the semi-diurnal variability in CH4 flux? This is more obviously seen in the 6-hr CH4 flux data, with peak flux values at around 1800 on 9th Jul and 0600 on 10th Jul (12 hours apart). More generally, adjacent 6-hr CH4 fluxes during this period always alternate between higher values and lower values every six hours.

P10, l278: same pattern that what? Semi-diurnal variability? That is not possible, this must be something else. . .

Yes we mean to say that CH4 flux varies on a tidal scale as a result of the outflow from the Tamar estuary. CH4 flux (and saturation) tends to be higher during rising tide than during falling tide.

P10, l 285-287: comparison is made on two set of data without the same number of monthly data. Not sure it is meaningful.

We will specify that this comparison (i.e. 32 uatm difference in the mean) is made only during months when we had flux measurements from both sectors.

P11, l 299-300: seems that the sentence should be reworded

We have revised the sentence to "It is worth noting that our implied seawater GHG concentrations would be overestimated if the actual gas transfer velocity were higher than the wind speed dependent parameterization of Nightingale et al. (2000)." We are calculating deltaC = flux / K. If the K values we're using is too low (e.g. because it doesn't include contribution from bottom-driven turbulence), we would be getting a deltaC value that is higher than the actual deltaC.

P11, 309: syntax? Missing word?

Yes it should've been "we first evaluate the spatial homogeneity of our study region using the shipboard seawater measurements"

P12, l 350: not the highest saturation, but highest absolute concentration.

We will specify "the highest dissolved CH4 concentration"

P12, l 353-354: data at L4 not on figure, could be added for comparison.

The April and July 2017 L4 data on shown in Figure 11 already.

P12, l 357: four "times" higher. Times is missing

Thanks for spotting our error.

P13, l 359: mentioned that it is the flux footprints for the open water sector

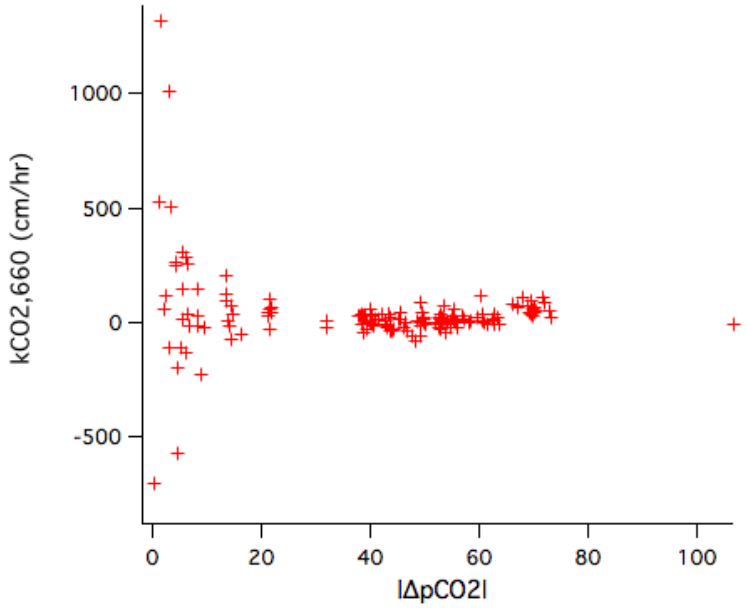
Suggestion accepted.

P13, l 383: how did you choose to discard interpolation more than four days away?

We chose this number because the pCO2 measurements were made approximately once a week. Thus per our filter, we keep the computed kCO2 values if they are sandwiched by pCO2 measurements that were made by a maximum of four days (~half a week) away.

P14 l 393: how this threshold of 20 µatm was chosen/determined? Any justification?

A dpCO2 threshold of 40 uatm is commonly used in gas exchange studies. Though we find that a 20 uatm threshold already filters out most of the noise as a result of dividing by a dpCO2 that is too close to zero. See plot below.

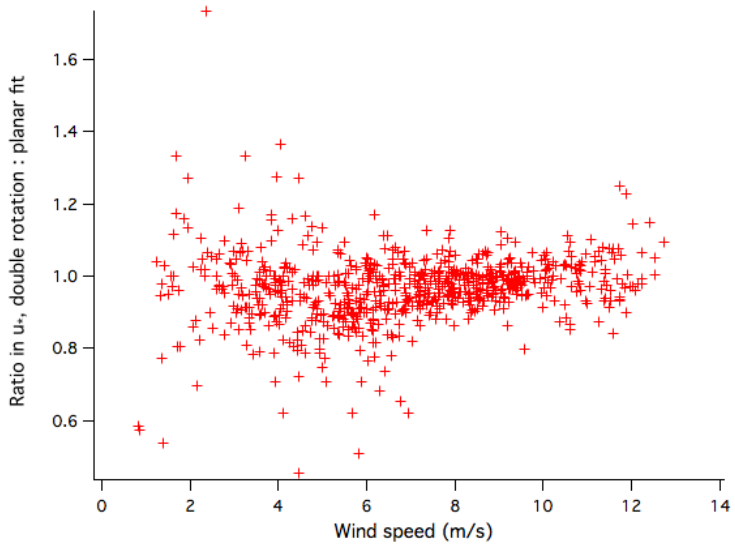


P14, l 397: be more explicit on what you call "measurements uncertainties in flux, variability in pCO2, as well as processes other than wind speed . . ."

Measurement uncertainties in flux here are due to random error in the flux measurements. pCO2 was only measured on approximately a weekly basis, and thus any variability in pCO2 at higher frequencies would contribute to scatter in kCO2. We will specify that processes other than wind speed are discussed in more detail in the rest of Section 5.

P14, l 413-414: why did not you check the effect of planar fit vs double rotation to confirm your assumption?

We did check the effect of planar fit vs double rotation in 2014 when the mast height was higher (27 m above mean sea level). As shown in the plot below, the u* values from the two methods agree pretty well (ratio around 1.0) at wind speeds over ~5 m/s. Below this threshold there is a bit more divergence. Because the difference in fluxes doesn't seem to be large between the two methods, and because the double rotation method is commonly used in the air-see exchange community, it is what has been used here as well. The planar fit angles will be different during this measurement campaign (2015 – 2016) compared to 2014 because the mast height was lower (18 m above mean sea level). We have not repeated this analysis for the new mast height but aim to do so in the future.



P15, l 441: what is the effect of the 40µatm threshold on that gap?

Not sure what the reviewer means here. A threshold on dpCO2 for the kCO2 calculation has no bearing on the actual gaps (i.e. missing data) in the pCO2 observations.

P15 : the highest Chla measurements in Plymouth Sound is well above the regression line. Any clue for that?

By regression line, I assume the reviewer is referring to Figure S8? Figure S8 is made when there were near-concurrent measurements of Chla at the two locations. There are occasions when the Chla within the Plymouth Sound were quite different from that at L4 due to natural spatial variability.

P14, l 467: Be more clear about "to reduce the temporal mismatch between the flux and pCO2 measurements".

We will remove this unnecessary phrase. The first part of this sentence explains already that since there is a strong diel cycle in the CO2 flux for the Plymouth Sound sector, it makes sense to look only at kCO2 during hours when pCO2 was measured.

P15, l 479: ". . .could result in biased annual mean flux estimates". Could this be more precisely quantified for example in the case of only daytime measurements?

This is already presented in the paragraph beginning on line 248 in the case of diurnal variability in CO2 flux. We will refer to Sections 3.1 and 3.2 here.

Figures P23: use consistent legend throughout the paper with: SW (open water) and NE (Plymouth Sound) all along.

Suggestion accepted.

P25: figure 5A: you should not display negative value for K which have no physical meaning. You could shade the night time period on the figure.

Suggestion accepted.

P27: figure 9: add units to the X and Y axis

Suggestion accepted. We will label them as PSU.