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Discussions

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

Anonymous Referee #1

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General comments:

Climate change is expected to enhance photochemical cycling of biogeochemically-important constituents in Arctic marine waters in complex ways. This study did a good job explaining the importance of photoammonification in these environments and providing the first local estimates of new nitrogen provided via this process. I would like to see uncertainty estimates on photoammonification rates, evidence showing that storage/refiltration of samples before irradiation doesn't affect results, and a more thorough discussion of biases stemming from potential dose-dependence of the reaction, which was largely uncharacterized in the authors' experiments.

Specific comments:

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.

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 a_{CDOM}? 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.

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 photoammonificable DON?) and probably a larger absorption coefficient than the other samples, which still could have exhibited (unmeasured) decreasing NH_4^+ production rates over 4-7d 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.

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.

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 S_R and high S_R 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?

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.

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_{CDOM}?

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.

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

Figure 5. This figure would be more effective (following the text discussion) if each panel were a scatter plot, with NH_4^+ production rate on the x-axis and the test parameter (a_{CDOM}, DON, TDAA) on the y-axis. Samples referred to specifically in the discussion (e.g., 691) can be labeled directly on the plot.

Technical comments (Not exhaustive; I suggest the authors take some time to thor-

oughly 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 [. . .]".

Interactive comment on Biogeosciences Discuss., 9, 4441, 2012.