

Reply to the Reviews

Interactive comment on “Absorption and fluorescence properties of the eastern Bering Sea in the summer with special reference to the influence of a Cold Pool” by E. J. D’Sa et al.

The authors would like to thank the two anonymous reviewers for the detailed and helpful comments that will improve the quality and clarity of the paper. The author’s responses are detailed below in italics.

Anonymous Referee #1

Received and published: 28 January 2014

Paper title: Absorption and fluorescence properties of the eastern Bering Sea in the summer with special reference to the influence of a Cold Pool

Authors: E. J. D’Sa, J. I. Goes, H. Gomes, and C. Mouw

General comments: The authors examined optical properties including both absorption and fluorescence of colored dissolved organic matter (CDOM) in the eastern Bering Sea (EBS) using a large dataset. Spatial/vertical distribution, sources, and photo-chemical/microbial degradation of CDOM are addressed together with hydrographic features and dissolved organic carbon (DOC). These types of analyses are important not only for better understanding of optical properties of but also for primary productivity of productive EBS as CDOM controls light penetration in the water column. However, this manuscript requires more work. I had to read the manuscript several times to understand exactly what the authors described in the text. The section of Results is particularly difficult to follow. The main reasons are as follows. First, linkages between optical properties of CDOM and hydrography are not well explained. Because these optical properties are explained based on water masses, the hydrography should be clearly examined. Second, spatial distributions of a series of variables (e.g., temperature, salinity, chl fluorescence, DOC, ag_{355} , etc) are not clear, which makes difficult to follow. Finally, some important relationships are missing (e.g., a spectral slope of CDOM (SCDOM) versus $a_{CDOM}(i)$, which provides a useful information about such as photo-bleaching; SCDOM versus a fluorescence component), is not presented. So the effect of photo-bleaching that the authors mentioned in the text reads like speculation without evidence.

We thank the reviewer for the above suggestions and have addressed the concerns through further analysis of the data that include (i) identifying the salinity ranges of the various water masses in the study region (Figure 2a, b; shown at the end of this comment) as described in Mathis et al. 2010 for the same study period in the EBS, (ii) adding density contours on the distribution plots (e.g., Figures 5 and 6) that has better revealed linkages between the water masses and the optical properties, (iii) showing the SCDOM versus ag_{355} relationship (Figure 2c) which revealed patterns associated with the marine (outer shelf and slope waters), intermediate (middle shelf) and terrestrial sourced (inner shelf) CDOM as well as the effects of photobleaching (Stedmon and Markager 2001; Matsuoko et al. 2012; Granskog et al.

2012), and (iv) examining the relationship between Apparent Oxygen Utilization (AOU) and CDOM optical properties such as S_{cdom} (Figure 2d; Table 4). A strong negative relationship between $AOU > 0$ and S_{cdom} ($r^2 = 0.79$) with S decreasing linearly in waters transitioning from the middle shelf, the outer shelf and into the deep slope waters of the EBS suggested the increasing aromaticity and molecular weight structure of CDOM in these waters (Blough and Del Vecchio 2002).

Several specific comments are also provided as below. Taking into account these comments would help for better describing optical properties of CDOM in EBS. After the revision, the paper would be appropriate to a publication in BG.

Specific comments:

-Page L19110 Line 15: $24 \pm 2.25 \mu\text{m}$? Not $24 \pm 2.25 * 10^{-3} \mu\text{m}$?

-Page L19118 Lines 13-15: "Relationships between the CDOM...". This sentence should be in section of discussion rather than in section of results.

This sentence will be modified and moved to the discussion section to reflect the new results of the relationship between salinity and S_{cdom} (inverse relationship, $r^2 = 0.46$) after excluding samples associated with sea ice melt waters (salinity < 31 , surface samples; Fig 2a, b). Also, samples obtained near the islands (St. Paul, Pribilof and Nunivak) tend to contribute to greater scatter in the data.

Lines 16-20: "However, a decreasing...". No these trends can be seen in Figure 2. Where do we see data points corresponding to cold pool waters? Same for warmer waters of the south middle shelf.

This sentence will be removed (the temperature versus a_{g355} plot has been replaced by the a_{g355} versus S_{cdom} plot in the revised Figure 2).

Lines 28-29: "This could be attributed...". Vague expression. Also, this sentence should be placed in the section of Discussion.

This sentence will be modified and moved to the discussion section. We have determined the relationship between salinity and a_{g355} (please see Table 4 in this comment) and observed an inverse correlation for the inner shelf (Table 4; $b = -0.19$, $r^2 = 0.34$) and an inverse weak correlation for the rest of the samples.

-Page L19119 Lines 1-3: "Similarly, the increase...". How can you prove that? It would be better to show relationship between SCDOM and aCDOM(i) to examine the effect of photo-bleaching. In Figure 2d, do $S_{275-295}$ values increase with increasing temperature significantly?

The relationship between a_{g355} and S_{cdom} illustrates the effect of photobleaching (new Figure 2c). The temperature versus S_{cdom} relationship did indeed show an overall positive correlation (slope $b = 0.42$, $r^2 = 0.41$, $n = 216$; Table 4) suggesting that CDOM in warmer waters experienced greater photo-oxidation likely due to increasing insolation as the sea-ice retreated.

Line 6: Shouldn't "Chl fluorescence" be converted into chlorophyll concentrations and shown as log-scale? It could provide a clearer relationship.

Chl fluorescence in Fig. 2e has been re-labeled to chlorophyll concentrations to reflect the units ($\mu\text{g/l}$) in the extracted CTD data (the CTD fluorometer onboard the ship was calibrated during the cruise). Chl is now shown on a log-scale (Fig. 2e).

Lines 7-10: “ag355...”. Do ag355 values increase with increasing DOC significantly in the inner shelf and the UP region? Provide statistical values. Again, which data points correspond to inner shelf and UP in figure 2f??

The relationship between DOC and ag355 were evaluated for the different regions and a weak increasing trend (Table 4) was observed for the inner shelf and the combined regions.

However, there was no relation between the two variables in the UP region.

Inverted triangles correspond to data points of the inner shelf and + symbol to that of the UP region.

Lines 10-13: “In the UP region...”. Low ag355 and high SCDOM in the UP are not clearly shown in Figure 3.

This pattern is better illustrated in the new ag355 versus Scdom plot (Figure 2c) wherein the samples from the UP region show higher Scdom and lower ag355 relative to the other regions.

-Page L19120 Lines 3-5: “Chl fluorescence and DOC...”. I don’t see similar trends between DOC and ag355 in the inner shelf and outer shelf/slope waters in figures 3c and d. Why don’t you examine directly DOC versus chl relationship and provide the related statistical values? Also, the latter half of this sentence is rather discussion.

There was no relationship between DOC and Chl. The sentence will be removed.

Lines 16-19: “Some of the highest...”. SCDOM versus aCDOM(i) relationship would provide a useful information for the effect of photo-bleaching. Again, the latter half of this sentence is rather discussion, not results.

We thank the reviewer for this suggestion. The Scdom versus ag355 relationship does indeed show the photo-bleaching effect on the surface water samples.

-Page L19121 Lines 25-28: “A lens...”. How about the effect of brine rejection during ice formation in winter [e.g., Dittmar, 2004; Matsuoka et al., 2012]?

The high salinity at the northern end of the 70m line during the 2008 summer has been attributed to brine rejection (Stabeno et al. 2012) which also show patterns of more elevated CDOM (Figure 6e) likely due to the effect of brine rejection during ice formation in winter (Dittmar 2004; Granskog et al. 2012; Matsuoka et al. 2012). As to “A lens....”, Stabeno et al. (2012) noted that the freshwater pool just north of 60° latitude (Figure 6b) was the result of ice melt; Figure 6e indicates ice melt waters to have relatively lower levels of CDOM.

-Page L19122 Lines 9-10: “The stratification appeared...”. Please add density contours to Figure 6 and check it.

Thanks for the suggestion. Density contours have been added to Figure 6; the presence of pycnocline observed in Figure 6 now supports the above statement.

Lines 10-15: “With ice covering”. Apparent oxygen utilization (AOU) would be useful to

examine the presence of ice in previous winter. These sentences should be placed in section of Discussion.

We thank the reviewer for suggesting the use of AOU in the analysis; the new data also supports the above statement. In the revised manuscript we have added vertical sections of AOU for the SL and 70m transects (please see Figures 10f and 11f in this comment). AOU was indeed elevated in the higher salinity cold bottom waters along both the SL and 70 m transects suggesting the presence of winter water at depths below the pycnocline. An AOU minimum observed in regions of high chlorophyll concentrations at depths just below the pycnocline was likely due to trapping of the oxygen (Matsuoko et al. 2012). Also, elevated negative AOU values in the inner shelf up to about 40 m depth could be due to the tidal/wind mixing of the cold inner shelf waters; offshore along the SL transect (Figure 10f) elevated negative AOU values were likely due to solar heating of winter mixed water (Matsuoko et al. 2012). The above sentences will be placed in the Discussion section.

Lines 15-19: “Patterns in...”. Why don’t you show Nutrient data?
Nutrient data for the same cruise have been shown and discussed in Mathis et al. 2010 and Goes et al. 2014. We will reference these two papers in the revised manuscript.

Lines 19-27: “DOC concentrations...”. Enhance the ranges of Figures 6d-f to see the patterns more clearly.
As shown in some example property plots (Figure 6 in this comment), the ranges have been enhanced and these new plots will be used in the revised manuscript.

Lines 21-22: “but was elevated...”. I cannot see clear relationship between ag355 and DOC in cold pool is shown in Figure 6. Line 22: “increased biological activity”. Apparently, there is no clear relationship between ag355 and chl fluo even in cold pool.
This statement was based on a visual assessment of the figure and will be removed in the revised manuscript.

Lines 22-24: “However, sections of the transect...”. Not clear.
This statement will be removed in the revised manuscript.

-Page L19124 Lines 7-8: “Fluorescence intensities in the...”. How can we know that?
Some of the stations identified as ice melt water (Figure 2a) appeared to have lower fluorescence (Figure 8); however, since these are not statistically different from the other samples the sentence will be removed.

Lines 8-10: “Inner shelf...”. Not clear.
This sentence will be removed as it was based mainly on a visual assessment of the figure.

-Page L19125 Lines 4-6 and 26-28: Avoid redundancy.
Thanks. The statement will be removed.

Lines 6-10: I’m confused here. Figure 4e suggest that high ag355 values in the inner shelf attributed to river input. If so, the source of CDOM would be of terrestrial origin, not marine source. However, in section 3.2.1, you clearly mentioned that C1 is marine component. C1 is

high in the inner shelf. These results suggest that in the inner shelf, both marine and terrestrial origin of CDOM were high. Please verify that.

Although component C1 has been designated as marine humic-like component resulting from biological activity and/or microbial reworking of plankton-derived DOM, it has also been found to be sourced from land (Murphy et al. 2008) which most likely explains the enhanced levels of C1 in the inner shelf.

-Page L19126 Lines 15-18: “However...”. Examining relationship between SR and ag355 would be useful to check your conclusion.

This is a good suggestion. In comparison to the relationships between Scdom and ag355 as well as AOU, the relationships between Sr and ag355 and AOU are weak indicating that Sr may not be a robust indicator of biological activity in these waters. We will therefore remove Lines 15-18 in the revised manuscript.

-Page L19127 Lines 16-19 & 20-23: According to figures 6 and 12, high chl fluorescence in the cold pool is not clearly correlated with high values in C4.

The statement was made based on visual patterns of Chl fluorescence and C3 & C4 in the outer shelf waters or the “green belt” region (Figures 3c, 4c, 9c, d, and 10c, d) where terrestrial influences or bottom mixing are minimal. In the case of the middle shelf where the cold pool is present, strong tidal mixing in the bottom 40 meters can quickly change the patterns of distribution of the different water properties such as the fluorescence components and Chl.

-Page L19128 Lines 8-10: “In the surface mixed later...”. How did you calculate the averages losses?

Differences between the surface and sub-surface values were calculated then divided by the sub-surface values.

Lines 10-13: “The earlier ice retreat...”. Again, SCDOM versus aCDOM(i) relationship is useful to check the effect of photo-bleaching.

This has been done and supports the statement.

Lines 14- 16: “Although, the protein-like...”. I cannot really see the clear correlation between chl fluorescence and C4 according to figures 6 and 12.

The statement was made based visual assessment of the patterns of distribution and not supported by statistical analysis.

Lines 17-19: Please see my comments on L19128 & lines 10-13 above.

The new Figure 2c showing the relationship between ag355 vs Scdom now supports the statement.

Line 20: “to some extent” is a vague expression. Eliminate this type of words in the text.

Thanks. This expression will be removed in the revised manuscript.

Lines 25-27: Figure 10f shows spatial distribution of SR at mid-depth (28 m). Does solar irradiation influence optical properties at this depth?

The Limitation of the Sr parameter in the study region has been pointed out earlier and Figure 10f will not be included in the revised manuscript (it will be replaced by the AOU distribution shown as Figure 9f in this comment).

Lines 26-29: Please consider the effect of brine rejection regarding σ_{355} values, S275-295, and SR.

The effect of brine rejection appears to be an important factor as also illustrated by the AOU distribution and will be considered in the revised manuscript.

-Page L19130 Lines 14-16: “In contrast, fluorescence...”. Relationship between SR (or S275-295) and each component of fluorescence (especially C4) would be useful.

This has been done (please see Figure new 8d and Table 4 in this comment).

Figure 2: Please add SCDOM versus aCDOM(i) relationship. This relationship is particularly useful to examine the effect of photo-bleaching. Add explanation for abbreviations (i.e., MS, IS, etc).

Thanks. This was an important suggestion and is shown in Figure 2c. The abbreviations have now been explained in the revised figure caption.

Figures 5&6: Add density contours.

Density contours have been added (please see example property distribution plots in Figures 5 & 6 at the end of this comment).

Figure 6d-f: Enhance the ranges.

This has been done. Please see example plots of Figure 6 in this comment.

Figure 8: SCDOM versus a C component might be useful to examine a source of CDOM.

We have added Figure 8d showing the relationship between Scdom versus sum of the humic-like and the C4 protein-like component.

Figures 11&12: Add density contours.

This has been done (please see example plots of new Figures 10f and 11f).

References

- Dittmar, T (2004), Evidence for terrigenous dissolved organic nitrogen in the Arctic deep Sea, *Limnology and Oceanography*, 49, 148–156.
- Matsuoka, A. and A. Bricaud, R. Benner, J. Para, R. Sempere, L. Prieur, S. Belanger, and M. Babin (2012), Tracking the transport of colored dissolved organic matter in Southern Beaufort Sea waters, Canadian Arctic: relationship with hydrographical characteristics, *Biogeosciences*, Vol. 9, doi:10.5194/bg-9-925-2012, 925-940.

Anonymous Referee #2

Received and published: 19 February 2014

We thank the reviewer for the helpful comments and suggestions. Responses to the comments/suggestions are detailed in italics.

The study explores the potential of optical properties as an indicator for dissolved organic matter sources and transformations in the Bering Sea by relating a variety of absorbance and fluorescence based parameters to hydrography and biological indicators. The methods used in this study are appropriate and all necessary corrections have been used in order to acquire comparable results to other studies. In general terms the results of this study are very heterogeneous with few consistent patterns throughout the data set. It must have been a difficult data set to work on, but sometimes that is what we have to work with. From my own experience in working in the Arctic regions it has been very helpful to relate chemical parameters to water masses. I am not sure what information the authors can access, but I would suggest to strengthen the portion of water mass characterization to see if the relationships to the optical properties become more convincing.

The authors appreciate the reviewer's comment regarding the heterogeneous data set which was collected from a large and complex region of the Bering Sea. Based also on comments from reviewer #1 we have strengthened the portion on the water mass characterization by i) identifying various water masses based on salinity (please see Figures 2a and 2b in this comment) and referencing the work of Mathis et al. 2010 who described in detail the hydrography during the same field campaign in the EBS, (ii) plotted the density contours on the two vertical sections showing the various water column properties (please see example plots of new Figures 5 and 6), (iii) examined the CDOM optical properties in relation to the AOU of the study area (e.g., Figures 2d, 10f, 11f, and Table 4 in the revised manuscript), and (iv) examined the slope $S_{275-295}$ versus a_{355} relationship. The above additional information we believe has strengthened the water mass characterization in relation to the optical properties of this study.

The authors mention the cold pool in their study region. Is this cold pool what physical oceanographers call "winter water" produced during the last freezing cycle? If so, I would stick to terminology that is used in this environment.

The cold pool we refer to is indeed the "winter water" produced during the previous winter. Since almost all studies of the eastern Bering Sea (e.g., Stabeno et al. 2012) refer to the "winter water" as the cold pool, we continue using the same terminology in this manuscript. However, we will note in the introduction that the two terminologies are the same.

The study would potentially also benefit from including oxygen concentrations, which should be available from an oceanographic data set like the one in this study.

This is a very good suggestion. As also suggested by reviewer #1, we calculated the AOU from oxygen concentrations and examined its relationship to CDOM optical properties (Figure 2d, Table 4). Relationship between AOU and $S_{275-295}$ for example showed a high negative correlation ($r^2=0.79$) suggesting the greater aromaticity and higher molecular weight of CDOM as the waters transition from the middle shelf, the outer shelf and into the deep slope waters of the eastern Bering Sea. High AOU distribution also corresponded to

elevated salinity especially in the north middle shelf cold bottom waters.

If available, stable oxygen isotope values of water would also be a good indicator for water masses in this region and would be extremely useful to interpret this heterogeneous data set. *The authors are not aware about the availability of the stable oxygen isotope data for this study.*

The other suggestion I would have is to expand on the observed ranges of optical properties published for the high latitude environments. Spectral slope values for example can vary from 12 to 40 in the Arctic environment, unrelated to photo-bleaching of CDOM but with strong relationships to water masses. There have also been other studies in the Arctic including information about Parallel Factor Analysis components of EEMs that could be related to this data set to identify similarities and differences, see work by Granskog et al., and Walker et al. *We have included some additional references as suggested.*

In terms of constraining the sources and transformations of organic matter it might be helpful to look at a property-property plot of S and a_{355nm} , this relationship has produced interesting patterns in other studies in the Arctic and might help with the interpretation of this heterogeneous data set.

The S versus a_{355} plot does indeed reveal three patterns associated with the different water masses (Figure 2c). Although the wavelengths used in the S versus CDOM relationship differed from that used in the model derived by Stedmon and Markager (2001) for distinguishing marine CDOM from terrestrial CDOM, the patterns observed in our study indicate CDOM mainly of marine origin in the outer shelf and slope waters and terrestrial CDOM in the inner shelf (see also Granskog et al. 2012). A third trend is also observed in waters of the middle shelf that suggest these waters to be intermediate between the terrestrial and marine end members.

One interesting observation in this study is that absorbance and fluorescence give you a somewhat different picture, particularly in terms of a potential sediment CDOM source. While the fluorescence components are mostly elevated in the lower water column the absorbance based parameters are not.

New distribution plots of AOU and the density contour further provide additional insights into the water column distribution of CDOM.

My last general comment would be to try to shorten the manuscript, may be fewer figures and a combined results and discussion section to improve the manuscript flow.

In an effort to shorten the manuscript we have removed Figure 11 (fluorescence spatial distribution at mid-depth), and also replaced 4 other figures in the original manuscript with the a_{355} vs S_{cdom} , AOU vs S_{cdom} , and 2 AOU distribution plots. Initially we had also considered combining the Results and Discussion sections, but the use of CDOM absorption and fluorescence data in this study made it more convenient to separate the sections.

Specific comments: Page 19129, line 11: CDOM loss is not a proxy for DOM loss! Fig. 1: Add (UP region) after Unimak Pass

The sentence will be removed. UP region added in the new Figure 1.

New/modified figures:

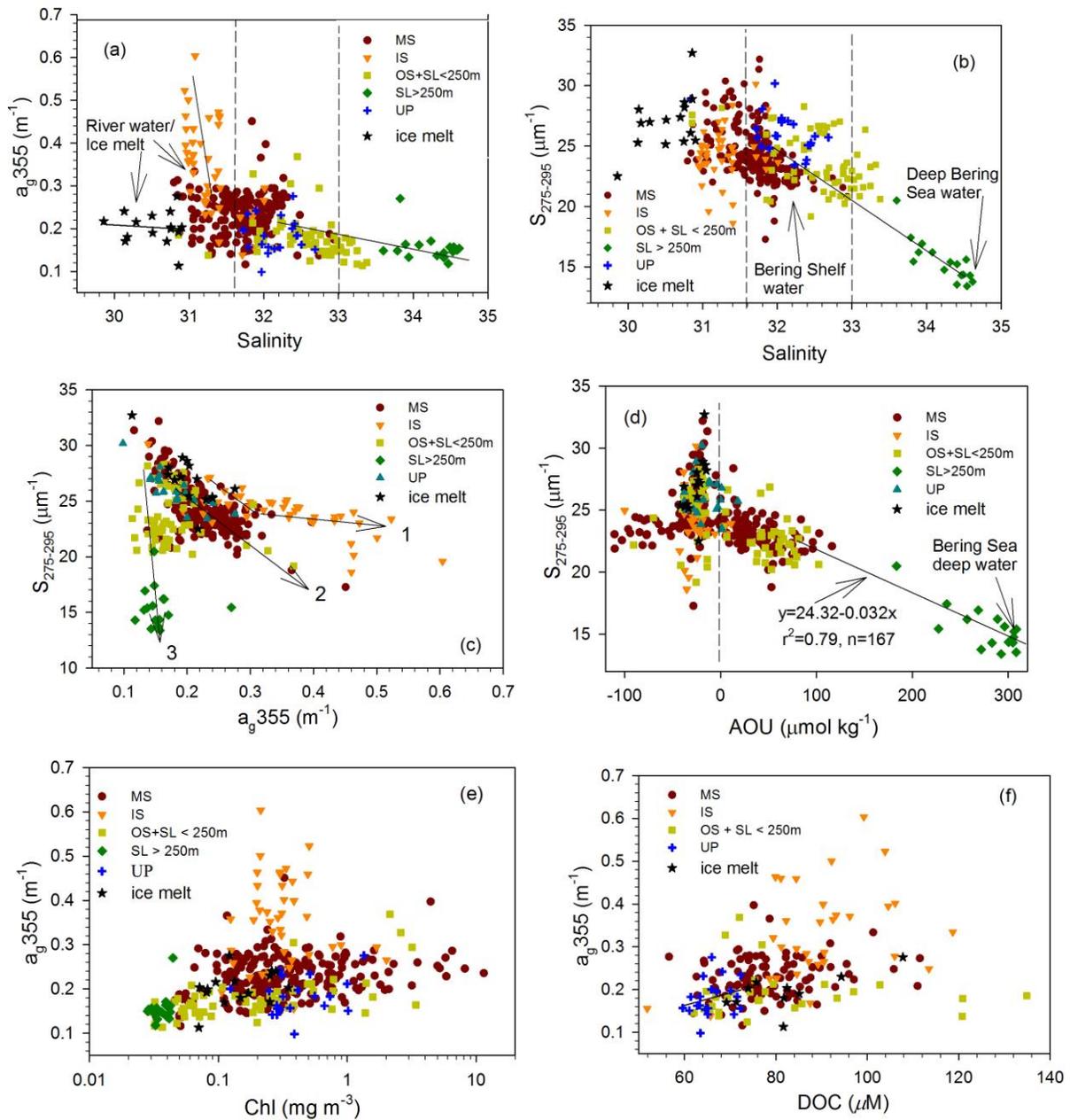


Fig. 2. Relationships between (a) salinity and CDOM absorption coefficients at 355 nm ($a_{g,355}$), (b) salinity and spectral slope (S or $S_{275-295}$), (c) $a_{g,355}$ and S , (d) apparent oxygen utilization (AOU) and S , (e) chlorophyll concentration (Chl) and $a_{g,355}$, and (f) DOC and $a_{g,355}$. The abbreviations MS, IS, OS, SL and UP represent the middle shelf, inner shelf, outer shelf, slope and Unimak Pass regions, respectively.

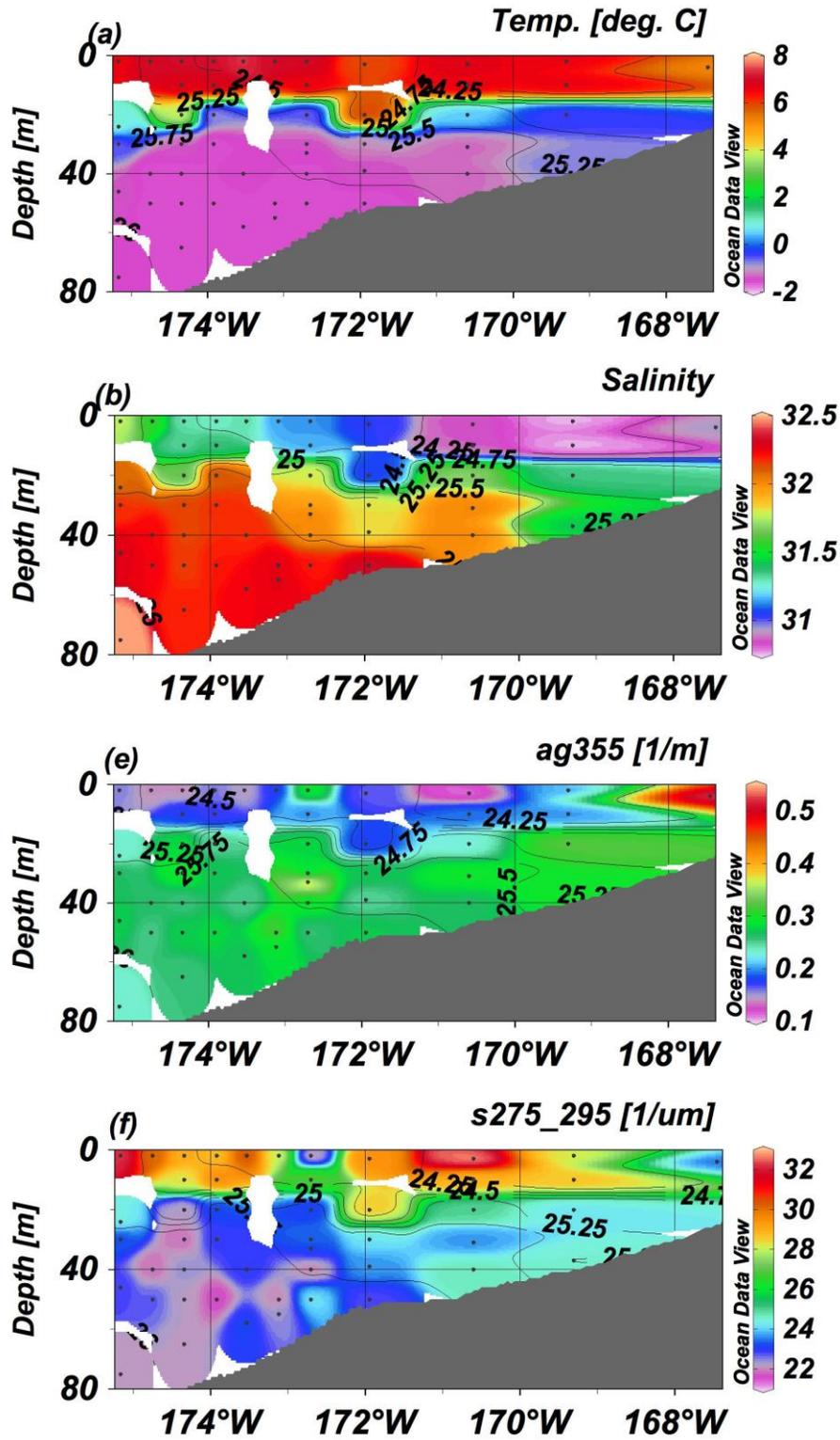


Fig. 5. (selected property distribution plots showing density contours)

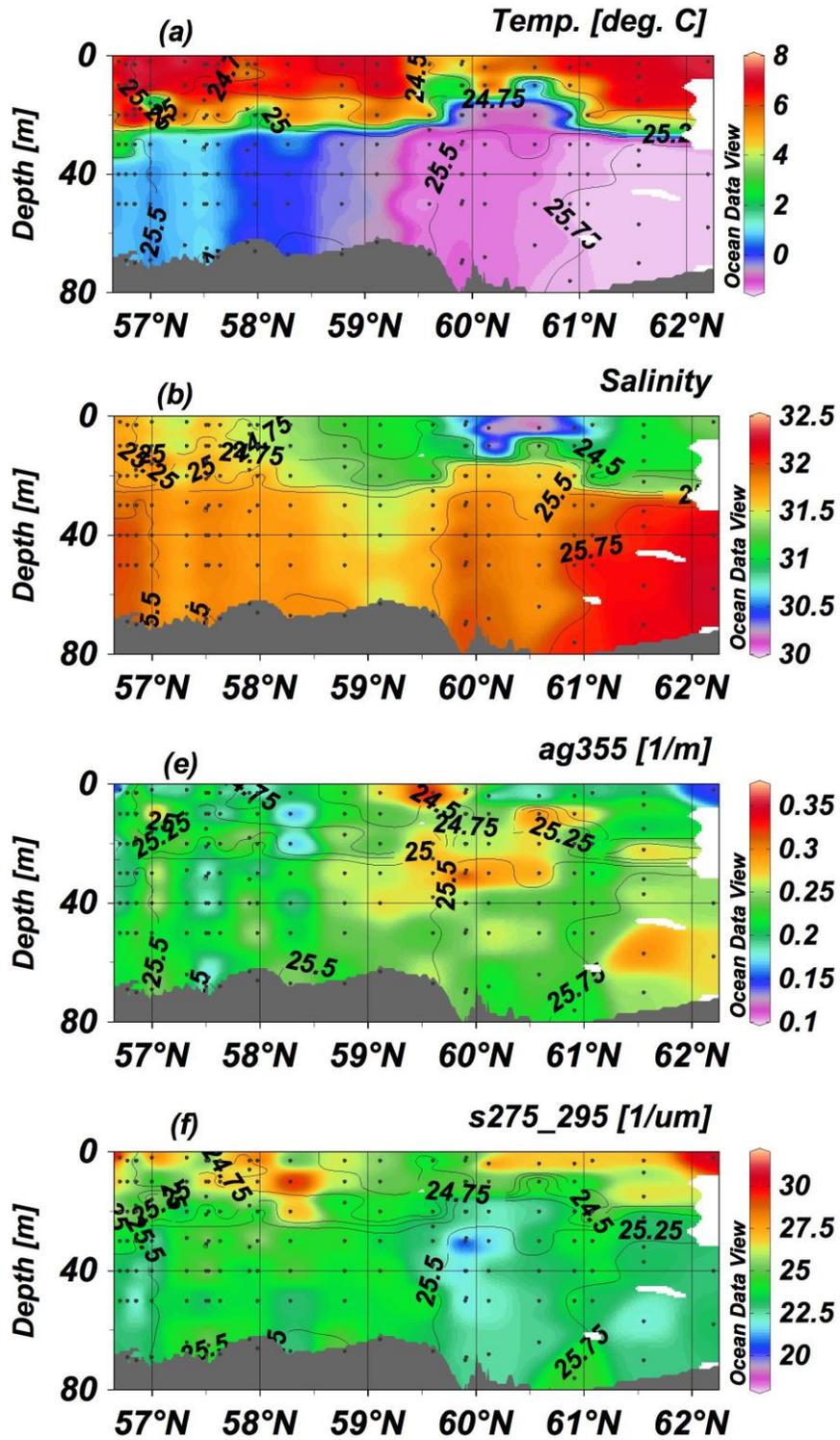


Fig. 6 (selected property distribution plots showing density contours)

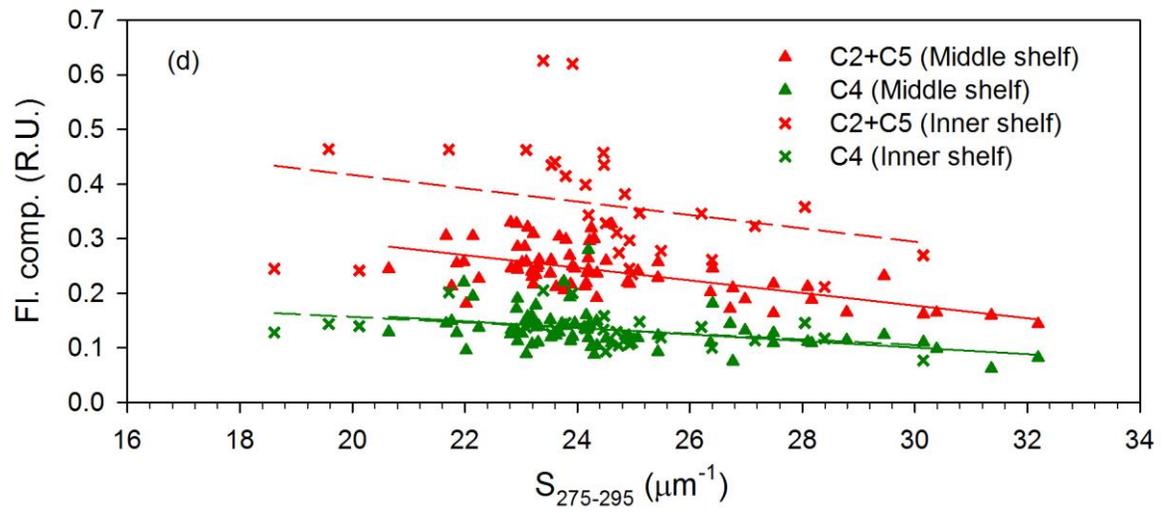


Fig. 8. (d) Slope $S_{275-295}$ versus fluorescent components for the inner and middle shelf stations

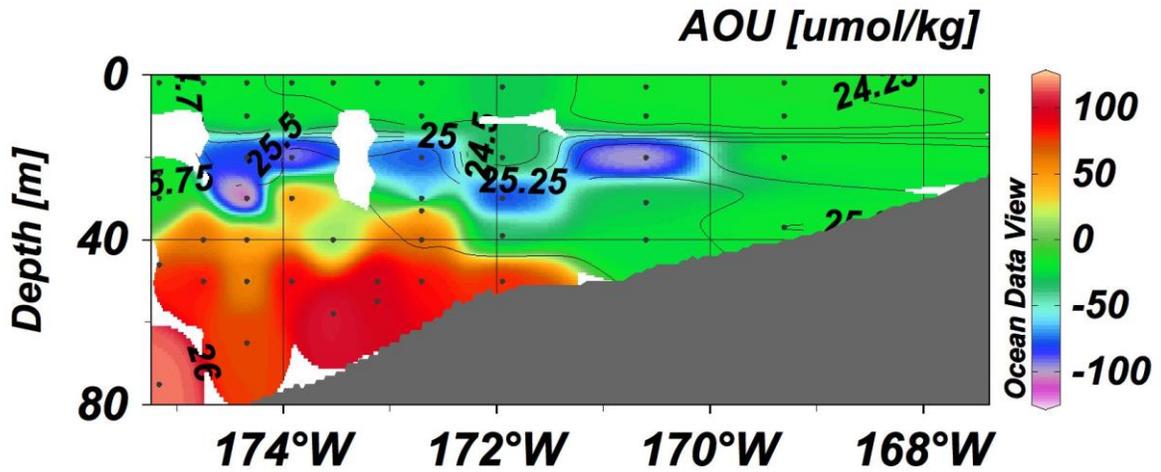


Fig. 10 (f) (distribution plot of AOU along the SL transect in the new Figure 10)

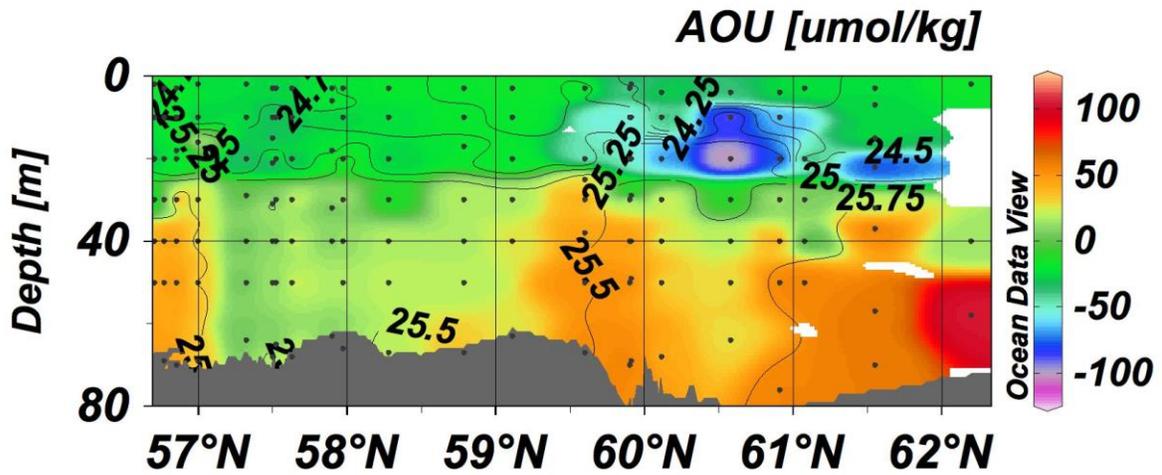


Fig. 11 (f) (distribution plot of AOU along the 70m transect in the new Figure 11)

New table:

Table 4. Relationships between the parameters: Apparent Oxygen Utilization (AOU) for values >0 ($\mu\text{mol kg}^{-1}$); S or $S_{275-295}$ (μm^{-1}); Temp. (temperature) ($^{\circ}\text{C}$); Chl (chlorophyll) (mg m^{-3}); DOC (μm); and fluorescent components C1, C2, C3, C4, C5 (R.U.). b, r^2 , and n correspond to linear regression slope, correlation coefficient, and number of samples, respectively.

Parameters	Inner shelf	Middle shelf	Other/comments
Salinity vs a_{g355}	b= -0.19, $r^2=0.34$ n=44	b= -0.19, $r^2=0.18$ n=216+99	+ os+sl, sl>250m, up
Salinity vs S	no corr.	b= -2.76, $r^2=0.46$ n=216+99	+ os+sl, sl>250m, up
AOU>0 vs S		b=-0.032, $r^2=0.79$ n=167	+ os+sl, sl>250m, up
AOU>0 vs S_r		b=-183.7, $r^2=0.19$ n=167	+ os+sl, sl>250m, up
Temp. vs S		b=0.42, $r^2=0.41$ n=216	
Chl vs a_{g355}	weak, +ve corr.	weak, +corr.	b=0.05, $r^2=0.37$ (OS+SL)
DOC vs a_{g355}	b=0.03, $r^2=0.17$	weak, +corr.	b=0.02, $r^2=0.13$ (all)
S vs C1	b= -0.02, $r^2=0.11$	b= -0.02, $r^2=0.35$	
S vs C2+C5	Weak, -ve corr.	b= -0.01, $r^2=0.38$	
S vs C4	b= -0.05, $r^2=0.16$	b= -0.07, $r^2=0.16$	

Additional references:

Dittmar, T.: Evidence for terrigenous dissolved organic nitrogen in the Arctic deep Sea, *Limnol. Oceanogr.*, 49, 148–156, 2004.

Granskog, M. A., Stedmon C. A., Dodd P. A. , Amon R. M. W., Pavlov, A. K., de Steur, L., and Hansen, E.: Characteristics of colored dissolved organic matter (CDOM) in the Arctic outflow in the Fram Strait: Assessing the changes and fate of terrigenous CDOM in the Arctic Ocean, *J. Geophys. Res.*, 117, C12021, 1-13, 2012.

Mathis, J. T., Cross, J. N., Bates, N. R., Moran, S. B., Lomas, M. W., Mordy, C. W., and Stabeno, P. J.: Seasonal distribution of dissolved inorganic carbon and net community production on the Bering Sea shelf, *Biogeosciences*, 7, 1769-1787, 2010.

Matsuoka, A., Bricaud, A., Benner, R., Para, J., Sempere, R., Prieur, L., Belanger, S., and Babin, M.: Tracking the transport of colored dissolved organic matter in Southern Beaufort Sea waters, Canadian Arctic: relationship with hydrographical characteristics, *Biogeosciences*, 9, 925-940, 2012, doi:10.5194/bg-9-925-2012.

Stedmon, C. A., and Markager, S.: The optics of chromophoric dissolved organic matter (CDOM) in the Greenland Sea: An algorithm for differentiation between marine and terrestrially derived organic matter, *Limnol. Oceanogr.*, 46, 2087-2093, 2001.

Swan, C. M., Siegel, D. A., Nelson, N. B., Carlson, C. A., and Nasir, E.: Biogeochemical and hydrographic controls on chromophoric dissolved organic matter distribution in the Pacific Ocean, *Deep Sea Res. I*, 56, 2175-2192.

Walker, S. A., Amon, R. M. W., Stedmon, S., Duan, S., and Louchouart, P.: The use of PARAFAC modeling to trace terrestrial dissolved organic matter and fingerprint water masses in coastal Canadian Arctic surface waters, *J. Geophys. Res.*, 114, G00F06, 2009, doi: 10.1029/2009JG000990.