Response to review comments on “DOM and its optical characteristics in the Laptev and East Siberian seas: Spatial distribution and inter-annual variability (2003–2011)” by Svetlana P. Pugach et al.

Anonymous Referee #2

Review of Svetlana et al DOM and its optical characteristics in the Laptev and East Siberian seas: Spatial distribution and inter-annual variability (2003-2011). The manuscript has the aims of reporting on the inter-annual variability in CDOM and DOC in the Laptev and East Siberian sea. It reads very much like a cruise report and would benefit from a more comprehensive data analysis and discussion of the results obtained.

SP: *Thank you for all your comments, which help us to improve our manuscript further.*

While we respectfully disagree that our manuscript is “like a cruise report”, we recognize there is indeed several aspects that we can improve. A more comprehensive data analysis and more detailed discussion is now facilitated, for instance, by five new figures (shown in the end of this response):

- vertical distribution of CDOM along two the west-to-east transects across the ESAS (Figure 1_add);

- relationship between DOM fluorescence (DOM-FL) measured using WETStar fluorometer and absorption coefficient at 370 nm (a_{370}) in the ESAS (our data) and Belzile data (Figure 2_add);

- depth profiles of salinity (a) and DOM-FL (b) measured at two typical stations in the ESAS (their locations are shown in Figure 3), and relations between DOM-FL and salinity (c) (Figure 3_add);

- relationship between the DOM-FL and salinity; S_R and salinity in the ESAS surface waters, September 2005 (a) and 2011 (b) (Figure 4_add),

- relationship between the surface salinity and DOM-FL (Figure 5_add).

This further analysis will be elaborated in the revised discussion section.

The referencing of previous literature is suboptimal and at times inappropriate. In my opinion there is a missed opportunity for a solid analysis on the linkage between CDOM absorption, fluorescence and DOC across several years.

SP*: The referencing of previous literature was now carefully reconsidered and complemented by several additional references. The linkage between CDOM absorption, fluorescence and DOC was considered in detail only for summer 2004, because only this year all these parameters were investigated simultaneously.*

Why not take more inspiration from the Belzile paper cited and include a comparison of your data with theirs from the East Siberian sea? Does the same FDOM to CDOM relationship exist?

SP: *In the revised ms, we have now compared the relationship between DOM-FL and absorption coefficient at 370 nm (a_{370}), which quantify CDOM, using the East Siberian Sea’ data reported by Belzile (2006) and our data obtained in the Laptev and East Siberian seas. Figure 2_add (shown below) demonstrates a good agreement between Belzile’ and our data. Correlation coefficient between DOM-FL and CDOM – in terms of a_{370}, have been found the same in the ESAS (r=0.97, N=92) and Belzile samples (Boothbay Harbor, West Harbor Pond, Beaufort Sea and East Siberian Sea): (r=0.98, N=74).*

Highest values of DOM-FL and a_{370} can be seen in the Laptev Sea (marked as grey circles) which is strongly impacted by the Lena River runoff.

The section on the inter-annual variability is difficult for the reader to follow as is. It would likely be easier if figure 5 and 6 were combined so that the sea level pressure maps could be compared with the CDOM and salinity distribution maps. Alternatively, the authors could just compare the maps of both salinity and SLP, then in a separate figure reveal how robust the salinity CDOM relationship was. In this form the manuscript is not suitable for publication and I recommend re-submission after revising the data analysis.

***SP**: As espoused above and further below, the ms is significantly revised to further the data analysis and interpretations. On the more specific reviewer comment, we tried to redo our Figures 5 and 6 according to the comment, but we found that of the output was not so useful because of different formats of the datatypes. Instead, we will add a separate figure, which reveals a relationship between the surface salinity and DOM-FL, to the existing figures 5 and 6.*

Whilst doing this you should consider splitting the results and discussion sections to allow for a better separation between your results and reflections on how your findings link to other studies.
***SP:** We have revised the data analysis and splitted up the results and discussion sections to allow for a better separation between our results and reflections on how our findings link to other studies.*

Other points to address:

Line 8. “amount” rather than “volume”.

***SP:** Corrected.*

Line 21. Replace “were” with “was”

Try to avoid use of “e.g.” in referencing and citing very many studies. Find the most relevant and limit it to 3-4.

***SP:** Agree. Corrected/adjusted throughout the ms.*

Line 46. Replace “gives input” with “supplies”.

***SP:** Corrected.*

Line 50-51. I suggest you specify this more. Many rivers and streams have high or higher DOC but few large rivers have concentrations this high at their mouth.

***SP:** Thank you. This part of introduction was rewritten as:*

Annually, the Arctic rivers transport 25-36 Tg of DOC to the Arctic Ocean, which is ~10 % of the global riverine DOC discharge (Raymond et al., 2007). The Siberian rivers have high DOC concentration with a mean of more than 500 µM (Gordeev et al., 1996; McClelland et al., 2012; Amon et al., 2012). These concentrations are an order of magnitude higher than in the inflowing Atlantic (60 µM) and Pacific waters (70 µM), but the volume flux of the latter is about 60 times larger than that of continental runoff (Anderson and Amon, 2015). Furthermore, Arctic and subarctic regions contain approximately 50 % of the global terrestrial OC in their frozen soils (Tarnocai et al., 2009; Hugelius *et al., 2011). Warming and intensification of the hydrologic cycle is leading to increased rate of water and dissolved organic matter (DOM) discharge from the Siberian rivers (Semiletov et al., 2000; Savelieva et al., 2000; Stein and Macdonald, 2004).*

Line 54. Replace “lead” with “is leading to”

SP: *Corrected.*

Line 56-68. This section should be rephrased and better references found. If you do not want to have too many references I recommend you pick either the original papers or first to demonstrate this in the Arctic. Currently there is a bizarre selection of studies cited and not all directly relevant.

SP: *This section is rephrased and referencing edited.*

Line 78-79. Several of these references are not even Arctic.

SP: *Agree. Corrected.*

Line 80. Were there not any additional scientific aims or hypothesises? Possibly developed during the data analysis for this study? Try to mention them here. As stated now the aim reads very much as a data report.

SP: *Thank you. It was edited to the following:*

The purpose of this paper is: (1) to study the inter-annual dynamics and optical characteristics of DOM in shelf waters of the Eastern Arctic seas on the basis of multi-year summertime (August – September) expedition data (2003-2005, 2008, 2011); (2) to examine the relationship between CDOM and DOC in order to validate a method for accurate prediction of DOC concentration from CDOM properties; (3) to show the possibility to determine the distribution of terrigenous dissolved organic matter and continental runoff in the surface water of East Siberian Shelf by CDOM optical characteristics.

Delete line 83-86. This has been established in the Introduction.

SP: *Deleted. Thanks.*

Line 95. Check your phrasing of “would be oxidised”.

SP: *Thanks. This sentence was replaced by:*

Moreover, it has been found that in the past the Lena River played a dominant role in sediment discharge, flushing out soil OM from its vast watershed (Tesi et al., 2016); a significant fraction of “fresh” terrestrial OM contributes to the DOM pool (Karlsson et al., 2016).

Line 133-134. Delete this. It is a standard fluorometer which is readily available. No need for this. Also the description of the interior optics can be removed. Not really necessary and appears to be copy pasted word for word from Belize et al 2006 paper, which is a little alarming.

SP: *Thanks. It was edited as following:*

3.3.1 In situ measurements of CDOM fluorescence

CDOM fluorescence (DOM-FL) was measured with a WETStar DOM fluorometer which is suitable for in situ measurements without prior filtration of water (Belzile et al., 2006).
Line 146. What ranges? I do not understand.

SP: *Thank you. It was a typo. This sentence is replaced by: «Water samples for CDOM underwent filtration through 0,7 µm GF/F filters (Whatman, Inc.).*

Lin 150. It is not valid to apply the fit across this range. The spectrum does not behave exponentially and in many samples there will be a shoulder at 280. Additionally the absorption below 240 will be mainly due to other constituents.

Line 156. Sr is not explained, and the whole this part if poorly written.

Line 157. SUVA is not that recent and include a citation of the original paper for this (Weishaar).

Line 158. I do not agree with this sentence. Starting "The last parameter. . ."

Line 161. I do not agree with this extrapolation. The relationship demonstrates the expected link between MW and SUVA but not does not mean that the relationship is fixed and one can use it to determine MW in other systems.

Line 168. "The value of S increases with the decrease of the CDOM absorption coefficient". This is not true. It depends on the values of the end members (see Stedmon and Markager 2003).

Line 169. Include reference for relationship between S and aromatic content/molecular weight

Line 172. Several of these references did not even measure or report the spectral slope at 275-295.

SP: *This section from line 150 was rewritten as following.*

3.3.2 CDOM optical properties

Spectroscopic analysis of CDOM samples was performed using a UNICO 2804 spectrophotometer with a 1 cm quartz cuvette over the spectral range from 200 to 600 nm at 1 nm intervals. Milli-Q (Millipore) water was used as the reference for all samples. Water samples for CDOM underwent filtration through acid-washed Whatman glass fiber filters (GF/F, nominal pore size 0.7 µm).

The absorption coefficient (aλ, m-1) was calculated as follows:

$$a (\lambda) = 2.303A(\lambda)/L, \tag{1}$$

where A (λ) is optical density at wavelength λ, and L is the cell pathlength in meters.

The absorption coefficient at 350 nm (a_{350}) was chosen to quantify the concentrations of CDOM because of its correlations to DOC and to permit comparison with other results (Spencer et al., 2009; Stedmon et al., 2011; Walker et al., 2013; Gonçalves-Araujo et al., 2015; Mann et al., 2016).

The dependence of a (λ) on λ is described using Equation (2):

$$a (\lambda) = a (\lambda_0) \exp \{-S (\lambda - \lambda_0)\}, \tag{2}$$

where $a(\lambda_0)$ is the absorption coefficients at reference wavelength λ_0, and S is a spectral slope defining spectral dependence of the absorption coefficient resulting from CDOM presence (Blough and Del Vecchio, 2002).

The spectral slope, S, indicates the rate at which the CDOM absorption coefficient decreases with wavelength increase (Carder et al., 1989). The value of S varies with the source of the CDOM, aromatic content, and molecular weight (Blough and Del Vecchio, 2002; Helms, 2008; Granskog et al., 2012). In near-shore regions, which are under the influence of terrestrial sources with high concentrations of CDOM, S values increases due to the conservative mixing of terrestrial CDOM (high $a\lambda$*, low S) with oceanic CDOM (low* $a\lambda$*, high S) (Stedmon and Markager, 2003). Therefore, it is also widely accepted that the spectral slope S can be used as a proxy for CDOM composition (Kowalczuk et al., 2003). However, its usefulness is limited by the fact that S depends on the wavelength interval over which it is calculated (Carder et al., 1989; Stedmon et al., 2000). Following recommendations by Helms et al. (2008) a wavelength interval of 275-295 nm was chosen for detailed spectral analysis because it demonstrates the biggest variability of optical parameters under mixing conditions of water with contrasting optical characteristics. The ratio of S values from the shorter (275-295 nm) and the longer wavelength region (350–400 nm), termed the slope ratio,* S_R*, was calculated as described by Helms et al. (2008).* S_R *values for terrestrial CDOM typically are <1 whereas oceanic CDOM and extensively photodegraded terrestrial CDOM are typically >1.5 (Stedmon and Nelson, 2015).*

Specific UV absorbance (SUVA) is defined as the UV absorbance of a water sample at 254 nm normalized for dissolved organic carbon (DOC) concentration is used to estimate the degree of aromaticity in bulk CDOM (Weishaar et al., 2003):

$$C_{Ar} = 6.52 * SUVA + 3.63, \qquad (3)$$

where C_{Ar} *is percentage of aromatic carbon of the total carbon.*

This equation is applicable for a wide range of aquatic environment(seas, bogs, lakes) since the authors used humic substances that have different chemical characteristics and demonstrated a strong correlation (r = 0.98) between the specific UV absorbance and aromatic carbon content (Weishaar et al., 2003).

To calculate concentration of lignin which is a well-established biomarker of terrigenous dissolved organic matter (DOM) in the ocean and has been successfully applied as a tracer of riverine inputs in the Arctic Ocean (Opsahl and Benner, 1997; Opsahl et al., 1999), we used model by Fichot et al., (2016). Exploration of lignin and CDOM relationships provided useful information for the development of two simple empirical models for the retrieval of the sum of nine lignin phenols (TDLP9, nmol L^{-1}*) from a (λ) in coastal waters (Fichot et al., 2016):*

when $a_{250} < 4\ m-1$*, a “low-CDOM” sub-model based on a simple linear regression was used,*

$$\ln(TDLP9) = 0.7672 \cdot a_{263} - 0.3987, \qquad (4)$$

When $a_{250} \geq 4\ m-1$*, a “high-CDOM” sub-model based on a multiple linear regression was used,*

$$\ln(TDLP9) = -2.282 \cdot \ln(a_{350} - 8.209 \cdot \ln(a_{275}) + 11.365 \cdot \ln(a_{295}) + 2.909 \qquad (5)$$

Line 182. First sentence is repetition.

SP: *Deleted.*

Line 190. What do you mean by spectral dependency of S275-295? The spectral range should be constant.

SP: *Thanks. This sentence was rewritten as following:*

Figure 3 shows CDOM absorption spectrum and calculated values of $S_{275\text{-}295}$ *for surface waters of three stations located in typical shelf zones: station 118 is under direct Lena River influence (the Laptev Sea), station 60 is located in the ESS (moderate zone of river and ocean waters mixing), and station 97 in Long Strait.*

Line 193-209. Why not expand the comparison of slope values and ratios with data available from other Siberian rivers Eg. In Walker et al 2013 doi: 10.1002/2013JG002320 (they have seasonal data to compare to). Stedmon et al 2011; Mann et al 2014 & 16. And Gonçalves-Araujo et al 2015 10.3389/fmars.2015.00108

SP: *Thank you. We will expand the comparison of slope values and ratios with data available from other Siberian rivers (citing refs, accordingly).*

Line 201-214. Is this analysis/interpretation only based on the 2004 data. Why not expand to include all data and compare where you see the qualitative change with where there also is a large drop in CDOM? Is it at the same region the drop in SUVA occurs across all years or is it more salinity that is driving the drop seen in the figure?

SP: *Yes, this analysis/interpretation is only based on the 2004 data. We will expand this to 2005, and 2011 (no spectral data are available for 2008) with a special emphasizes at the areas with large drop in CDOM. To answer this question the Figure 4 was redrawn and shown below.*

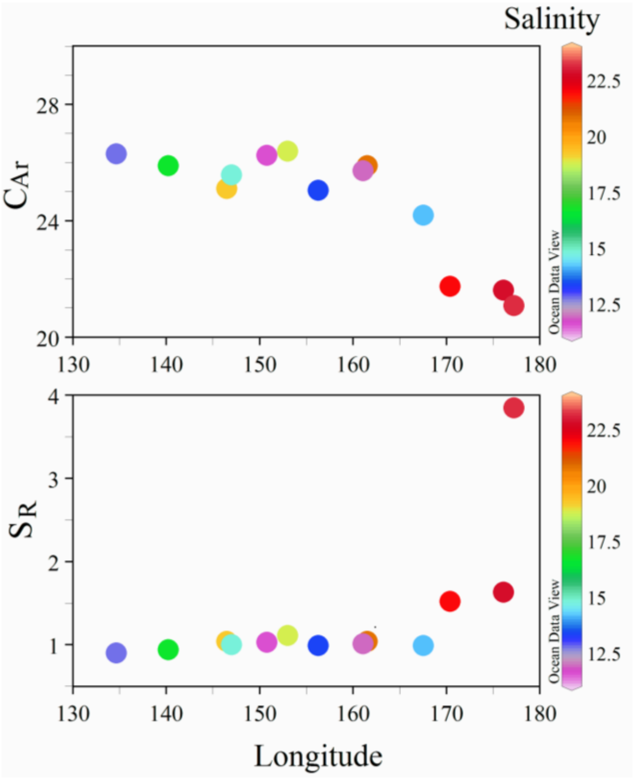


Figure 4. *The relationship between the aromatic carbon content* (C_{Ar}, *%) and salinity,* S_R *and salinity in the ESAS surface waters, September 2004.*

*As can be seen from new Figure 4, SUVA (C_{Ar}= 6.52*SUVA + 3.63) is strongly correlated with salinity (r= -0.7). SUVA and CDOM are also closely related (r = 0.71). Then we can say that large drop in CDOM, Sr and SUVA values is driven by increased salinity across all years; position of the region of large change of CDOM and other parameters demonstrated inter-annual dynamics.*

Figure 9a and b. It would be more robust to derive the relationship for the 2004 data and test in on the data from other years. I wonder if you carried out the regression analysis between DOC and salinity if you get the same predictive power. The data here look to be very conservative. Mixing is dominating.

SP: *Thanks. It seemed that this comment is targeted on Figure 8a and 8b. Yes, mixing is dominating. Following your comment we joint all the data for 2004 and 2008 in new Fig. 8c.*

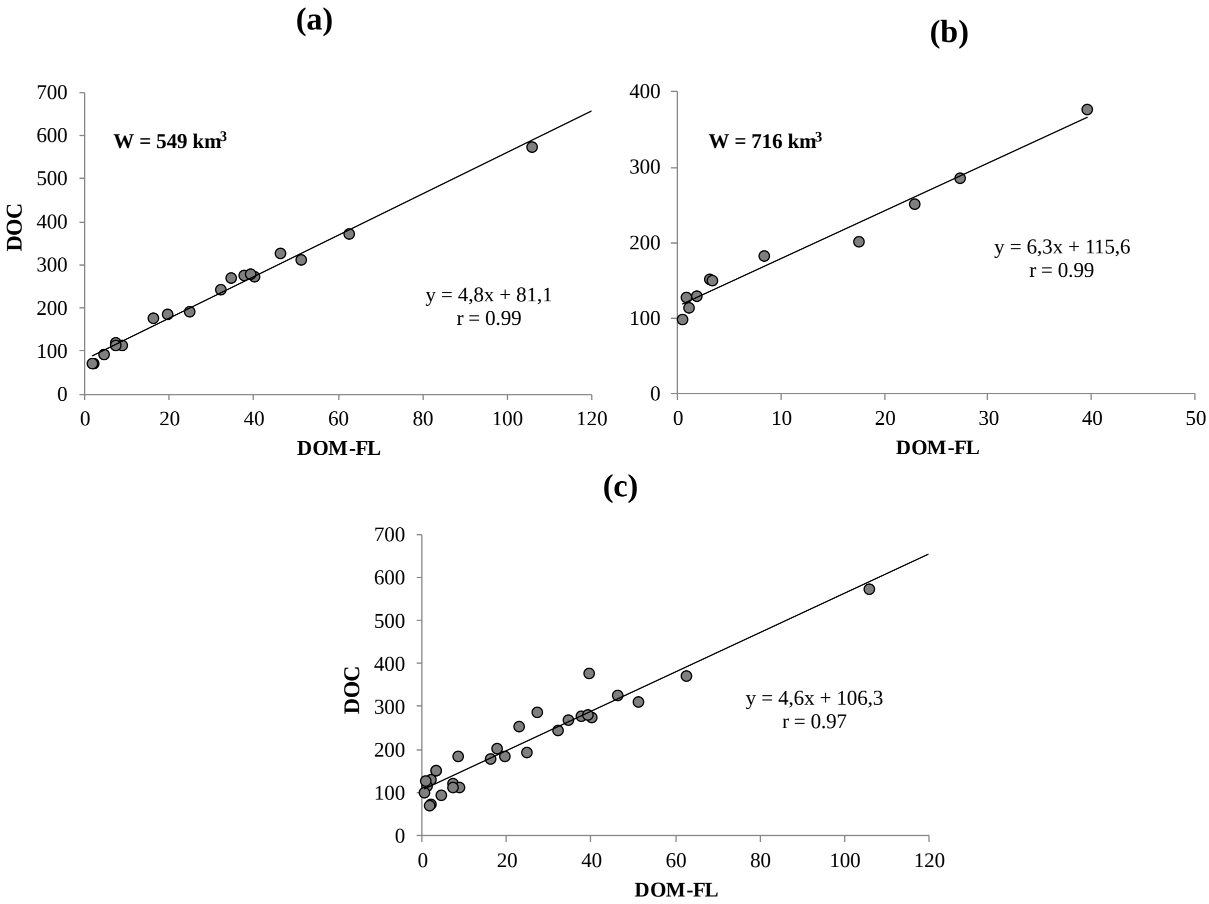
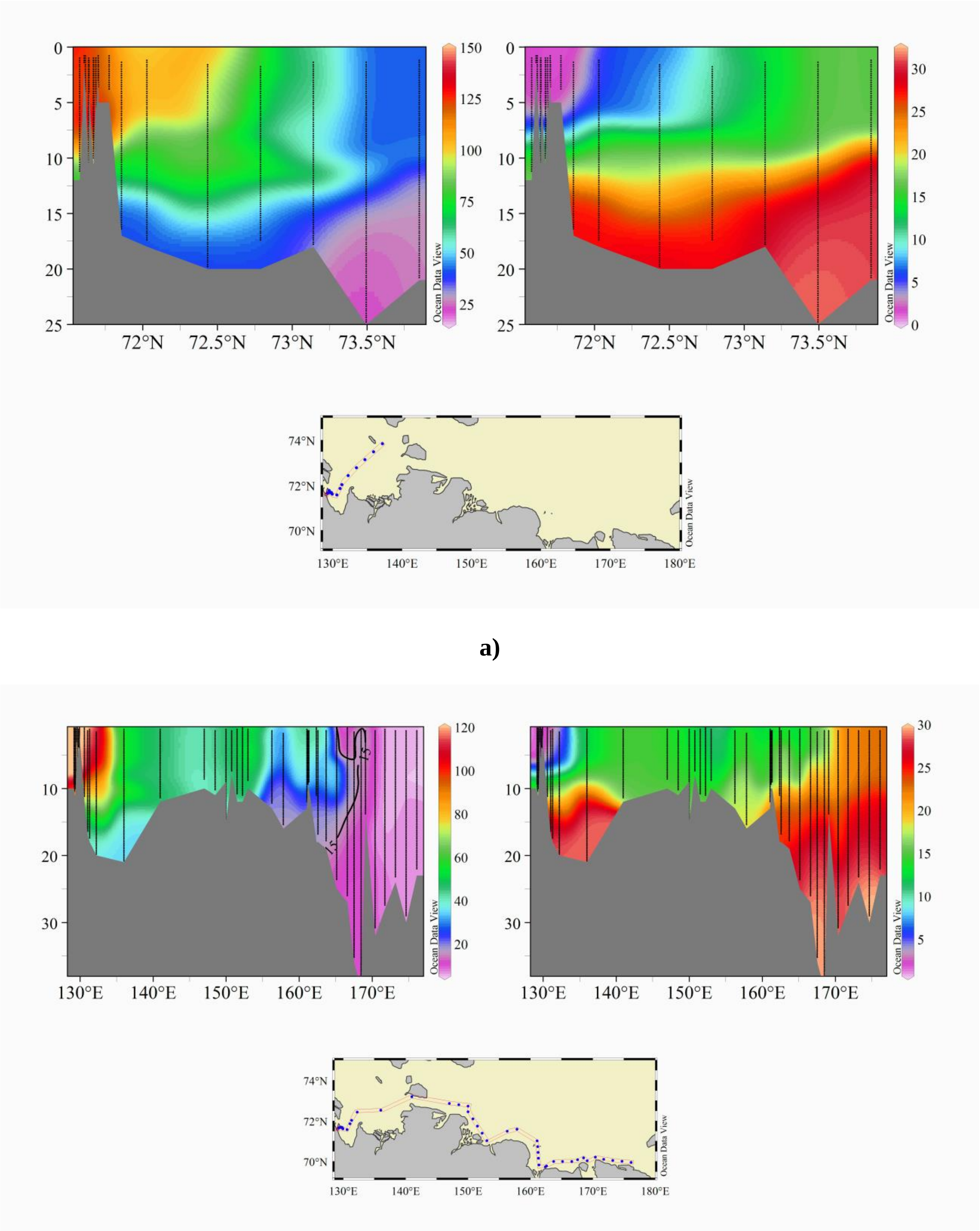


Figure 8. *DOC concentration (µmol l^{-1}) versus DOM fluorescence measured using the WETStar fluorometer (DOM-FL, QSU) in the ESAS surface water, September 2004 (**a**), 2008 (**b**) and combined for two years (c); **W** - annual Lena River discharge.*

As can be seen the DOM-FL-DOC predictive power is high and can likely be used in other studies. Unfortunately, the relationship between DOC and salinity is not so strong, because of melt water that lowers this correlation. For example, in 2004 the pair salinity-DOC demonstrates high negative correlation (0.9) in the ESS nearshore zone, while this correlation drops down to - 0.7 in 2011 in the LS and ESS, because of more meltwater. Thus, the relationship between salinity and DOC can be used only for river-freshened areas (limited by isohaline 24.5) and with caution.

Additional Figures



a)

b)

Figure 1_add. *Vertical distribution of DOM-FL (left panel) and salinity (right panel) along the Lena River transect (a) and the west-to-east transect across the ESAS (b) in September, 2004.*

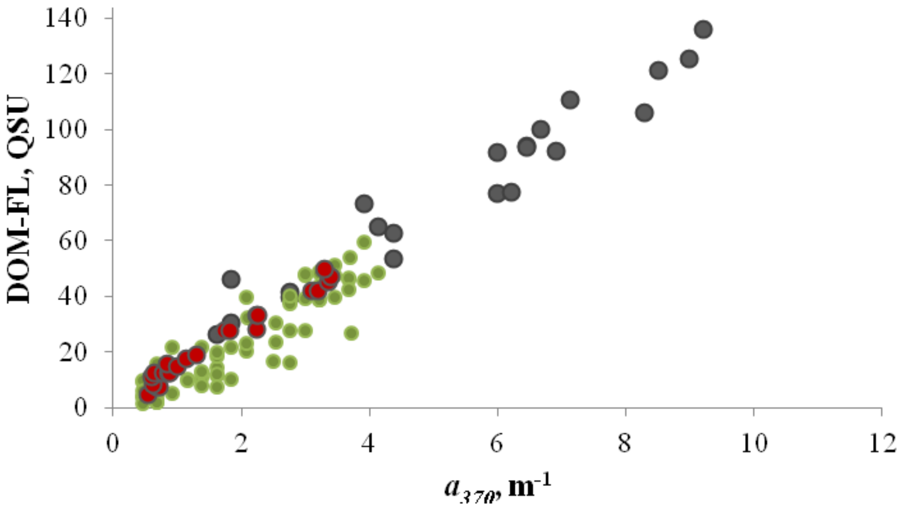


Figure 2_add. *Relationship between DOM fluorescence (DOM-FL) measured using WETStar fluorometer and absorption coefficient at 370 nm (a_{370}). Grey – our data in the LS (N = 23), Green – our data in the ESS (N = 69) and red – data from Belzile et al., 2006 (N = 23).*

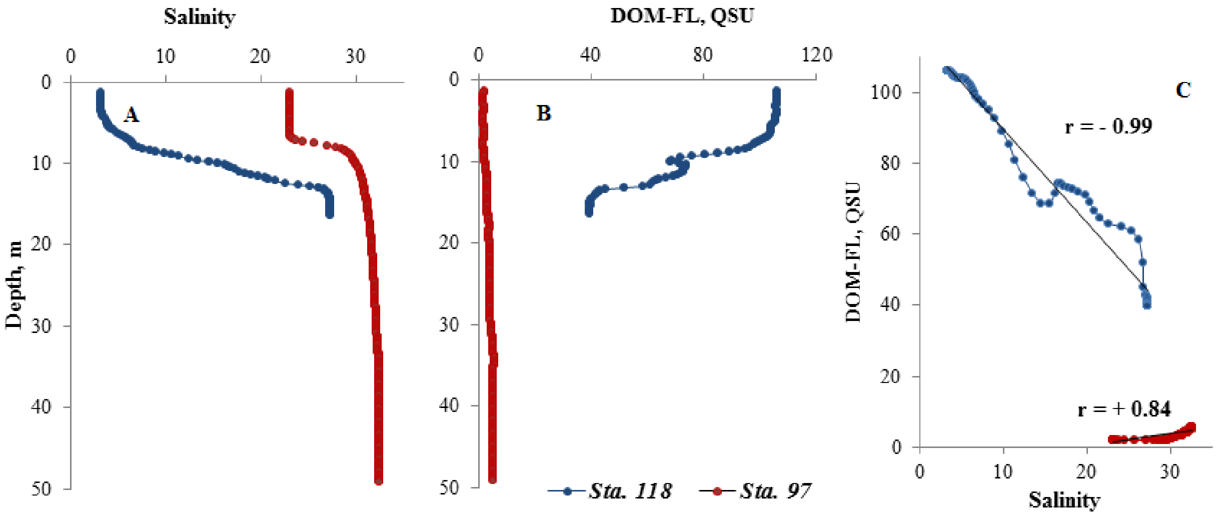


Figure 3_add. *Depth profiles of (A) salinity and (B) DOM-FL measured at two stations on the ESAS, and (C) relations between DOM-FL and salinity.*

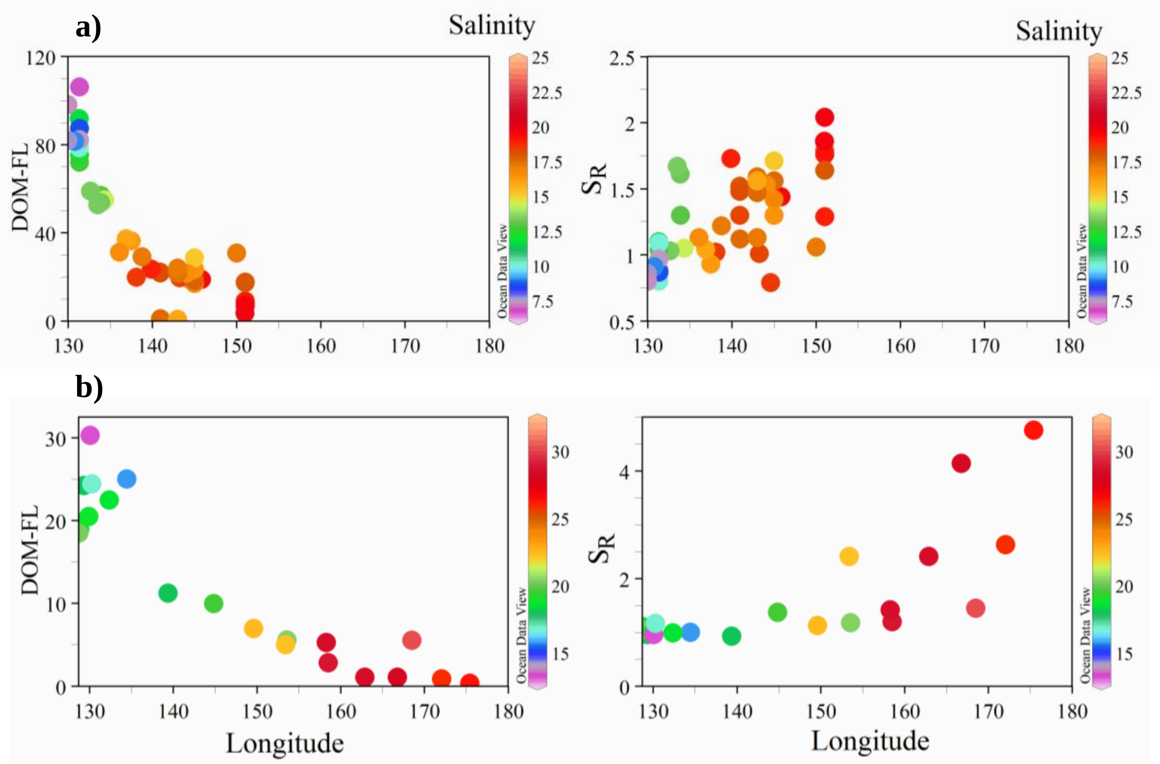


Figure 4_add. *The relationship between the DOM-FL and salinity;* S_R *and salinity in the ESAS surface waters, September 2005 (a) and 2011 (b).*

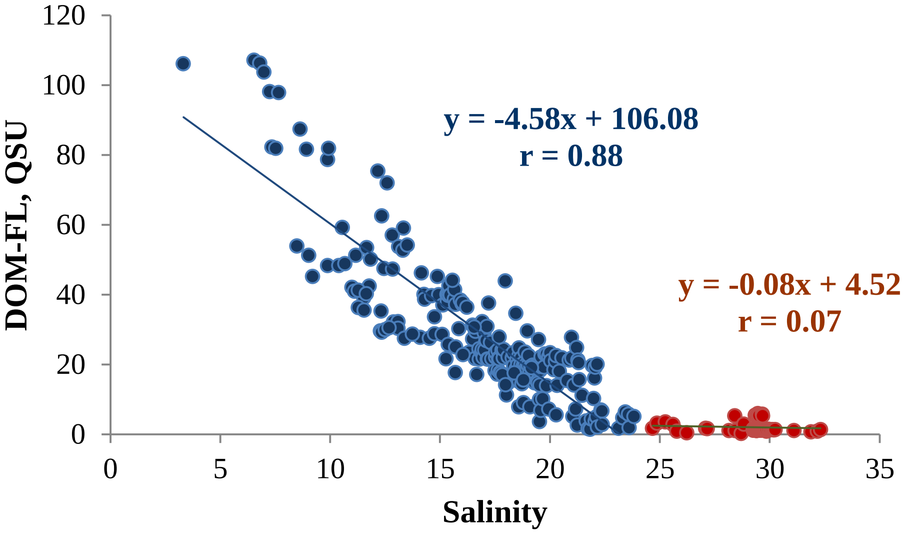


Figure 5_add. *The relationship between the salinity and DOM-FL in the ESAS surface water in August-September 2003-2005, 2008 and 2011(blue circles – salinity < 24.5, red - > 24.5).*