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 #3

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In freshwaters and the coastal ocean, a large part of the CDOM is "terrestrially-derived", i.e. it is derived from the decomposition of terrestrial plant matter that is trans- ported from the land. CDOM has important effects on the penetration of solar UV ra- diation into aquatic environments and it also can interfere with remotely sensed obser- vations of primary production. Microorganisms do not readily decompose terrestrially- derived CDOM, but its transformation can be accelerated when it is exposed to solar ultraviolet radiation. Recent research has provided additional evidence that two major decomposition processes are induced by exposure of the CDOM to solar UV radia-tion. These processes are direct photoproduction of both dissolved inorganic carbon (DIC) and biologically labile organic substances that are readily assimilated by mi- croorganisms and oxidized to DIC. Carbon dioxide (CO_2) and carbon monoxide (CO) are the two major identifiable photoproducts that make up the DIC. Past research has indicated that photoproduction of CO_2 from CDOM occurs over an order of magni- tude more rapidly than does photoproduction of CO. Although CO is not produced as rapidly as CO_2, other marine sources are sparse and thus its photoproduction could provide an important source of this gas. Because CO rapidly scavenges OH radicals in the atmosphere, its photoproduction from CDOM could have a significant influence on chemical reactions in the marine boundary layer. Marine scientists have long puzzled over the fate of terrestrially-derived organic matter on entry to the ocean. Experimental studies indicate that the DOC in the open ocean is primarily of marine origin, although some terrestrial character would have been expected. Past experimental and modeling research indicates that photodecomposition can potentially consume all of the input of CDOM from land. However, these previous estimates are based on very sparse data and limited relationships that use the data to predict rates and concentrations. This paper provides unique and valuable new data and analyses related to CO_2 and CO photoproduction that potentially will enhance the ability to model the role of photoreac- tions in the cycling of carbon in estuarine and coastal shelf systems. The paper is well written and generally well referenced. It should be of general interest to the readership of BGD. However, I have several suggestions that should be addressed.

(1) The authors use the Rundel approach to derive algorithms that describe spectral AQYs for photoproduction of CO_2 and CO. This approach involves use of broad-band irradiation with cutoff filters. This approach was originally developed for developing biological weighting functions for microorganisms that have complex responses to dif- ferent wavelengths. The process involves

statistical fitting of the data sets using as- sumed non-linear fitting routines. Please provide some comparisons of the AQY esti- mated here with AQY that have been determined with the traditional techniques using monochromatic radiation.

Response: Added the following sentence to text (just prior to 2.5, page 11): "Previous published work on CO and CO2 AQY has shown that this multispectral approach compares well with traditional monochromatic studies, particularly in the important UV region of the spectrum, and both do a credible job of predicting measured full spectrum photochemical production rates (White et al., 2010; Ziolkowski & Miller, 2007)."

(2) The equations used to account for inner filter effects are C2928certainly consistent with those discussed by Hu et al. However, there is another effect that potentially could lead to serious underestimates of the AQY using the technique employed in this study. The equations described by Hu et al assume that the photore- action is well mixed during the period of irradiation. Some of the samples used in this study absorb most of the incident UV radiation in the upper part of the irradiated water samples and thus gradients in photoproducts and photobleaching of the CDOM likely occurred due to mixing limitations. Among the basic problem that this mixing effect could lead to underestimates of the AQYs, it also could confound estimates of the CO to CO2 production ratios. Because CO is much more readily detected than CO2, the irradiations in the CO2 experiments required longer exposure times. This exposure differential could have further exacerbated the any problems related to mixing. See the paper by Morowitz that is cited in the Hu et al paper for background.

Response: While this is a valid concern, and could certainly be occurring to some extent in our darker samples and longer irradiations, it was not deemed to be a problem for the following reasons. We always ensured mixing of the samples prior to analysis thus evenly distributing the products throughout the sample. Additionally, photochemical fading over the entire sample was never more than 1% as stated line 17, pg. 8 (even in the longest CO_2 irradiations and the darkest samples) and in most cases, it was far less. Since we account for the total photon absorbance in the entire sample (eqs 3 & 4; page 10), and account for fading in AQY calculations, regardless of where the photons are absorbed and where the product is generated, AQY calculations consider both total moles of product in the sample and total moles of photons absorbed in the sample over the time of exposure. No changes were made to the text since the items mentioned above should be sufficient to explain our approach.

(3) A recent series of paper by Blough and Del Vecchio have provided new information about the optical and photochemical properties of CDOM that may be relevant to analysis of these data sets. In essence these scientists have provided

evidence that the long wavelength part of CDOM absorbance is largely attributable to charge transfer (CT) transitions involv- ing hydroxylated aromatic (phenolic) donors and carbonyl-containing acceptors. These are linked to spectral slope coefficients that range from the UV into the visible spectral region. The E2/E3 ratio of absorption coefficients at 250 nm to 365 nm also correlates with the degree of CT character of the CDOM. Photochemical AQYs of the CDOM decrease with increasing CT character and this happens to correlate with increasing molecular size. I do not believe that DIC photoproduction has been examined taking these findings into account. The spectral slope coefficients used in this study do not use a sufficiently wide spectral range but perhaps E2/E3 ratios could be used. Here are a few lead references: Golanoski, K. S.; Fang, S.; Del Vecchio, R.; Blough, N. V., Investigating the mechanism of phenol photooxidation by humic substances. Environ. Sci. Technol. 2012, 46, (7), 3912-3920. Ma, J. H.; Del Vecchio, R.; Golanoski, K. S.; Boyle, E. S.; Blough, N. V., Optical properties of humic substances and CDOM: Effects of borohydride reduction. Environ. Sci. Technol. 2010, 44, (14), 5395-5402. Sharp-
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less, C. M., Lifetimes of triplet dissolved natural organic matter (DOM) and the effect of NaBH4 reduction on singlet oxygen quantum yields: Implications for DOM photo- physics. Environ. Sci. Technol. 2012, 46 (8), 4466-4473.

Response: This is a good point, and while E2:E3 ratio was investigated in our work, we did not see any relationship to CO and CO_2 AQYs. We have added the following text to section 4.3, third paragraph:

"The E2:E3 ratio (i.e. the ratio between absorption at 254nm and 365nm) is similar to spectral slope, and has been shown to be an indicator of the charge-transfer character of CDOM (Del Vecchio and Blough, 2004). Del Vecchio and Blough (2004) have shown that increased absorption at long wavelengths is an indication of higher charge-transfer character. This charge-transfer character has been shown to be a potential predictor of the photochemical activity of reactive oxygen species, such as $^1O_2$ and H_2O_2 AQYs (DaryImple et al, 2010). We investigated the relationship between our CO and CO_2 reaction efficiencies and E2:E3, but found that there was no significant relationship between them (data not shown). As with the spectral slope, it is possible that the limited range of E2:E3 ratios present in our data set (4.95-7.24) is not enough to show a definitive relationship."

(4) Section 4.1 on seasonal changes. The changes likely are linked in part to residence times of the CDOM in the rivers. CDOM is photoreactive and as it moves down rivers to the ocean its degree of photoreaction is affected by residence time. CDOM that shoots rapidly down the river during wet periods has much less chance to photoreact than CDOM that moves slowly down the river

during droughts. Salinity is conservative and thus the DIC /salinity correlations looked for here are likely to be strongly system specific.

Response: This is a good point, as is number (5) below. The following text has been added to the discussion in section 4.1 (new paragraph at line 413 (second paragraph):
"   Fluctuations in riverine discharge and coastal hydrology may also add to the observed variability of photochemical reactivity in our samples. Due to higher sediment loads and reduced residence times during high-flow events in the Altamaha river, CDOM reaching our sampling sites during these periods would have minimal pre-exposure to sunlight and could influence its photochemical reactivity relative to CDOM delivered during low-flow with a longer pre-exposure to sunlight. It is also documented that estuarine Fe is usually positively correlated with river flow and particulate loading (e.g. Lippiatt et al., 2010) and that its complexation with DOM can greatly effect photochemical reactions in estuarine systems (Gao & Zepp, 1998; White et al., 2003). These potential variations in the chemical nature of CDOM would certainly add to the variation of AQY in coastal systems and may not be directly related to salinity."

(5) Iron plays an important role in CDOM photochemistry in the colored rivers and nearby coastal regions of the SAB. Variation in iron content could help explain the variability observed with the CO2 AQYs. See the paper by Xie, Zafiriou et al for lead references (but Miller knows this area well). Please add discussion of this point.

See Above

(6) Did you check the effects of DIC removal by acidification on the CO AQYs? Miller and Zepp checked a few sam- ples and found no change but this assumption needs examination with a wider range of water samples,

Response: While this is certainly a relevant question to the general study of CO:DIC ratios and in some studies could alter results, this was not part of the present study since all of the CO experiments were done on un-acidified samples as specified in the text. Consequently the CO AQY results will be more generally comparable to other studies. No changes were made in the text.

(7) What fraction of the DOC that drains into the SAB is chromophoric? If only a small fraction is chromophoric (which is the case with the Savannah River for example) then even complete photochemical loss of the CDOM would have little effect on loss of coastal DOM. See papers by Blough et al on the CDOM content of the Orinoco River for example.

Response: Data from our lab over several seasons and several years in this region show that depending on location, time of year, and hydrological conditions in the SAB the fraction of DOC that is chromophoric is extremely variable, between ~50% and ~90%. This ratio is also not constant over all absorption ranges (i.e. ag <5, ag>10 etc.). Because of this large variability, we do not believe that we can report a single definitive number for this system. No changes were made in the text.

(8) The figure are hard to read in general. Fig 2 is one of the hardest to read. The symbols on other figures could be enlarged to help. Terms such as CDOM normalized production need to be defined
Response: Figure 2 was re-drawn to make it easier to read. The sheer number of samples is high, but this figure shows that they fall within previously published ranges. CDOM normalized production and its calculation are explained in the methods (Section 2.5).

(9) I suggest presenting the production data as area normalized results as in the Miller et al paper on BLPs. It would be easier to compare the results to past work. Please do not use system specific units such as nmol CO2/s.

Please see our response to Reviewer#2 on this matter.