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Discussions

Interactive comment on "Variability of carbon monoxide and carbon dioxide apparent quantum yield spectra in three coastal estuaries of the South Atlantic Bight" *by* H. E. Reader and W. L. Miller

Anonymous Referee #1

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Title: Variability of carbon monoxide and carbon dioxide apparent quantum yield spectra in three coastal estuaries of the South Atlantic Bight

Authors: H. E. Reader, and W. L. Miller

General Comments The authors present data from a seasonal study of CO and CO2 photoproduction, including valuable data on the apparent quantum yields (AQY) for these processes. Furthermore, the simultaneous determination of CO and CO2 photoproduction allows the authors to examine the CO2:CO photoproduction ratio. Both the

AQYs and CO2:CO ratio will be useful for biogeochemical modelling studies, particularly for the spatial and temporal extrapolation of CO2 photoproduction which poses more analytical difficulties. The paper concludes with an estimate of CO/CO2 photoproduction in the South Atlantic Bight. The paper is within the scope of BG and is generally well-written with appropriate equations, tables and figures. Nevertheless, I have a few comments/suggestions which I would like the authors to address. Most importantly, I would like to see a brief discussion of AQY uncertainty resulting from self-shading (see comment 5 below). Some figures are unclear and may have to be redrawn. Other comments follow below.

Specific Comments 1. Introduction: The introduction is well written with appropriate references. The authors may wish to add a recent paper on CO photoproduction and AQYs (Kitidis, Tilstone, Smyth, Torres, Law, 2011. Carbon Monoxide Emission from a Mauritanian Upwelling Filament, Marine Chemistry 127, 123-133). 2. Methods; Section 2.1: Please refer the reader to Table 1 for sample properties (salinity, DOC, CDOM). The sites are referred to as "coastal", but the salinities would suggest they are very much "estuarine". This may be a matter of opinion, so a reference to Table 1 would allow the reader to make up their own mind. 3. p. 6953, Line 23-27: Were any of the CO2-degassed samples irradiated for CO photoproduction? How did these compare with the standard protocol for CO? It is not critical if this was not done, but I would be interested to know in future. 4. p. 6955, Line 18-20: What was the phase ratio for equilibration (Sample volume to headspace volume)? 5. p. 6956, Line 21-23: Please discuss Qa error as a source of error for the determination of AQY. These samples are highly colored and according to Hu et al. (2002) the first order approximation for the error of Qa (given ag320 in Table 1 and 0.1 m path) would be 16-121% here. This will propagate through to the AQY determination and I am sure will be the biggest source of AQY uncertainty by far. 6. Methods; p. 6960, Line 21: Figure 2 is very unclear. I couldn't separate out the lines. I strongly recommend redrawing this figure. 7. p. 6961, Line 26: I would make the preceding statement less definitive unless the authors can back it up with statistics. There is a lot of variability in Figure 4a. 8. p.

6962, Lines 4-6: Not so sure if CDOM is the "carbon fuel" for CO/CO2. Either back it up with references or remove. CDOM certainly plays a central role in CO/CO2 photochemistry, but I wouldn't go as far as saying it is the substrate (fuel). 9. p. 6964, Lines 19-21: Alternatively, the observed trend in lower CO photoproduction efficiency could be explained by bleaching (prior radiation exposure). Looking at Fig. 3, the seasonal trend seems to be driven mainly by summer months (June-July-August). 10. p. 6964, Line 28: Spelling "dominant" 11. p. 6965, Lines 13-19: The authors suggest that "Pre-exposure of the CDOM to sunlight could explain the variation of CO2 to CO production ratios . . . since samples from riverine sources, presumably having had less sunlight-exposure showed higher ratios (see Fig. 3) . . .". Why not look at the ratio against salinity? If a positive correlation between CO2:CO and salinity was found, this would make the argument much stronger . 12. p. 6965, Line 19: Spelling "consistent" 13. p. 6965, Lines 19-20: The authors suggest that ". . . CO2 photoproduction is more variable than CO photoproduction (which) . . . is consistent with CO2 AQY spectra being more affected by pre-exposure to sunlight than . . . CO ". Fair enough, but earlier the authors suggested that CO2 photoproduction was more variable due to differences in the molecular composition of source material (p.6963, line 20-23). I don't object to either explanation, but please make it more obvious that there are alternatives. 14. p. 6965, Line 26: "Conversely. . .Delaware River". Please also refer to Stubbins et al. (2011) here. 15. p. 6966, Lines 4-7: The authors suggest that the absence of a salinity-AQY relationship here may be due to the relatively limited salinity range of their samples (most fall between 29 and 33). Yet, 10 of 38 experiments have salinity <29 (26%) and as low as 0.1, so I don't think this is a valid argument. I think the presence/absence of such a relationship is more likely to be specific to the system of study. The St. Lawrence estuary and Beaufort Sea have much longer residence times (presumably). This may be comparable or longer than photochemical turnover, so that bleaching of CDOM and concomitant changes in AQY are apparent. In contrast, in short residence-time estuaries, CDOM may be "flushed out" faster than it is turned over photochemically, resulting in lower rates at high salinity (due to lower CDOM), but

constant AQY. Alternatively, Xie et al. (2009) and Stubbins et al. (2011) have a much larger range of CDOM absorbance, 2-orders of magnitude as opposed to 1 here. This may be more important in separating out AQY differences than salinity and we know that CDOM and salinity are generally inversely related in estuaries. 16. Conclusions, p. 6968, Lines 25-27: This statement may be missleading. Photochemical production efficiency under constant light (solar simulator) varries by 21.7% seasonally, but CO photoproduction "over all of Georgia coastal environments" will vary by more than that due to seasonal insolation differences. 17. Table 1: Headings appear to be offset (e.g. DOC is above psu). Please correct. 18. Figures 4-7: In the respective figure legends use the word "symbols", not "circles". Also for CO, "grey symbols". What do the lines represent? Presumably CO2 (black) and CO (grey). Make these solid and thicker and explain what they are in the legend.

Interactive comment on Biogeosciences Discuss., 9, 6947, 2012.