

## **Response to review comment 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 #2**

The paper illustrates the surface pCO<sub>2</sub> distributions in the Arctic Ocean and the associated air sea CO<sub>2</sub> fluxes within wide and shallow shelves of the Eurasian sector, which can be affected by intense exchanges at the air sea interface. In addition, spatial and temporal variabilities are presented together with different drivers of the marine carbonate system in one of the most sensitive region to climate change and ocean acidification. The region has been undergoing rapid changes for the last decades. The collected data refers to three seasonal campaigns, conducted in late summer/fall 2006, 2007 and 2009, characterized by different meteorological conditions. The spatiotemporal variability and the different drivers are thoroughly analyzed and well discussed, while results are clearly presented. In my opinion, the objectives of this study are clearly presented and fully reached. The paper can add valuable contribution to the knowledge of CO<sub>2</sub> fluxes in a polar region, where dearth of data is limiting. I enjoyed the paper, in particular the introduction and the discussion on the response of marine carbonate system to the different drivers well enlightening the complexity of the system. I believe it is worth of publication.

We would like to thank Anonymous Referee #2 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) It seems to me that title does not fully mirror the focus of the paper, mainly addressed to the upper layer properties, distributions and dynamics. . . . If you agree would you mind suggesting this even in the title?

We followed the suggestion; the title has been changed for:

“The spatial and inter-annual dynamics of the surface waters carbon dioxide system and air-sea CO<sub>2</sub> fluxes in the outer shelf and slope of the Eurasian Arctic Ocean”.

2) Line 30: more caution should be used about “a growing CO<sub>2</sub> evasion occurs . . .” as the estimated fluxes from the sea to the atmosphere (in Tab 1) are really very low ! Wanninkhof and McGillis (1999) are reported to underestimate fluxes at low wind speed, that seems the case. I don't mean to open discussion about the best parameterisation (for instance Nightingale et al. 2000 might be suggested). I accept the author's choice but please be cautious about results. I

rather would say that uptake was strongly weakening under 2007 environmental conditions as surface seawater appears in equilibrium with atmosphere . . .

The text will be re-written as:

“In contrast, the uptake of CO<sub>2</sub> was strongly weakening in the outer shelf and slope waters of the East Siberian Arctic seas during the 2007 environmental conditions. The surface seawater appears in equilibrium or slightly supersaturated by CO<sub>2</sub> relative to atmosphere because of increasing influence of river runoff and its input of terrestrial organic matter that mineralizes, in combination with the high surface-water temperature during sea ice-free conditions.”

3) Paragraph 2.2.2: author should provide the temperature conditions of analysis. Titration has been performed at constant temperature ? and which one ? Due to the variety of analytical methods and measurement units, the international community working on marine carbonate system has decided to adopt common protocols (requiring the analysis at constant temperature, and common measurement units) Protocols reported by Dickson et al 2007 that authors cite, are recommended.

Thank you for pointing this out. The text will be re-written as:

“Samples for A<sub>T</sub> were analyzed in the lab within one month using an indicator titration method in which 25 ml of seawater was titrated with 0.02 M HCl in an open cell according to (Bruevich, 1944; Pavlova et al., 2008). Measurements were performed at 20°C, with the temperature in the cell controlled to within 0.1°C. In 2000 the Carbon Dioxide in the Ocean working group of the North Pacific Marine Science Organization (PICES) performed an intercalibration of A<sub>T</sub> in seawater using CRMs. The results of the intercalibration showed that the alkalinity values obtained by the Bruevich method are in agreement with the standard within ±1 μmol kg<sup>-1</sup> when state-of-the-art analytical practice is applied (Pavlova et al., 2008)”.

Pavlova, G. Yu., Tishchenko, P. Ya., Volkova, T. I., Dickson, A., and Wallmann, K. (2008) Intercalibration of Bruevich's method to determine the total alkalinity in seawater, *Oceanology*, 48, 3, 438-443. DOI: 10.1134/S0001437008030168.

4) Paragraph 2.2.3: indicate the scale of the pH measurement and again the temperature. The international community working on CO<sub>2</sub> fluxes, ocean acidification and impacts, has decided to adopt common protocols and common measurement units in order to increase utilization of data among different scientific communities. This uniformity would increase a wider utility of the paper. Protocols reported by Dickson et al 2007 that authors cite, are recommended. Please refer to them for units and scale. Line 140-141: authors should provide the accuracy of the method, for consistency with TA. This can be done by calibration against the reference materials (CRM's supplied by Dickson) and using CO<sub>2</sub>SYN for calculating the pH<sub>T</sub> of CRMs at the temperature of analysis. Specific comments at point 3 and 4 are necessary also for the next paragraph (2.2.4),

where CO2SYS programme is mentioned. This could be useful to non expert (of carbonate system analysis) readers.

The text will be re-written as:

### “2.2.3 pH

A potentiometric method was applied to determine pH in the Pitzer pH scale (Pitzer, 1991) using a closed cell thermostated at 20°C with a sodium and hydrogen glass electrode pair without liquid junctions (Tishchenko et al., 2001, 2011). The buffer solution TRIS–TRIS–HCl– NaCl–H<sub>2</sub>O (Tishchenko, 2000a) was used for calibrations in the Pitzer pH scale. Using this buffer not only the hydrogen glass electrode but also the sodium glass electrode was calibrated. Together with thermodynamic data (Dickson, 1990) the pH values were converted from the Pitzer pH scale to the total hydrogen ion concentration scale (Dickson et al., 2007). The accuracy of pH measurements was about 0.004 pH units”.

Note, that pH values were measured potentiometrically in the Pitzer pH scale and reported at total scale according to method, developed by Prof. Pavel Ya. Tishchenko, the contributor of “Guide to Best Practices for Ocean CO<sub>2</sub> Measurements”, edited by A.G. Dickson, C.L. Sabine, J.R. Chistain (2007). Direct comparison between these potentiometric and spectrophotometric pH values (both in “total” scale) demonstrated a good coincidence (Tishchenko et al., 2001). More details can be found in (Tishchenko et al., 2000ab, 2001, 2002, 2011).

Dickson, A.G. (1990). Standard potential of the reaction:  $\text{AgCl(s)} + 1/2 \text{H}_2\text{(g)} = \text{Ag(s)} + \text{HCl(aq)}$ , and the standard acidity constant of the ion  $\text{HSO}_4^-$  in synthetic sea water from 273.15 to 318.15 K, *Journal of Chemical Thermodynamics*, 22, 113-127.

Pitzer, K.S. (1991). Ionic interaction approach: theory and data correlation. In: Pitzer, K.S. (Ed.), *Activity Coefficients in Electrolyte Solutions* second ed. CRC Press, London, pp. 75–153.

Tishchenko, P.Ya. (2000a). Non-ideal properties of the TRIS–TRIS - HCl–NaCl–H<sub>2</sub>O buffer system in the 0–40 °C temperature interval. Application of the Pitzer equations, *Izv. Akad. Nayk. Ser. Khim.*, 49, 670–675 (in Russian).

Tishchenko, P.Ya. (2000b). Standardization of pH measurements based on the ionic interaction approach, *Izv. Akad. Nayk. Ser. Khim.*, 49, 676–680 (in Russian).

Tishchenko, P.Ya., Wong, C.S., Pavlova, G.Yu, Johnson, W.K., Kang, D.-J., and Kim, K.-R. (2001). pH measurements of seawater by means of cell without liquid junction. *Oceanology*, 41, 6, 813–822.

Tishchenko, P.Ya., Il'ina, E.M., Chichkin, R.V., and Wong, C.S. (2002). pH measurements in estuary by means of cell without liquid junction. *Oceanology*, 42, 1, 27–35.

Tishchenko P. Ya., Kang D.-J., Chichkin R.V., Lazaryuk A.Yu., Wong C. S., Johnson W. K. (2011). Application of potentiometric method using a cell without liquid junction to underway pH measurements in surface seawater, *Deep-Sea Research I*, 58, 778–786.

5) Paragraph 2.2.4, lines 148-149: in order to prevent misunderstanding and not confuse direct continuous pCO<sub>2</sub> measurements (by SAMI CO<sub>2</sub> sensor) with the calculated pCO<sub>2</sub> from discrete samples (collected by Rosette), I suggest to specify “At oceanographic stations surface pCO<sub>2</sub> values were calculated, on discrete samples, from pH<sub>T</sub>25, AT and inorganic nutrients data using CO2SYS. . .” In addition authors should say which constants for sulfate and borate (KSO<sub>4</sub> and KBorate) have been chosen in the CO2SYS programme.

It will be specified accordingly.

6) Lines 367-374: rephrase the two paragraphs as “In order to compare our estimates with those calculated by Lauvset et al. (2013) which carefully assessed the seasonal cycle of air-sea CO<sub>2</sub> fluxes in the Barents Sea, daily wind speed and quadratic parameterization of gas transfer velocity (Wanninkhof, 1992) were used for calculating CO<sub>2</sub> fluxes in the northern Barents Sea. The CO<sub>2</sub> uptake during the 2007 fall season reached an average . . . As the dataset by Lauvset et al. (2013) did not cover the north of the sea comprehensively, the data obtained during our cruise adds information enabling more accurate estimation of the absorption capacity of the whole Barents Sea in the fall season.”

Thank you very much for suggestion, text will be replaced.

7) Lines 408-409: again I feel necessity of a clear indication that pCO<sub>2</sub> data of the selected transect, reported in fig 10, are calculated for discrete samples (from AT, pH<sub>T</sub>25 and inorganic nutrients data) by means of CO2SYS programme.

It will be clarified in the text.

8) Fig 10 seems underutilized in the text, as only surface data are compared without any further discussion about vertical distributions. As the figure is very informative could you please comment a bit more ?

We have added a bit more details in describing the data of Figure 10. This text will be incorporated in the manuscript instead of the sentence on Line 410.

“The salinity distribution along the transect during the three cruises shows a similar general pattern, but with some significant variations especially in the top 30-50 m. Of the three years, 2007 had the lowest surface salinity and the most pronounced halocline (Figure 10). However, the largest interannual differences were in the seawater temperature distribution. In late summer of 2007 the surface layer was the warmest and underlain by a sharp thermocline coinciding in depth with the halocline to form a strong pycnocline that restricted vertical exchange. A

characteristic feature of the vertical distribution of  $p\text{CO}_2$  over the transect in late summer 2007 was a pronounced subsurface maximum of  $p\text{CO}_2$  (Figure 10) and higher  $p\text{CO}_2$  values in the surface waters. Subsurface maximum was found exactly at the slope, and coincided with a layer of the brine-enriched south-eastern Laptev Sea bottom waters (Bauch et al., 2011). During years with prevalent offshore wind setting, such brine-enriched waters are exported to the Arctic Ocean halocline at about 50 m water depth (Bauch et al., 2009, 2011).

Westerly winds during the ice –free period in the summer 2007 advected the Lena River plume to the northeast. Thus, the low surface salinity was mainly related...” (Followed by text on Line 411).

The reference will be added in the manuscript:

Bauch, D., I. A. Dmitrenko, C. Wegner, J. Hoilemann, S. A. Kirillov, L. A. Timokhov, and Kassens H. (2009). Exchange of Laptev Sea and Arctic Ocean halocline waters in response to atmospheric forcing, *J. Geophys. Res.*, 114, C05008, doi:10.1029/2008JC005062.

9) Line 421: I find a bit “dangerous” using here the word “supersaturation” as this make me to wonder if supersaturation has been really computed

Actually, it was “a weak supersaturation” in the south of the transect. It will be re-written.

10) Line 422: I find not fully proper to say that  $\text{CO}_2$  outgassing into the atmosphere was observed . . . (Fig 10), as the calculated fluxes for the Laptev and East Siberian seas were really very low (see Tab 1). I would prefer rephrase as “Thus  $\Delta p\text{CO}_2$  conditions (Tab 1) favoring  $\text{CO}_2$  outgassing into the atmosphere were observed”

Thank you. It will be changed accordingly.

11) Line 456-458: I suggest authors to rephrase as “. . . resulting in an increase of the area where seawater  $p\text{CO}_2$  was in equilibrium with atmosphere and consequent reduction of  $\text{CO}_2$  adsorption in the East Siberian Arctic seas”.

It will be done.