Response to review comments on “The dynamics of the carbon dioxide system in the outer shelf and slope of the Eurasian Arctic Ocean” by Irina I. Pipko et al.

Anonymous Referee #1

This paper presents pCO_2 data and associated air-sea flux of CO_2 from the Eurasian sector of the Arctic Ocean for three years (2006, 2007 and 2009). Data in this region are extremely scarce due to the logistical difficulties involved. As such, this paper makes a valuable contribution to our understanding of CO_2 exchange between the atmosphere and the Arctic Ocean at a time when the latter is undergoing rapid change. The authors have followed up various lines of thought to explain inter-annual and regional differences. I particularly liked the separation and apportionment of freshwater sources (MW and RW). The work presented is substantial, the analysis is very thorough and the paper is well structured and well written. The written style varies slightly between sections, probably reflecting the fact that different authors had written different section – a consistent writing style may slightly improve the manuscript in this respect. I enjoyed this paper and have no hesitation to recommend its publication. I have some specific comments, which are outlined below. I would leave most of my comments at the authors’ discretion, but I would urge them to address comments 6 to 9 in particular.

We would like to thank Anonymous Referee #1 for his thoughtful and positive review as well as helpful advices to improve our manuscript. Our responses to all of the Referee’s comments are shown in blue below.

Specific Comments:

1) Lines 79-84: A couple of useful references might also be: Mann et al., 2012, doi:10.1029/2011JG001798 and Mann et al., 2015, doi: 10.1038/ncomms8856.

Thanks, references will be added.

Mann, P. J., Davydova ,A., Zimov, N., Spencer, R. G. M., Davydov, S., Bulygina, E., Zimov, S., and Holmes, R. M. (2012). Controls on the composition and lability of dissolved organic matter in Siberia’s Kolyma River basin, J. Geophys. Res., 117, G01028, doi:10.1029/2011JG001798.

Mann, P.J., Eglinton, T.I., McIntyre, C.P., Zimov, N., Davydova, A., Vonk, J.E., Holmes, R.M., and Spencer, R.G.M. (2015). Utilization of ancient permafrost carbon in headwaters of Arctic fluvial networks, Nature Communications, 6, 7856, doi: 10.1038/ncomms8856.

2) Line 129: At what depth was the intake for the pumped seawater?

Seawater was taken from a depth of about 4 m. This information will be added to the text.

3) Line 135: Please give batch numbers for carbonate CRMs

Batch #96 was used in 2009, in the 2006 and 2007 cruises the hydrochloric acid concentration was determined using a standard solution of Na_2CO_3 made up by carefully weighing Na_2CO_3 of 99.995% purity (DOE, 1994; Pavlova et al., 2008).

This information will be added in the manuscript.

4) Line 146-147: Does the 30-minute averaging have an effect on accuracy? Over 30 minutes a moving ship may cross fronts, river-plumes, marginal ice zones etc. Averaging would therefore smooth if not obscure any gradients in pCO_2.

Thank you for pointing this out. For comparison, plots of pCO_2 (and hydrological parameters) with 15 min averaging have been constructed (Figure 1). Comparison of the graphs did not reveal additional features in the distribution of these parameters.

Nevertheless, we will use the 15-min averaging for a more detail presentation of the available data.

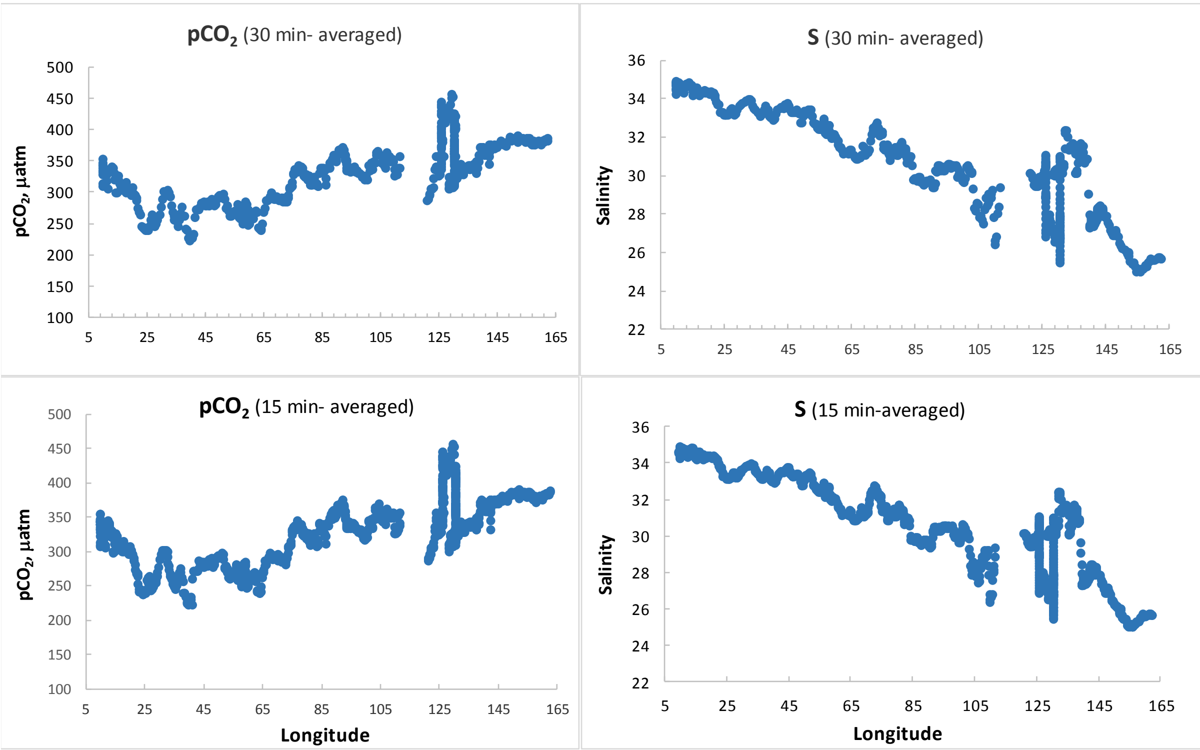

Figure 1. Distribution of pCO_2 and salinity: 30-min averaged –upper panels, 15-min averaged – bottom panels.

5) Line 255: The high Oxygen supersaturation observed in the Barents Sea is intriguing. Clearly, temperature alone explains 84% of the variance in pCO_2 and the authors are correct to point out

the air-sea exchange may not have fully compensated for earlier biological drawdown of CO_2. Typically, the turnover of the surface mixed layer CO_2 via gas-exchange is in the order of months because of carbonate buffering. In contrast, Oxygen will re-equilibrate with the atmosphere in days/weeks. Simultaneous CO_2 undersaturation and O_2 oversaturation would therefore suggest very recent PP. Satellite Chlorophyll might give additional insight should the authors wish to expand their analysis.

Thank you for suggestion. We have noted the remaining effect from primary production late in the season, i.e. close to our study. Unfortunately, we do not have field information regarding the distribution of chlorophyll-a and oxygen concentrations in the Barents Sea in autumn 2007, and the available satellite images do not allow to reliably estimating the intensity of photosynthetic processes throughout the photic zone. To avoid confusion, we will remove an information about the values of oxygen saturation observed in 2006 and 2009.

6) Line 318-320: The authors state that "optically-active OM and suspended material... promotes the accumulation of solar radiation... which increases the heat content [leading to further ice melt]". I don’t think that OM and SPM contribute hugely to the heat content of surface waters. The big switch from high albedo with ice-cover to low albedo in ice-free water would have a much bigger effect than the absorbing constituents such as OM.

Sure, the reduction in albedo due to increase in the area of ice-free water is a main driving factor in increasing the heat content of surface waters. However, the elevated concentrations of CDOM and SPM also can contribute to the surface waters heating and subsequent melting of sea ice by absorbing shortwave visible radiation (Granskog et al., 2007; Hill, 2008; Logvinova et al., 2016). For example, Granskog with co-authors (2015) noted that high concentrations of CDOM in the surface polar waters resulted in 50–60% more heat deposition in the upper meters relative to clearest natural waters.

We will add these references to support this statement:

Granskog, M. A., A. K. Pavlov, S. Sagan, P. Kowalczuk, A. Raczkowska, and C. A. Stedmon (2015). Effect of sea-ice melt on inherent optical properties and vertical distribution of solar radiant heating in Arctic surface waters, J. Geophys. Res. Oceans, 120, doi:10.1002/2015JC011087.

Granskog, M.A., Macdonald, R.W., Mundy, C.J., Barber, D.G. (2007). Distribution, characteristics and potential impacts of chromophoric dissolved organic matter (CDOM) in Hudson Strait and Hudson Bay, Canada. Cont. Shelf Res. 27, 2032–2050.

Hill, V.J. (2008). Impacts of chromophoric dissolved organic material on surface ocean heating in the Chukchi Sea. J. Geophys. Res. 113, C07024. http://dx.doi. org/10.1029/2007JC004119.

Logvinova, C. L., Frey, K.E. and Cooper, L.W. (2016). The potential role of sea ice melt in the distribution of chromophoric dissolved organic matter in the Chukchi and Beaufort Seas, Deep-Sea Research II, 130 28–42.

Nevertheless, I do believe that OM is hugely relevant here since OM will undergo photolysis to CO_2 (e.g. Mann et al., 2012, doi:10.1029/2011JG001798). This is in addition to microbial OM mineralization which the authors have covered.
Thank you for pointing this out. We did not pay an enough attention to the role of photolysis, because we assumed that biomineralization is the dominant mechanism for removal of terrestrial DOM (Belanger et al., 2006; Fichot and Benner, 2014; Kaiser et al., 2017), and some authors demonstrate that sunlight exposure does not substantially degrade DOM on Arctic shelves (~1% DOC loss, Osburn et al., 2009). On the contrary, photomineralisation has important role in the Siberian Rivers, particularly in samples collected during the spring freshet (Mann et al., 2012). We will note in the manuscript that photochemical transformation of terrestrial DOC and direct photomineralisation of OM also has an effect on increasing concentrations of CO_2 in surface waters.

Bélanger, S., H. Xie, N. Krotkov, P. Larouche, W. F. Vincent, and Babin, M. (2006). Photomineralization of terrigenous dissolved organic matter in Arctic coastal waters from 1979 to 2003: Interannual variability and implications of climate change, Global Biogeochem. Cycles, 20, GB4005, doi:10.1029/2006GB002708.

Fichot, C. G., and Benner, R. (2014). The fate of terrigenous dissolved organic carbon in a river-influenced ocean margin, Global Biogeochem. Cycles, 28, doi:10.1002/2013GB004670.

Kaiser, K., Benner, R., and Amon, R. M. W. (2017). The fate of terrigenous dissolved organic carbon on the Eurasian shelves and export to the North Atlantic, J. Geophys. Res. Oceans, 122, 4–22, doi:10.1002/2016JC012380.

Osburn, C. L., Retamal, L., and Vincent, W. F. (2009). Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea, Marine Chemistry, 115, 10–20.

7) Line 330: In relation to pCO_2 supersaturation in the East Siberian Sea, the authors state that this was due to the atmospheric pressure gradient which diverted river water offshore. I presume that this would carry high OM to the ESS which would be further mineralized to CO_2, hence the elevated pCO_2. It would be worth stating this explicitly as the current text leaves it up to the reader to make that connection. If the reader fails to make the connection, then the message is lost.
We will clarify this point in the paper.

8) Line 351-355: Regarding the flux of CO_2, the authors state that the highest influx coincided with high wind, while the highest DpCO2 did not result in very high influx because of low wind. The authors have used the cubic relationship of Wanninkhof and McGillis (1999) between k and wind speed for calculating the flux. There is a wide spectrum of Kw-wind relationships and the one used here returns k values at the upper end of the range. I wonder whether a middle of the range formulation might be better while the separate debate regarding the Kw-wind relationship goes on in the air-sea gas exchange community. Wanninkhof, 1992 would certainly be ok here.

We used a cubic relationship between gas exchange and wind speed (Wanninkhof and McGillis, 1999) because this parametrization is appropriate for short-term winds (as a quadratic dependence of gas exchange on wind speed (Wanninkhof, 1992)). Moreover, a cubic relationship (Wanninkhof and McGillis, 1999) demonstrates a better agreement with eddy covariance CO_2 flux measurements in comparison with Wanninkhof, 1992 parametrization over the East Siberian and Laptev seas in the late summer season (Pipko et al., 2008). We agree with Referee that each relationship has its limitations and uncertainties. However, even if we used W92 parametrization, we found that the highest CO_2 fluxes were not coincide with maximum in ΔpCO_2 (Figure 2).

Pipko, I.I., Repina, I.A., Salyuk, A.N., Semiletov, I.P., and Pugach, S.P. (2008). Comparison of Calculated and Measured CO_2 Fluxes between the Ocean and Atmosphere in the Southwestern Part of the East Siberian Sea, Doklady Earth Sciences, 422, 7, 1105-1108.

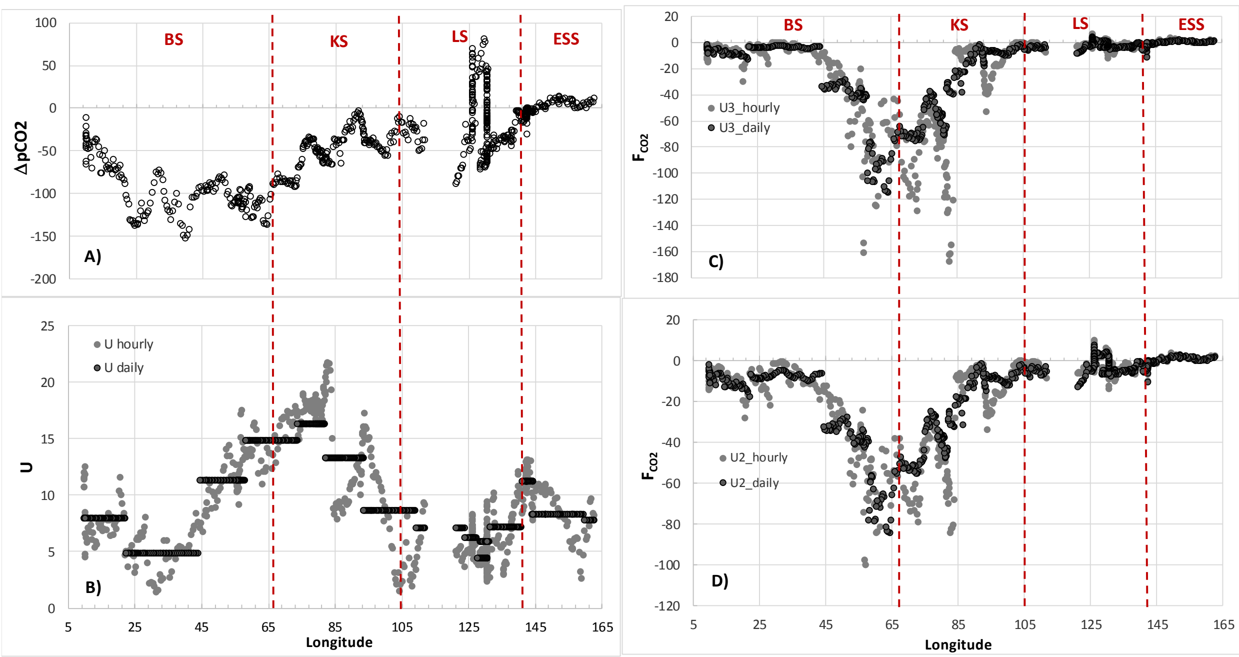

Figure 2. Distribution of ΔpCO_2 (μatm) (A), wind speed (U, m s^{-1}) (B), and air-sea CO_2 fluxes (F_{CO2}, mmol m^{-2} day^{-1}) (C –for cubic parametrization (Wanninkhof and MacGillis, 1999), D – for quadratic parametrization (Wanninkhof, 1992)) along the ship's route in 2007. Grey color corresponds to the hourly averaged wind speed and the hourly-based air-sea CO_2 fluxes; black color corresponds to the daily averaged wind speed and the daily average based air-sea CO_2 fluxes.

On line 190 it is stated that the W92 formulation was used, but there is no further mention of it in the results (?).

We used CO_2 flux calculations based on Wanninkhof, 1992 formulation for comparison with Lauvset et al. (2013) data for autumn 2007 (Lines 367-371).

9) Lines 363-364: The authors state that hourly wind speed improves the estimate of CO_2 uptake capacity (line 363-364). I have a technical objection to the use of the term "uptake capacity" (or "uptake intensity" on line 368). What do these mean? Surely, we are talking about "flux", so why not stick to that term and avoid ambiguity?

Thank you, we will replace these terms.

Whether hourly wind-speed improves the estimate of the flux is somewhat irrelevant given that the flux depends so much on one's choice of k formulation. This alone makes a difference of 50%, if not more at high wind speeds. Each parameterization of Kw has its limitations and is calculated over different time-scales so it may or may not be appropriate to apply this to hourly wind data. I would simplify this discussion by not going into such details of air-sea exchange. In my opinion, it's fine to clearly state how the flux is calculated here and move on to the other sections. Statements regarding improvements of the flux by hourly vs. daily wind speed are beyond the scope of this paper.

We agree with the reviewer, and will remove this part of the discussion from the text.

10) Figure 1: It would be informative to also plot the 2007 sea-ice extent on panel b of Figure 1.

Thank you, it will be added.