

Reply to reviewer 1

As the reviewer's three general comments are also included in the specific comments, we here only make responses to the specific comments (but mentioned which specific comment also belongs to a general comment)

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

**p. 4443, lines 9-11: I suggest rewording this a little - the words "controversial" and "conflicting" connote a field of study overwhelmed by human error, and underemphasize the real environmental variability of this process.**

*Now changed to "The extent and ecological relevance of  $\text{NH}_4^+$  photoproduction (i.e. photoammonification) are, nonetheless, not well constrained because of the large variability of results obtained by different laboratories and from different samples."*

**p. 4445, lines 20-24 and p. 4446, lines 4-6: How do you know that storage and the refiltration step didn't affect DIN, DON, DIC, or aCDOM? You specifically state that DIN and DON were measured on fresh samples (so months before the AQY determinations), and it's not clear when the other measurements were made. In particular it is important to provide evidence that storage/refiltration didn't affect your observed patterns along the inshore-to-offshore transition (one of the three general comments)**

*All parameters reported in our study were measured on stored samples except salinity, temperature, and DIN. We followed well-accepted collection and storage protocols for DOC, TDN (DON = TDN - DIN), and TDAA (Davis and Benner 2005). The collection and storage methods for DOC, TDN and TDAA are now added in the methods section: "Samples for dissolved organic carbon (DOC), total dissolved nitrogen (TDN) and total dissolved amino acids (TDAA) were gravity-filtered (Whatman GF/F filters) directly from Niskin bottles into clean Nalgene HDPE bottles (60 mL) and stored frozen until analysis in the home laboratory (Davis and Benner 2005)."*

*Because of technical and/or time restrictions (in our case, the shipboard irradiation system was used for measuring CO photoproduction), marine photochemical studies, particularly those for determining AQYs, often rely on stored samples (a few weeks to 12 months in published studies) combined with re-filtration prior to irradiation (e.g. Johannessen and Miller, 2001; Toole et al., 2003; Bouillon and Miller, 2005; Osburn et al., 2009; White et al., 2010; Stubbins et al., 2011). The direct effect of storage/re-filtration on the specific photoprocess in question is hard to evaluate due to the lack of analysis of the initial samples freshly collected shipboard. Instead, such effects are usually assessed by monitoring  $a_{\text{cdom}}$  during the storage period. Several studies have confirmed that the storage/re-filtration method does not significantly affect  $a_{\text{cdom}}$  for up to 12 months (e.g. Johannessen and Miller, 2001; White et al., 2010). In our study, we monitored temporal variation in  $a_{\text{cdom}}$  over a storage period of 34 months (see an example in Fig. 1 below) and found  $a_{\text{cdom}}$  decreased by 8% averaged from 250 to 500 nm. Our photochemical studies were conducted within 2 months of sample collection, which gives an essentially negligible 0.5% decrease in  $a_{\text{cdom}}$ , assuming that the  $a_{\text{cdom}}$  decay followed first-order kinetics. As the photoammonification rate was linearly correlated*

with the initial  $a_{cdom}$  (Fig. 2 below; Fig. 5A in the new version), we expect that the sample storage effect should be minimal.

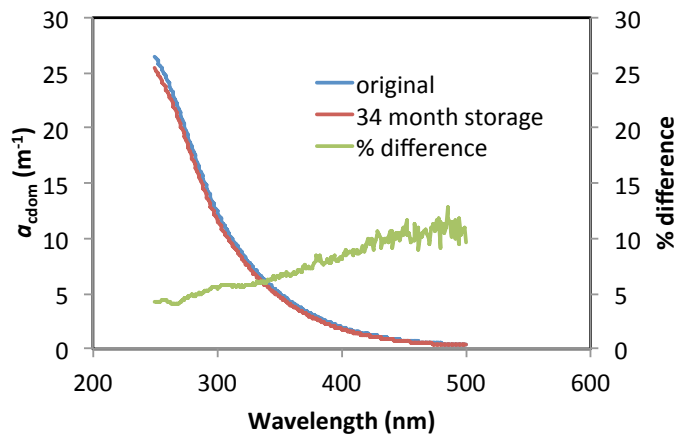


Fig. 1. The difference in  $a_{cdom}$  at Sta. 640 between time zero (original) and after 34-month storage at 4°C in darkness.

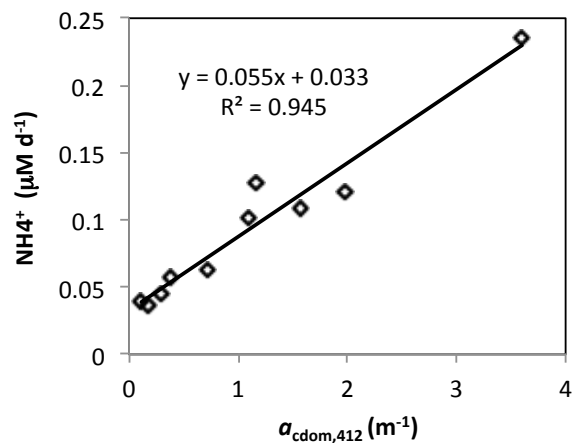


Fig. 2. Relationship between ammonium photoproduction rate (cutoff 280nm) and initial  $a_{cdom,412}$ . The highest  $a_{cdom,412}$  data point was from the sample collected from the Mackenzie River off Inuvik.

Furthermore, even if reoccurrence of bacterial degradation of DOM during storage could not be strictly ruled out, any potential microbial DON uptake would tend to be faster in offshore waters on a percent basis because of the increasingly higher quality of DOM (higher DON/DOC ratio) with distance from land (Fig. 8 in the manuscript). Therefore, bacteria-related storage effect, if any, is not expected to change the spatial pattern of  $NH_4$  AQY we observed (higher offshore than nearshore). It also should be noted that our AQY pattern is similar to that observed by Aarnos et al. (2012) in the Baltic Sea.

We added a brief discussion of the storage effect in section 3.3 in the new version:

“Use of aged samples (see Sect. 2.1) might lead to lower  $\Phi_{NH_4^+}$  values as well if loss of photoammonifiable DON occurred during sample storage. Nevertheless,  $a_{cdom}$  remained rather constant over the two-month storage period (Fig. SM2 in Supplement), which, combined with the linear relationship between the photoammonification rate and  $a_{cdom}$ , suggested that the storage effect was minimal.”

**p. 4446, lines 12-13 and 25-27; p. 4449, lines 18-27; p. 4453 lines 8-9 and 12-14; p. 4458 lines 3-4: You justify your assumption of constant  $NH_4$  production during your experiments based on one time-course irradiation using water collected well upstream of your estuarine samples, and 6 weeks earlier in the year. Presumably this water had different chemical characteristics (maybe more photoammonifiable DON?) and probably a larger absorption coefficient than the other samples, which still could have exhibited (unmeasured) decreasing  $NH_4$  production rates over 4-7 d irradiations under intense simulated sunlight. This linearity test therefore doesn't rule out the (fairly strong, I think)**

**possibility that your AQY spectra are underestimates because of uncharacterized dose-dependence. The best remedy would be if you could provide data from a second time-course experiment with a marine end-member sample; if this isn't possible, at least provide the composition and optical characteristics of the Inuvik sample so the reader can see how similar (or different) it is from the other estuarine samples. Finally, in comparing your AQY magnitudes and overall rate estimates to other studies I think you need to be very upfront about this methodological caveat (one of the three general comments).**

*The linear relationship shown in Fig. 2 above, which contains the data from the upstream of the Mackenzie estuary, provides stronger support that the effect of dose-dependence on AQY in our study was unimportant. Samples under the WG280 cutoff filter received the highest UV irradiance. DOM absorbed widely different photon fluxes among different samples due to varying CDOM levels and differing exposure times. However, the ammonium photoproduction rate linearly increased with the initial (prior-irradiation)  $a_{cdom}$ , suggesting substrate (photoammonifiable DON) was not the limiting factor over the adopted irradiation durations. We added the following lines in section 3.3 to further elaborate the dose-dependence issue:*

*“The linear correlation between the photoammonification rate under the WG280 cutoff filter and  $a_{cdom}$  (Fig. 5A) further corroborated that substrate-limitation was unimportant, since samples under the WG280 cutoff filter received the highest UV irradiance and DOM absorbed very different amounts of photons among different samples.”*

*The absorption spectrum of the upstream sample was now added to Fig. 4A.*

**p. 4449, lines 3-5: Move this statement (“An intercomparison by [ . . . ]”) to the first half of the paragraph, as it refers to polychromatic curve-fitting in general, not to the specific functional form you've chosen for this study.**

*Revised according to reviewer's suggestion.*

**p. 4451, lines 11-12: The cutoff between Groups 1 and 2 seems arbitrary, looking at the mixing curve in Fig 3b. I don't see an obvious distinction between the low SR and high SR samples. Also, the “Group 1” vs. “Group 2” slope ratios are only briefly discussed once more at the very end of the paper, and aren't really used to further interpret the data. Perhaps just strike the references to these groups?**

*The  $S_R$  for Group 2 (1.36) was 35% higher than that for Group 1 (1.01). This was a big difference for  $S_R$ . The substantial difference in AQY between the groups (Tables 2 and 4) justifies this classification. Actually, a large part of section 3.3 uses this grouping to discuss the results.*

**Section 3.3; Table 2: The uncertainty bounds presented here for the AQY at 330 nm are (I assume) just the variability among different stations. Can you provide also the uncertainty around each AQY estimate by, for instance, using a Monte Carlo technique to propagate through your analytical uncertainties (from your reproducibility estimate) into the spectral fitting parameters? Then, when you compute area-normalized and -integrated photoammonification rates, you can provide a true measurement uncertainty (one of the three general comments).**

*Right, these are the variability among different stations. As stated in the methods section, because of irradiation time restriction and limited sample volume available, the reproducibility was evaluated only for Sta. 430 under full-spectrum irradiation. As the measurement uncertainty was expected to increase with increasing cutoff wavelength of the cutoff filters, the lack of replicate irradiations under each cutoff filter makes it difficult to evaluate the errors of the spectral fitting parameters. In the new version, we made an approximate assessment of the uncertainty (coefficient of variation, CV) in the AQY by combining the variability of the factors used for AQY determination ( $\text{NH}_4$  production rate, photon flux, and  $a_{\text{cdom}}$ ) and by assuming that the reproducibility from the Sta. 430 was applicable to all other samples and to the entire wavelength range of interest (280-500 nm) (while acknowledging that this potentially underestimated the CV at long wavelengths). We then combined the CVs from AQY and satellite-derived solar irradiance,  $a_{\text{cdom}}$  and  $a_{\text{cdom}}/a_t$  to estimate the uncertainty in the area-integrated  $\text{NH}_4$  production rates.*

**p. 4454 lines 15-18: Can you provide information on how you determined the wavelengths at which to switch from the linear, to the exponential 1-parameter, to the exponential 2-parameter models of AQY vs.  $a_{\text{CDOM}}$  ?**

*The switch was based on the adjusted  $R^2$  from the regression between the predicted and determined AQYs. This information was added in the new version.*

**Section 3.6: I am not sure that this discussion of photochemical stoichiometry adds much to the paper. It could be expanded (after p. 4461 lines 4-5, perhaps further discuss the possible photoproduction/environmental control mechanisms?) or just struck in its entirety.**

*Simultaneous measurements of several important photoproducts are not often available. These data for the first time provided the photochemical stoichiometry among  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{NH}_4$ . We think this information is useful, as agreed by reviewer 2. We hence decided to retain this section. An expanded discussion on mechanisms appears premature, given the lack of sufficient chemical structure characterization of the DOM.*

**Figure 3b. Please consider splitting into two panels (one with the  $a_{\text{CDOM}}$  -based mixing curve, the other S-based) to make this easier to read.**

*Yes, now split into two panels.*

**Figure 5. This figure would be more effective (following the text discussion) if each panel were a scatter plot, with  $\text{NH}_4$  production rate on the x-axis and the test parameter ( $a_{\text{CDOM}}$ , DON, TDAA) on the y-axis. Samples referred to specifically in the discussion (e.g., 691) can be labeled directly on the plot.**

*Revised according to reviewer's suggestion.*

**Technical comments (Not exhaustive; I suggest the authors take some time to thoroughly**

proofread the manuscript for grammar and typos):

p. 4443, line 25 and elsewhere in the manuscript: capitalize “Arctic”

p. 4443, line 26: change “its inorganic counterpart” to “dissolved inorganic nitrogen” p.

4444, line 8: Begin a new paragraph with “DOM photochemistry becomes [ . . . ]” p. 4448, line 27: Change “non-simple” to something else like “complex”

p. 4450, line 25: Begin a new paragraph with “The spectral slope ratio [ . . . ]”.

*Revised according to reviewer’s suggestions. We proofread the manuscript for grammar and typos.*

## References

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- Bouillon, R.-C., and W. L. Miller (2005), Photodegradation of dimethyl sulfide (DMS) in natural waters: Laboratory assessment of the nitrate-photolysis-induced DMS oxidation, *Environ. Sci. Technol.*, 39(24), 9471-9477.
- Johannessen, S. C., And W. L. Miller. 2001. Quantum yield for the photochemical production of dissolved inorganic carbon in seawater. *Mar. Chem.* 76: 271-283.
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- Toole, D. A., D. J. Kieber, R. P. Kiene, D. A. Siegel, and N. B. Nelson (2003), Photolysis and the dimethylsulfide (DMS) summer paradox in the Sargasso Sea, *Limnol. Oceanogr.*, 48(3), 1088-1100, doi:10.4319/lo.2003.48.3.1088.
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