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Interactive comment on “Photoproduction of ammonium in the Southeastern Beaufort Sea and its biogeochemical implications” by H. Xie et al.

Anonymous Referee #2

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This paper provides a new estimate of the photodecomposition of DOM to ammonium in the Arctic Ocean. Given that global warming will significantly affect both the composition of DOM in the Arctic Ocean, and the exposure of oceanic waters to solar irradiation, this paper is both timely and provides useful information. However, I do have several general and specific comments that should be addressed and / or considered before the paper is published.

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. Rela-

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tively 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 photoammonification 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.

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.

Third, the authors present some very interesting data about the stoichiometry of photodegradation, based on rates of NH_4 photoproduction (this study) versus CO and CO_2 photoproduction. The CO and CO_2 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 CO_2 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 CO_2 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.

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

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warranted. The large Siberian rivers have a chemistry that is quite different from the Mackenzie; I would expect that photoammonification rates could be quite different in the Siberian nearshore.

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

Specific comments:

Page Line Comment

4442 29 “would”. This is strong wording, given that what is being presented is a modeled result.

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

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.

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?

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

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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?

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

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.

4450 14-17 “CDOM removal at the onset of estuarine mixing” causing the lowest salinity 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?

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 sunlight in the ocean? Given that you show measureable photoammonification, it seems likely that some change in Sr related to photobleaching could be occurring.

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?

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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?

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.

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*?

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?

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 mis-leading 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.

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

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-

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ology for CO and CO₂ measurements – perhaps as an appendix?

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 relative to your written discussion of this effect.

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