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Biogeosciences 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 #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 transported from the land. CDOM has important effects on the penetration of solar UV radiation into aquatic environments and it also can interfere with remotely sensed observations 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-

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tion. These processes are direct photoproduction of both dissolved inorganic carbon (DIC) and biologically labile organic substances that are readily assimilated by microorganisms and oxidized to DIC. Carbon dioxide (CO2) and carbon monoxide (CO) are the two major identifiable photoproducts that make up the DIC. Past research has indicated that photoproduction of CO2 from CDOM occurs over an order of magnitude more rapidly than does photoproduction of CO. Although CO is not produced as rapidly as CO2, 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 CO2 and CO photoproduction that potentially will enhance the ability to model the role of photoreactions 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 CO2 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 different wavelengths. The process involves statistical fitting of the data sets using assumed non-linear fitting routines. Please provide some comparisons of the AQY estimated here with AQY that have been determined with the traditional techniques using monochromatic radiation. (2) The equations used to account for inner filter effects are

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certainly 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 photoreaction 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. (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 involving 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 photophysics. Environ. Sci. Technol. 2012, 46 (8), 4466-4473. (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. (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. (6) Did you check the effects of DIC removal by acidification on the CO AQYs? Miller and Zepp checked a few samples and found no change but this assumption needs examination with a wider range of water samples, (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. (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 (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.

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