

## Reply to anonymous reviewer #2

**General comment:** The manuscript presents the UV/PAR radiations and some DOM properties for the surface samples of a 27-stations cruise at the Beaufort Sea during summer 2009. As the authors state on the manuscript, this area has special interest as it is an important source of organic material to the oceanic circulation, and furthermore, it is mostly sure that this contribution will increase due to climate change. In general, the focus of the manuscript it is appealing, but as the reviewer #1 stated, data set is very limited, data analysis is very superficial and the conclusions are not clear and deficient in new contributions. Also, there are some inconsistencies in the methodology used that I am explaining below. The article should be rewritten, authors should avoid trivial information like some of the figures and tables, and they should do a better data analysis, for example studying the correlations of the residuals for some of the variables with the salinity. In addition, some of the paragraphs of the manuscript are not easy to understand, specially the conclusions which also should not include references

**Reply :** The manuscript was rewritten taking account the reviewer comment's.

The methodology inconsistencies were corrected in the revised manuscript (MS). The figure panel was simplified and reorganized. The structure of the paragraphs in the results and discussion chapter were deeply modified. Trivial information on  $K_d$  values were removed in the revised MS. The paragraph on radiometric data was shortened and rewritten in the revised MS (pages 10-11, lines 241-264). Chapter 3.2.1. (pages 11-15) and 3.2.2. (pages 15-18) were shortened and reorganized. The conclusion chapter was changed for a Summary Chapter.

Please find below the detailed responses to the reviewer #2 comments.

**Comment# 1: "... authors should avoid trivial information like some of the figures and tables"**

**Reply:** We agree with this comment, thus, when justified, the figures were deleted or simplified.

- **The Figures 4, 6 and 10** of the submitted MS were removed

- **The Figure 3** was simplified with only one panel ( $K_d$  at 325 nm) and the legend modified as follows (Figure caption, page 28, revised MS):

*"Diffuse attenuation coefficient of light for  $K_d$  at 325 nm .....Similar pattern was observed for 340 and 380 nm wavelengths and for PAR spectral domain.*

- **Panel C of the Figure 5** of the submitted MS was removed in the revised MS. (Now Figure 4, revised MS)

We believe that such new configuration will provide more appropriate information.

**Comment # 2: Page 15571, line 1: I don't understand the meaning of "and radiation in the Easter sector contamination."**

**Reply:** This sentence results of an error when formatting pdf.

The appropriate sentence (Page 5, line 106 of the revised MS) is:

*"Samples were collected using Niskin bottles equipped with Teflon O-rings and silicon tubes to avoid chemical contamination".*

**Comment # 3: "Do the authors use one use one Polycap AS75 cartridge per sample? They should**

**also add how they cleaned it, even more if they reuse the filter for several samples.”**

**Reply:** Yes we used one cartridge per sample, the cartridge were cleaned with HCl 5 %, rinsed with Milli-Q Water, then washed with 4-5 L of sea water before sampling.

The method paragraph was corrected and changed as follows (pages 5-6, lines 108-124 of the revised MS):

*“For fluorescence determination, samples were directly transferred from the Niskin bottle ..... and flame sealed. During sampling, in situ hydrological context (temperature & salinity vs. depth) was determined with a SeaBird Electronics 911 CTD profiler (Table 1)”*

**Comment # 4: “Why they use a different filtration/filters for DOC and CDOM/FDOM?”**

**Reply:** We used appropriate method for each parameter. For CDOM, samples were filtered using 0.2 µm GHP filters (Acrodisc Inc.), whereas Polycap AS75 (porosity 0.2 µm) that avoid bacteria cell lysis during thawing (Yamashita et al., DSR II, 2010) were used for FDOM determination. Such filters are easy to use and blank tests did not show any contamination. For DOC determination, water samples were filtered by using precombusted (450°C) 0.7 µm Whatman GF/F filters as recommended by JGOFS (Knap, et al., (eds.). 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements. JGOFS Report Nr. 19, vi+170 pp. Reprint of the IOC Manuals and Guides No. 29, UNESCO 1994).

**Comment # 5: “The term SZA is not defined”**

**Reply:** SZA (Solar Zenith Angle) is now defined in the Table 2 in the revised MS.

**Comment # 6 “Chlorophyll a concentration is set to a nominal value of 0.1 µg/L, nevertheless, elsewhere (Fig 3, for example) a value of about 7 µg/L is associated with stn 170. Authors should explain these differences”**

**Reply:** The Chl *a* content were used for the calculation of the Fresnel reflection albedo ( $\alpha$ ) for irradiance from sun and sky. This  $\alpha$  factor allowed us to calculate  $Ed_0^-$  (the downwelling irradiance just beneath the sea surface) and then used to determine  $K_d$  values.

The complete data set of HPLC pigments Chl *a* was not initially available and initial fluorescence data suffered of uncertainties and were closed to 0.1 µg l<sup>-1</sup>. This explained that the chlorophyll content was initially set to 0.1 µg l<sup>-1</sup> for all stations in the submitted version. HPLC pigments (unpublished data) are now available and were now used in the revised version of the MS. It is important to note that the results changed only slightly: For instance, for the station ‘170’ (highest Chl *a* content of the radiometric stations)  $\alpha$  was found to be 0.064 (Figure S1) when calculated with the previous Chl *a* concentration of 0.1 µg l<sup>-1</sup> whereas  $\alpha$  was found to be 0.059 for Chl *a* concentration of 1.72 µg l<sup>-1</sup> (Figure S2).

$\alpha$  factor is also used for  $Ed_0^-$  calculation ( $Ed_0^- = Es/(1+\alpha)$ ). The  $Es$  measured at 325 nm at this station was 10.41 µWm<sup>-2</sup>, thus  $Ed_0^- = 9.78$  µWm<sup>-2</sup> (for Chlorophyll concentration of 0.1 µg/l) and 9.83 µWm<sup>-2</sup> (for chlorophyll concentration of 1,72 µg/l) which is only 0. 3% lower. Thus this difference doesn’t induce significant change in the  $K_d$  calculation (< 0.1 % lower than difference between duplicate profiles i.e. 3%). However, to avoid any misunderstanding and be more accurate the text was modified accordingly as follows:

*“ where  $\alpha$  is the Fresnel reflection albedo for irradiance from sun and sky determined using a ‘look up table’ (Jin et al., 2004; <http://snowdog.larc.nasa.gov/jin/getocnlut.html>) based on the validated Coupled Ocean-Atmosphere Radiative Transfer (COART) model. Because...”*



Figure S1. Result for the calculation of the Fresnel reflection albedo ( $\alpha$ ) for irradiance from sun and sky using the “look up table” by Jin et al. (2004) for Station 170 with Chl *a* concentration set at 0.1  $\mu\text{g l}^{-1}$  at wavelength 325 nm

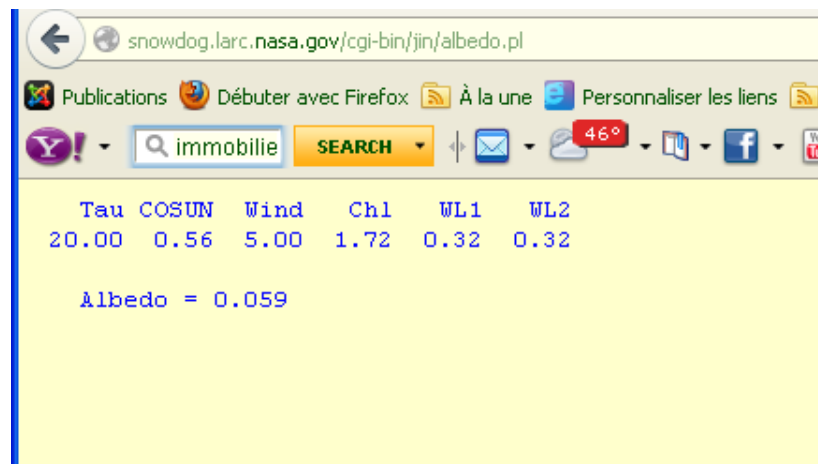


Figure S2. Result for the calculation of the Fresnel reflection albedo ( $\alpha$ ) for irradiance from sun and sky using the “look up table” by Jin et al. (2004) for Station 170 with Chl *a* concentration set set at 1.72  $\mu\text{g l}^{-1}$  at wavelength 325 nm.

**Comment #7: “Authors should explain the calibration of the TOC analyzer”**

**Reply:** the following sentence was added in the revised MS (pages 7-8, lines 169-183, revised MS)

*“Calibration of the instrument was performed daily ..... The average DOC concentrations in the DAW and in the LCW reference standards were  $45 \pm 2 \mu\text{M C}$  ( $n = 24$ ) and  $1 \pm 0.3 \mu\text{M C}$  ( $n = 24$ ), respectively. Carbon levels in the LCW ampoules were similar to and often higher than the Milli-Q water produced in our laboratory. The nominal analytical precision for the procedure was 2% or less.”*

**Comment # 8: Regarding the CDOM, I miss the data from 250-350 nm, that is an important part of the absorbance spectra, which also would permit to calculate ratios and compare them with previous articles**

**Reply:** During MALINA cruise, our CDOM measurements were done mainly in terms of ocean color application. A 2m optical pathlength using an UltraPath was used to obtain accurate measurements of CDOM absorption for both oceanic and coastal waters in the spectral domain ranging from 350 to 700

nm. Below 350 nm, we often observed the light saturation of a sample especially for coastal waters when using a 2m optical path length. Thus, UV spectrums were not used in this study.

**Comment #9: FDOM should be measured within the first 24 hours after sampling. After that time the sample loses the entire protein-like signature (very labile material). The measurements made by the authors, 3 months later, can be used to study the humics acids dynamics, but not protein-like compounds, i.e. peak T or component C3 in this study. Authors have to state this fact on the manuscript.**

**Reply:** We agree with this comment. We initially forgot to indicate in the Materials and Methods paragraph that the samples were filtered at 0.2  $\mu\text{m}$  then stored frozen until analyze. We did not consider possible to keep the sample at "room" temperature during all the time until their reception in the laboratory and their analysis. Yamashita et al. DSR (2010) consider that 0.2  $\mu\text{m}$  filtration should prevent lost of fluorescence properties during freezing-thawing of the samples: "it is likely....some of the changes in fluorescence upon freezing may be attributed to rupture of microbial cells or particulate origin, which would not be expected in our study where 0.22  $\mu\text{m}$  filters were used for sample preparation". Thus, the Materials and Methods paragraph in the revised MS (pages 5-6, lines 108-124 of the revised MS) was modified accordingly (see comment # 3).

**Comment # 10: In addition, I am not sure that 54 EEMs are enough to do the PARAFAC, authors should prove if the results of this methodology are significant with this number of samples**

**Reply:** EEM's higher number would be certainly better for PARAFAC modeling and the interpretation of results. However, our experience indicated that 50 samples give reliable results, this was also indicated by Stedmon & Bro (Limnol. Oceanogr.: Methods 6, 2008, 572–579) stating that "When dealing with complex mixtures such as DOM, where both the number and characteristics of the underlying fluorescent signals are unknown, it is generally preferable to model datasets with 20-100 samples" and "In our experience with DOM fluorescence, best results are often obtained with datasets spanning a gradient (e.g., mixing) or following a process (e.g., production or removal), depending on the focus of the study".

**Comment # 11: Results and discussion: DOM characteristics: Authors observed how DOC and  $a_{\text{CDOM}}$  correlates with S (also observed previous works), they should calculate the residuals of these correlations and compare them to study the processes involving DOC and CDOM independently of the salt gradient, this new correlation would conduct to new insight**

**Reply :** We calculated residuals from the different linear regressions observed within our data and the following paragraph was added in the revised MS (pages 13-14 lines 315-322)

*"DOC or  $a_{\text{CDOM}}(350)$  residuals calculated as the vertical distance to the regression line represent non-conservative variations in DOC or  $a_{\text{CDOM}}(350)$  with higher values implying production of DOC..... residuals correspond, except at station 696, to the lowest chlorophyll values (data not shown)."*

**Comment # 12. Page 15579, line 13: It is not clear to me how you relate this bibliography to the previous result.**

**Reply:** We agree with this comment, thus we deleted the following sentence in the revised MS :"*Previous study showed comparable discharge for particulate and dissolved organic carbon on an annual basis (Macdonald et al., 1998; Dittmar and Kattner, 2003).*"

**Comment # 13. “Third plot of Figure 10 is not consistent with protein-like dynamics. In addition the fluorescence characteristics of this C3 component (Figure 8) are not similar to the ones of the protein-like substances.”**

**Reply:** The C3 component exhibited a homogeneous distribution along the Mackenzie and Beaufort Sea surface waters without any clear trend. Moreover its fluorescence range is relatively narrow compared with the C1 and C2 components. This distribution is coherent with a low productive area (depletion in nitrates, turbid waters). Coble (1996), Yamashita and Tanoue (Mar. Chem., 2003) and Jørgensen et al., (Mar. Chem., 2011) attributed this fluorophore to Amino acids.

The Figure 10 was removed in the revised MS

**Comment # 14: I am not sure to understand the dynamics of C1 and C2 components as described in the manuscript. Looking at the results it seems that the allochthonous material (C2 component) is degraded very fast along the delta, this process generates a different kind of autochthonous compounds (C1 component) which is present in all oceanic waters of the study. The last long line of this section is not clear to me.**

**Reply :** This paragraph was rewrite in order to clarify the C1 and C2 dynamics (pages 17-18, lines 398-411, revised MS) “*There were significant .....C1 and C2 did not match Chlorophyll-a content or primary production*”

**Comment# 15. “in situ DOM production coupled with a limited DOM photodegradation process” this sentence is not discussed along the text, and it is stated in the conclusions.**

**Reply:** We agree with this comment, thus the following sentence was added in the revised MS (page, 14 lines 327-329) “*The low light availability during summer 2009 probably prevented CDOM photobleaching and thus allow  $a_{CDOM}(350)$  as acceptable proxy for DOC for the saltiest waters.*”

**Comment #16: Figures: Figure 5, plot A. At least one DOC concentration (stn 118) has a different value from the one listed in Table 1. Authors should revise all the values**

**Reply:** Indeed the right value in table 1 is 188  $\mu\text{M}$ , this type mistake was corrected in the revised MS. The values in Table 1 and 2 were checked. This was not wrong in the figure.

**Comment #17.** Figure 9. A, B, C and D labels are not corresponding with the figure caption.

**Reply :** The Figure legend was corrected in the revised MS

**Comment #18. Conclusions: They are not clear, they lack of new insights, and they contain references as they were part of the results and discussion.**

We believe that we provide interesting information related to UV/PAR radiations, DOC, and CDOM in the Beaufort Sea and in the Mackenzie Estuary. The conclusion in the submitted version was more a summary than a real conclusion. Such paragraph was rewritten and indicated as a summary in the revised version of the MS (pages18-19, lines 441-453).

**The authors acknowledge the anonymous reviewer for the constructive comments on the manuscript.**