Reply to reviewer 2

Reviewer's comments are **bolded** and authors' responses are *italicized*.

General comments: I have several overarching comments related to this paper. First, the authors often compare their results to previous studies of photoammonification from other regions (the Baltic Sea). While it is always useful to make comparisons to other studies, I find that the authors do not sufficiently acknowledge the uncertainty in their, and previous, photoammonification estimates when making their comparisons. Relatively broad statements are made about the large difference between this study and previous, without much note of the fact that the large error bounds on many photoam- monification estimates make these differences much smaller than the authors state. I have provided detailed comments related to this below. In addition, a clear statement of what types of error bounds are being presented (I assume standard deviations are being provided, but this is not always explicitly stated), and whether the error bounds being used are more appropriate than – for example – 95% confidence intervals, is warranted.

In the new version, we added a more detailed uncertainty estimate of our own data and acknowledged the uncertainty and variability in previous studies (see our response to a similar comment raised by reviewer 1).

Second, I find many of the figures and tables a bit difficult to follow, and have provided more detailed comments and suggestions related to this below.

See responses to the relevant specific comments.

Third, the authors present some very interesting data about the stoichiometry of photodegradation, based on rates of NH4 photoproduction (this study) versus CO and CO2 photoproduction. The CO and CO2 data appear to come from other studies that are in preparation, and therefore no methods have been presented, or are available by reference, for this work. Thus, it is not possible to assess the techniques used to measure CO and CO2 photoproduction. This is of potential concern to me, given the additional difficulty related to measuring gas production. This component of the paper is certainly very useful, and the findings are both novel and broadly applicable. I would suggest adding the CO and CO2 methods to a supplemental section. If this is not possible because the authors wish to keep this information for later publications, then perhaps the stoichiometry should be published at a later date. This would be unfortunate, but the methodology of this component of the work should be made available at the time of publication.

The reviewer is right that we should provide methodological information on CO and CO2 photoproduction either by reference or publishing it in the present paper. These methods actually have been published in detail several times by our team (e.g. Belanger et al., 2006; Zhang et al., 2006; Xie et al., 2009). Sorry for the omission of this point. In the new version, we referred the reader to these papers for CO and CO2 methodologies.

Fourth, a brief (1-2 sentence) discussion of the fact that the patterns that the authors observe are relatively consistent across a fairly broad expanse of the Beaufort Sea would be worthwhile. This is certainly an important aspect of the paper that was not explicitly discussed. At the same time, a brief caveat to readers that the rates presented in this paper are unlikely to apply to other coastal areas of the Arctic Ocean is also

A brief discussion of these two aspects following the reviewer's suggestions has been added to section 3.3 (for the pattern) and 3.4 (for the rates).

Finally, there are several typos in the manuscript, which would benefit from a re-read for spelling and grammar.

We proofread the entire paper and made appropriate corrections.

Specific comments: Page Line Comment
4442 29 "would". This is strong wording, given that what is being presented is a modeled result.

Replaced with "could".

4444 11-12 Do you have a reference for permafrost thaw increasing DOM delivery to the ocean? Although this appears to occur in Siberian rivers, studies from western North America suggest that deepening active layers may decrease DOC concentrations in streams and rivers. See for example Striegl et al. 2005 GRL, doi: 10.1029/2005GL024413

Thanks for providing the new reference. Obviously, Striegl et al's results contradict common presumptions, on which our statement is based. We now rephrased the statement by leaving out DOM:

"Rising temperatures lead to sea ice decline, allowing more solar radiation available for DOM photooxidation in the water column."

4444 14-18 See also comments elsewhere about discussions of uncertainty. This paper also discusses a wide range of uncertainty in their estimates, rather than a single point estimate.

Authors of this paper reported a single rate and a range across an order of magnitude (without giving specific rates). We suppose the reported rate is their best estimate based on their reasoning of choosing the specific AQY spectrum. The large range is now acknowledged in the new version.

4446 12-13 "Irradiation lasted from 4-7 d". This statement would be much more useful if it was presented as the total amount of radiation that an unfiltered sample would have received, or if the lamp output was stated so that the reader could do the calculation. It would also be useful to compare how the unfiltered radiation compares to typical Arctic values. For example: is 4 days of lamp output equivalent to 1 day of sunlight at Arctic solstice? 30 days?

Note that these irradiations were not intended to simulate the solar radiation condition over the Arctic Ocean. They were designed to derive the AQY by incrementally removing UV radiation incident on the samples. Therefore, each sample received different spectral radiation. The lamp output under the WG280 filter (least filtered radiation) (706.3 W m^{-2}, 280-800 nm) is reported in the new version.

4449 12-14 +/- 1.8 is the standard deviation for these samples? In this case, a 95% confidence interval would be more useful.

Yes, it is the standard deviation. Now changed to 95% confidence level, i.e. +/- 2 s.d.

4449 19 "mid channel off Inuvik". If I understand where you have taken your samples, stating this as "East Channel of the Mackenzie Delta, near Inuvik" would be more correct – there is also a "Middle Channel" that is in the middle of the delta. Also, upstream of the town of Inuvik?

Thanks. Now changed to "…from the east channel of the Mackenzie Delta slightly upstream of Inuvik…"

4449 20 Do you think that your late summer samples would react differently to irradiation than this freshet sample?

The linear relationship between the photoammonification rate and a_{cdom} for all the samples tested (see Fig. 2 in reply to reviewer 1 and Fig. 5A in the new version, now containing the data point from the freshet sample) suggested that all samples reacted similarly to irradiation with respect to photoammonification.

4450 3-8 See comments elsewhere about the organization of figures and tables. I would find Table 1 much easier to interpret if it was presented in the same order as given here (ie, transect 690, transect 390, offshore stations). Adding an additional column as the first column which gives the transect number or states 'offshore' would also help with the accessibility of the data in this table.

Table 1 was revised according to reviewer's suggestion.

4450 14-17 "CDOM removal at the onset of estuarine mixing" causing the lowest salin- ity sample to have lower than expected absorbance. Could you explain your reasoning here? It's unclear to me why CDOM removal at the onset of mixing would not be seen throughout the mixing curve. Also, are you assuming that molar absorptivity is constant, and that this is actually a DOM removal effect? If so, is an assumption of constant molar absorptivity valid? Or, does this statement imply unexpected changes in absorbance characteristics per unit of DOM/DOC?

Shortly after the submission of this manuscript, we realized that the mixing plot, which curves upward between Sta. 697 and Sta. 694, suggests that there was input (not removal) of CDOM somewhere between these two stations. This is a simple CDOM mixing plot: a convex-like shape

(curved upward) suggests input while a concave-like shape (curved downward) suggests removal of CDOM. No assumption of constant molar absorptivity is implicated. We now revised this part in the new version as follows:

"However, $a_{cdom,412}$ at the innermost Sta. 697 was 20% lower (1.98 m^{-1} vs. 2.38 m^{-1}) than expected from the linear fit for the outer section of transect 690, suggesting CDOM input slightly downstream of Sta. 697. The process responsible for this input was unclear but could be linked to episodic sediment resuspensions due to shallow water depths there."

4451 17-18 Conservative behavior of Sr and photobleaching. Please also explain this statement further. Could photobleaching not also vary predictably across the salinity gradient, as a result of the length of time that riverine DOM has been exposed to sun- light in the ocean? Given that you show measureable photoammonification, it seems likely that some change in Sr related to photobleaching could be occurring.

The largely undetectable photobleaching in the study area was due primarily to a combination of high CDOM abundance, competition for light absorption by high loads of particles and vertical mixing in the study area. These three factors greatly reduce the exposure of an average CDOM molecule to solar radiation. However, even if the solar radiation received by an average CDOM molecule is not enough to produce measurable photobleaching, the ammonium photoproduction contributed by numerous such CDOM molecules in the mixed layer could still be significant in the euphotic zone. We agree that photobleaching must be occurring in situ but not to the extent that can be clearly ascertained from the CDOM and S_R mixing plots. We now re-worded this statement as follows:

"The largely conservative behaviors of S_R (Fig. 3B) and a_{cdom} (Fig. 3A), however, suggested that photoleaching should not be the dominant factor controlling S_R in the study area. The lack of substantial photobleaching observed in the present study is consistent with the conclusion of a previous photobleaching modeling study for the Mackenzie Shelf area (Osburn et al. 2009).

4452 15 "Group 2 stations". This terminology is seen throughout the remainder of the manuscript, but has not been introduced. You are talking about the two different transects?

Group 1 and Group 2 stations are defined on page 4451, line 12-15 (old version).

4452 18-22 See detailed comments about discussions of uncertainty. Previous studies acknowledge wide ranges of uncertainty in their estimates. Given this, comparing means is likely not the best way to compare across different estimates. Comparing the upper bound of your estimate to the lower bound of the estimate from other studies, for example, results in a much smaller difference. Also, please provide units, and state what the error bounds represent. Standard deviation?

We now included a comparison of our upper bound with the lower bounds of other studies in the new version. Units and meaning of error bounds have been added.

4453 5-10 Could the Baltic also have more photosensitive DON? It is certainly much more strongly impacted by agriculture and human settlement than the water flowing into the Beaufort.

This is certainly a possibility. Now added in the new version as follows:

"Our lower AQY values, particularly in the most photochemically active UV wavelengths, may indicate a lower photoreactivity of DON in our sample area, reflecting the fact that the water discharged into the Baltic Sea is much more strongly impacted by human activity (e.g. agriculture) than the water flowing into the Beaufort Sea."

4454 19-20 Perhaps clarify this statement to indicate that this pattern is not necessarily a causative one – it's not acdom per se that is driving high photoammonification; rather, likely differences in molecular structure. Is this relationship better / more informative with Sr than with acdom?

Reviewer's opinion is certainly right. That's why we related acdom to the origin of CDOM (terrestrial vs. marine) when we discussed this pattern (p4454, line 18-20 in old version). This is now more explicitly expressed as:

"It should be noted that the $\Phi_{NH_4^+}$ patterns identified here do not necessarily imply a causative relationship between the two parameters. $\Phi_{NH_4^+}$ is more likely controlled by the chemical characteristics of CDOM than by CDOM abundance. "

The relationship between $\Phi_{NH_4^+}$ and SR is not as good as that of $\Phi_{NH_4^+}$ vs. acdom (see Fig 1.) below. However, it is obvious that lower $\Phi_{NH_4^+}$ values correspond to lower SR values (Group 1 stations) and higher $\Phi_{NH_4^+}$ values to higher SR values (Group 2 stations). This is already discussed in section 3.6.

An important advantage of establishing $\Phi_{NH_4^+}$ and acdom relationships is that such relationships allow us to evaluate NH4 production rates from satellite-derived ocean color data, as we have done in this paper.

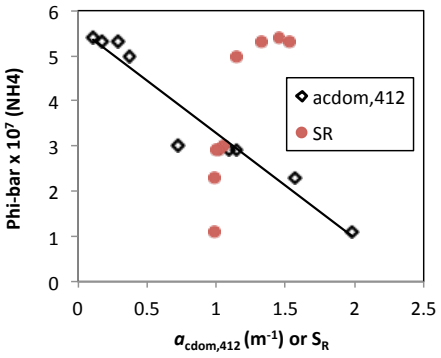

Fig. 1. Plots of phi-bar (NH4) (defined by eq. 5 in section 3.6 in the manuscript) and acdom,412 and S_R.

4456 26-27 "riverine CDOM more extensively spread over the shelf in August . . .". Is this directly from SeaWIFS data? This is an interesting result – could you provide some more explanation of why this occurs? Is the freshet water held close to shore by ice in June?

Yes this is from satellite observations and interpretation. In June, CDOM is blocked by ice. After the breakup, the plume extends offshore. In August CDOM is dominant over the shelf.

Now explained in the new version as:

"The maximum $P_{NH_4^+,0}$ *on the shelf, however, occurred in August (8.3 nmol* L^{-1} d^{-1}*), two months later than the maximum* $P_{NH_4^+,col}$*, due to the much higher* a_{cdom} *in August as compared to June (*$a_{cdom,412}$*: 0.57* m^{-1} *vs. 0.21* m^{-1}*). This pattern could be attributed to the characteristic CDOM dynamics occurring on the Mackenzie Shelf revealed by satellite-derived ocean color data (Bélanger et al., 2006). CDOM from freshwater runoff is held close to the shore by sea ice in spring and extends offshore after sea ice breakup in early summer. Consequently, riverine CDOM is more extensively spread over the shelf in August, about two to three months after the peak discharge of the Mackenzie River, resulting in a larger amount of photochemically active solar energy being absorbed near the sea surface."*

4457 14-27 Please provide the confidence intervals for your estimates, and state what type of interval you are providing for previous studies (standard deviation? 95% confidence interval?). Again, I find it somewhat misleading that you compare means between studies, given the very wide confidence bounds. Given the uncertainty presented, previous estimates are not really 26 and 5 times greater than yours.

Revised according to reviewer's suggestions. See reply above to a similar general comment.

4457-58 27-4 This study also discusses the fact that there is a wide range of uncertainty in their estimates.

The range of uncertainty in this publication is now acknowledged. See reply above to the same general comment.

Section 3.6 See also detailed comments. The studies of Song and Taalba are both unpublished, which makes it difficult to assess these results. Please provide the method ology for CO and CO2 measurements – perhaps as an appendix?

See reply above to the same general comment.

Tables 1, 2, 4 See comments above. I would find these data much more accessible if the stations were ordered as they are initially presented in the text, and an additional column was used to specify either offshore station, or the transect that the station was derived from.
Figure 1 The addition of some sort of indication of the extent of the Mackenzie Delta would be useful. Many readers will be confused as to where the potential river outflows are, given your current map.
Figure 3 I would find Figure 3b much easier to read if it were presented as 2 panels.

Figure 5 These figures are a bit hard to follow, and are not best presented as line plots. A series of scatterplots with NH4 on the x axis and acdom/DON/TDAA on the y axis would convey these data much more clearly; different symbols for the different sample locations (similar to Fig. 3) could be used to provide more information. I would also find a plot of salinity vs NH4 photoproduction to be a useful addition to this series of figures. I realize that you are trying to convey very specific information by including the station numbers, but I just find myself flipping between this figure and Table 1 to try to figure out where all your stations lie.
Figure 8 Similar to Fig 5, I find this hard to interpret, and these data are not best presented as a line figure. A scatterplot of NH4 production (y axis) vs DON:DOC would be much more useful. Using different symbols and/or addition information on salinity vs DOC:DON would aid in understanding sample location.
Fig. 10 Superimposing DOC:DON vs acodm on this figure might tell a nice story rela- tive to your written discussion of this effect.

Figures and tables were revised according to reviewer's suggestions.

References

Osburn, C. L., Retamal, L., and Vincent, W. F.: Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea, Mar. Chem., 115, 10-20, 2009.

Bélanger, S.: Response of light-related carbon fluxes in the Arctic Ocean to climate change: Quantification and monitoring of dissolved organic matter photo-oxidation in the Beaufort Sea using satellite remote sensing. Ph.D. thesis, Université Pierre et Marie Curie (UPMC– Paris XI), Paris, France, 2006.

P.S. In the original version, we forgot to acknowledge Max Holmes for help with collecting the spring sample from Mackenzie River near Inuvik. This is now added to the acknowledgments.