

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

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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

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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.

Reference to table one added to section 2.1

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.

Degassed samples were not analysed for CO photoproduction in this experimental set-up. As mentioned in the discussion, Miller and Zepp (1995) have performed one of the only dual irradiations on degassed samples, and did not find a significant difference in CO photoproduction in degassed samples, suggesting that the process of degassing does not affect CO photoproduction. Additional not yet published data from our lab (Powers and Miller) confirms this observation.

4. p. 6955, Line 18-20: What was the phase ratio for equilibration (Sample volume to headspace volume)?

The following text was added to section 2.3: To provide an initial CO-free headspace for equilibration, 13 mL of room air was drawn slowly through a 50 cc column of Schutze Reagent (Fisher Scientific) into the spectrophotometric cells. The exact volume of each cell varied slightly (all 30 mL), and thus the sample volume to headspace ratio varied around 2.3 and this was accounted for in the calculations by using the exact total volume for each cell.

5. p. 6956, Line 21-23: Please discuss Q_a 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 Q_a (given ag320 in Table 1 and 0.1 m path) would be 16-121

The reviewer is correct that using the first order approximation of Hu et al (2002) would lead to a large uncertainty in samples of this absorption range. However, we did not

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use the first order approximation of Qa (top of second column, page 1263 of Hu et al), we used the full expression of the equation (equation 1 in Hu et al, equation 4 in this manuscript). We specifically used this full expression of the Qa in order to account for inner filtering effects, as stated in the text.

6. Methods; p. 6960, Line 21: Figure 2 is very unclear. I couldn't separate out the lines. I strongly recommend redrawing this figure. Have redrawn the figure to separate the lines further. 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.

The text has been generalized to say: Measured production appears to decrease with increasing salinity for both photochemical products seen in Figure 4a but this is likely due to a negative correlation between CDOM and salinity.

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).

Text has been generalized and a reference to Equations 4 and 5 added: Because the absorption of a photon by CDOM must occur for a photochemical reaction to occur, a relationship between CDOM "concentration" and measured production should exist (see Equations 4 and 5).

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).

Text has been amended: Additionally, this seasonal trend with lower efficiencies seen in the summer months could be driven by increased solar irradiation and pre-exposure of the CDOM to extensive sunlight, leading to photobleaching and potentially lowering the efficiency of the photochemical reaction. CDOM released in the fall and winter months

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would have less prior exposure to sunlight and this could lead to the higher efficiencies seen in those months. In reality, both of these situations are likely to co-exist.

10. p. 6964, Line 28: Spelling "dominant"

This has been corrected.

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 .

The relationship between CO₂:CO ratio and salinity was examined, but as there was no relationship found, an additional figure was determined to be superfluous and was not added.

12. p. 6965, Line 19: Spelling "consistent"

This has been corrected.

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.

Text clarified to reflect both alternatives as: This is consistent with both CO₂ AQY spectra being more affected by pre-exposure to sunlight than CO AQY spectra, and differing molecular compositions of the source material for the two different photoproducts as discussed above in section 4.1.

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14. p. 6965, Line 26: "Conversely...Delaware River". Please also refer to Stubbins et al. (2011) here.

Reference to Stubbins et al added: Stubbins et al (2011), also found an inverse trend between CO AQYs and salinity in the Tyne River estuary. This was not explained by simple conservative mixing and suggests that this relationship is more strongly tied to CDOM.

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

29 was a typo, we meant 20 (has been corrected). Samples falling within the range of 20-30 represent 35/38 samples or 92%. The discussion of CDOM, which we agree is likely to be more important, follows this section immediately.

16. Conclusions, p. 6968, Lines 25-27: This statement may be misleading. Photochemical production efficiency under constant light (solar simulator) varies by 21.7

This sentence was clarified to refer to the variation of the EFFICIENCY of photoproduction rather than TOTAL photoproduction: The photochemical efficiency of CO production over all Georgia coastal estuarine environments studied varied annually within 21.7

17. Table 1: Headings appear to be offset (e.g. DOC is above psu). Please correct.

This was a typesetting error. Corrected.

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.

The word "circles" was a typo, it has been corrected in all legends. The lines were calculated as a linear regression, however they are only there to guide the reader's

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eye, and due to low R² values, they should not be used predictively.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/9/C4325/2012/bgd-9-C4325-2012-supplement.pdf>

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

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