Comments on the research article in BG, "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 (MS No.: bg-2012-200)


General comments

The manuscript presents seasonal measurements of apparent quantum yield spectra for the photoproduction of DIC and CO at three estuaries of South Atlantic Bight. Such seasonal studies are rare and the present study is a welcome addition to the scientific community assessing the rates of DOM-photochemistry in surface waters. The photochemical reactivity of DOM varied less than ca. 20% among the seasons being least reactive during spring and summer compared to more reactive seasons, fall and winter. The photochemical reactivity was poorly explained by the optical characteristics of DOM, and the most likely explanation (although not proved) for the variability of AQY was the magnitude of DOMs pre-exposure to solar radiation.

The large parts of results were presented in a way, which was not explained in the methods detailed enough. The presentation of results was also such that the comparison of the results of the present study to those of other studies is difficult. I encourage the authors to recalculate their results or at least explain the calculation methods clearly enough.

The discussion would get stronger by comparing the results of present study to those of similar earlier studies highlighting apparent quantum yields and the role of photochemical reactions in the carbon cycling in the coastal waters.


Detailed comments

P 6950, L 2: The PhD-thesis of Johannessen may not be available for everyone, please, add an additional reference e.g., Wang et al. 2009.

P 6952 L 23: The AQYs were determined sometimes with fresh samples and sometimes with samples stored 6 months. There is a possibility for abiotic transformation (e.g., the aging of iron associated to DOM) and biotic transformations of DOM under long storage. Did the authors observe any changes in DOM during the storage? How such changes could have influenced AQYs?

P 6956 L 11: How did you get $E_0(\lambda)$ referred as the scalar irradiance entering the top of cell? If you measured it with a spectroradiometer with a cosine corrected entrance for the incoming irradiance, you likely measured irradiance incident on a plane. This is referred as vector irradiance or just irradiance (not scalar). If you irradiated your samples in air, you should account for the reflection of irradiance at the interface between air and quartz cell. The refractive index of air is 1 and that of quartz ca. 1.4-1.5. The difference in the refractive indices reflects some of irradiation from the interface between air and quartz reducing the amount irradiance entering the cells (compared to values measured in air). If you irradiated the samples in water (RI = 1.34), such a reflection is small, because the refractive index of water and quartz is similar. Please, report your $E_0(\lambda)$ in more detail.

P 6957 Eq. 5: I believe you used spectral values in Eq. 5. Please, use AQY($\lambda$) and Qa($\lambda$) (instead of AQY and Qa) in Eq. 5 following their earlier use in Eq. 2-4.

P 6958 L 1-17: The purpose here is to examine variability in AQY (or the photoreactivity of DOM). It is possible to carry out these examinations as indicated here. However, the results of these calculations in units e.g., mol CO s$^{-1}$ reported in Figs 3, 4, 5, 6, and 7 are not environmentally relevant. I believe that most readers of this paper are not interested in the rates taking place in a 30 mL irradiation cell under artificial irradiation. At least it is very hard to compare the results of this

study in mol CO s-1 30 mL-1 under artificial irradiation to other studies. I encourage the authors to report their results differently so that the results are comparable to other studies. There are many ways to assess the variability of AQY.

Here, I suggest a simple modification of Eq. 7 as an alternative. Eq. 7 actually estimates the photochemical rate per volume and time (mol vol-1 time-1) at the given $E_0(\lambda), a_g(\lambda)$ and $AQY(\lambda)$. The units for these parameters are [mol m-2 s-1 nm-1] for $E_0(\lambda)$, [m-1 nm-1] for $a_g(\lambda)$ and [mol CO mol photons-1 nm-1] for $AQY(\lambda)$. In this case, the unit is [CO mol m-3 s-1 nm-1] for d[product]dt-1.

When Eq. 7 is normalized with arbitrarily selected $a_{g,Nov08}(\lambda)$, it will be modified to:

$E_0(\lambda) *a_g(\lambda) * a_{g,Nov08}(\lambda)-1 * AQY(\lambda)$.

Now $a_g(\lambda)a_{g,Nov08}(\lambda)-1$ will have an arbitrarily unitless spectrum for each time. The unit for d[product]dt-1 will be modified to [mol m-2 s-1 nn-1]. In order to get the units [nmol product s-1 cell-1; given at the page 6958 line 5) authors must have accounted for the area, the dimensions, and volume of their irradiation cells. Additionally, the Eq. 7 must have been integrated over the some spectrum of wavelengths. These details are not given in the methods, so it is hard to understand how the normalized rates were actually calculated.


I suggest that the authors simplify their Eq.7 to

$$d[product]dt-1 = \int_{290}^{450} E_0(\lambda) \, AQY(\lambda) \, d\lambda \qquad modified \ Eq. \ 7$$

where d[product]dt-1 has units [mol product m-2 d-1], $E_0(\lambda)$ is the $EdO-(\lambda)$ is the daily annual mean downwelling solar irradiance at their study site used later in Eq. 10 with a unit [mol photons m-2 d-1 nm-1] and $AQY(\lambda)$ is the spectrum of AQY determined for each sample [mol product mol photons-1 nm-1]. In this case, the modified Eq. 7 would estimate the mean daily photoproduction of CO or CO2 over the entire water column at their study site assuming that CDOM is responsible for the absorption of photolytic solar radiation. The modified Eq. 7 is the same used earlier by the present research group — see Eq. 8 of Miller et al. 2002 L&O-paper. The values of modified Eq. 7 would be environmentally relevant and comparable to estimated made by Eq. 10 of this study and many other earlier and future studies.

P 6959 Eq. 8: If you followed Helms et al. your Eq. 8 for the calculation of spectral slope coefficient should be:

$a_g(\lambda) = a_g(275)e^{-S(\lambda-275)}$

where $a_g(275)$ is the absorption coefficient of CDOM at the reference wavelength selected to 275 nm by the authors of present study. Please, modify your equation and recalculate your results so that they are comparable to the other studies following the method of Helms et al.

P 6960 Eq. 10: Please, re-place the integral sign between '=' and '$E_{d0-}(\lambda)$'.

P 6960 L 5: [mol photons yr-1 m-2 nm-1]

P 6960 Eq. 11: This is a nice and infrequently done approach to account for the absorption of photolytic photons by CDOM in the water column. However, in strict sense one should address the ratio of CDOM absorption to the total absorption in the water column (rather than the attenuation of solar radiation). In addition to the absorption of photons, the attenuation of solar radiation is influenced also by scattering (mainly from particles). In terms of photochemistry, the scattered photons will be eventually absorbed by water column and they contribute to photochemistry if absorbed

by CDOM (unless they exit the water column to the atmosphere or sediment). In the present approach (Eq. 11), scattered photons are lost and not involved in the photochemistry in the water column. The use of Eq. 11 will underestimate the rate of photochemical reactions in the water column. On the other hand, the modified Eq. 7 assumes that CDOM absorbs all photolytic solar radiation and lead to overestimation of photochemical rates (by not accounting the absorption of photons by other optically active components – mainly particles in the coastal waters studied here). Therefore, the comparison of photoreaction rates by two methods would be interesting in the results of this study (compare the modified Eq. 7 to Eq. 10 with embedded Eq. 11).

P 6960 L 15: Please, explain how you calculated means. Notice that typical arithmetic averages at linear scale do not work with your non-linear parameters. For example, the arithmetic mean of 1 and 2 is 1.5. But if 1 and 2 are exponents like in AQY-spectrum $e^1$ and $e^2$, their mean is 5.05 (not $e^{1.5} = 4.48$).

P 6960 L 21 and Fig. 2: Please, add the data from Aarnos et al. 2012 JGR to Fig. 2 A.

Table 1. There is a mismatch between Salinity, DOC and ag320, and their respective units. Additionally DOC is obviously given as $\mu mol\ L-1$ (not as mg L-1).

P 6961 L 6-14 and Fig. 3: Consider presenting your data differently. It is impossible to compare your results reported in mol $CO_2$ or CO s$^{-1}$ to other studies. Please, explain also how you calculated SE. Calculating SE helps to identify the source of variability in the spectral AQY. For example, it seems that that the CDOM-normalized photoproduction of CO2 varied typically <20% (Fig. 3). However, AQY at 480 varied over more than four-orders of magnitude i.e., > 1000000% (Fig 2 A)!!! Do you think AQY(480) represents AQY correctly within 20% SE at 480 nm? Or is there a possibility that the measured photoproduction of DIC under GG475 filter was detected with an error > 20%?

Figures 4, 5, 6 and 7: Try to express your data in a way, which makes it environmentally relevant and comparable to other studies. It is very hard to tell anything about the measured photoreaction rates given in units given nmol CO or $CO_2$ s$^{-1}$. Please, give your measured rates e.g., in units mol L-1 s-1. Please, try to relate your results e.g. to values representative of daily rates at the surface conditions of your study sites.

The CDOM normalized production is given in units mol $CO_2$ or CO/s/L although the methods explain other units (nmol products s-1 cell-1; P 6958 L 15). I do not understand how you obtained the CDOM normalized production. Please, revise your manuscript so that a reader can understand the way how you got your results.

I do not understand all symbols used in Figures 4-7. The symbol key gives nice explanation for the samples at your study sites at high or low tide – this is OK. I do not understand the additional black circles and grey squares. What are they?

R2 values in Fig. 4 and 7: How is possible to have negative $R^2$ value (-0.08) in Fig. 4? In Fig. 7, the $R^2$ value for the normalized data looks much lower than 0.46 given. Mistake?

The section 3.3: It is possible to follow the relative differences in the data presented. However, I did not fully understand how the data presented in Figures 3-7 was obtained. Please, revise the methods, the results and the figure legends for clarify the results obtained.

Fig. 6: Please, calculate the $S_{275-295}$ correctly. You values for $S_{275-295}$ should be between 0.010 nm$^{-1}$ and 0.035 nm$^{-1}$, not unitless and between 0.0065 and 0.0085 as shown in Figure 6.

P 6962 L 4-5: Please revise the expression "carbon fuel", since CDOM is a simple optical parameter and does not measure carbon directly. Please revise "CDOM concentration" to "the absorption by CDOM" and refer to Eq. 7, which shows that the photochemical rate per volume depends linearly on CDOM

P 6962 L 26 and P 6963 L 3: SAB instead of SABi.

3.4 and Table 3. Please, give error estimates for the annual photoproduction rates. For example, the range of $CO_2$ production spans from $0.25 \times 10^{11}$ g C yr$^{-1}$ SAB$^{-1}$ to $4.33 \times 10^{11}$ g C yr$^{-1}$ SAB$^{-1}$ when estimated over the observed range of CO2:CO ratio (Table 2).Because the maximum estimate is nearly 20-fold larger than the minimum estimate, CO2:CO ratio is not a good way to estimate CO2-production. There must be an error associated to your estimate based on AQY — please, report the magnitude of error and explain where it comes from. Please, report also the rates per square meter basis. These values are most frequently reported in the literature. For example, Miller et al. 2002 estimated that photoreactions produce ca. 2000-3000 umol biologically available photoproducts m-2 d-1 in your study region. If I calculated correctly the photoproduction of CO and CO2 were 36 and 636 μmolm-2 d-1, respectively, in your present study. The photoproduction of CO and CO2 in this study is low compared to the production of BAPs. More data for similar comparisons in found e.g., in the review by Vähätalo 2009 Encyclopedia of Inland Waters (Light, Photolytic reactivity and chemical products).

4.1: Please, compare your data to that reported by Aarnos et al. 2012 (JGR), which also addressed seasonality of photoreactions.

It seems that the previous exposure of CDOM to solar radiation can explain the photoreactivity of CDOM (Andrews et al. 2000 L&O, Vähätalo & Wetzel 2004 Mar Chem). Therefore, the marsh CDOM with little exposure to solar radiation can be expected to be more photoreactive that CDOM exposed to intense solar radiation during spring and summer.

4.2: For example, Belager et al. 2006 and Aarnos et al. 2012 have made estimates about CO2 photoreactions at the coastal seas based on AQYs. Accounting for the large variability in CO2:CO ratio, it is better to measure CO2 production directly than through CO-production.

P 6966 L 25: The absorption coefficient of CDOM and spectral slope coefficient are frequently linked. High CDOM absorption correlates with low slopes. This may explain the results in Fig. 6 A.

4.4: Please, include a section to discussion, where you compare your AQYs to those obtained earlier. Please, extend your discussions also to cover the estimated photoreaction rates. SAB in perhaps the most intensively studied coastal sea in terms of environmental photochemistry. The discussion of present study ignores the numerous earlier photochemical studies done in SAB and rivers draining into it. For example, please, compare your results to those published by Vodacek et al. 1997 L&O and Moran & Zepp 1997 L&O followed by many other studies where e.g., Bill Miller, Moran and Zepp have been involved. These studies have been done at the same coastal region, where the present study was carried out.

You concluded that ca. 2% of terrestrial DOC can be photochemically removed to CO and CO2 in SAB. Please, compare this conclusion to earlier studies where similar estimates have been done (Kieber et al. 1990 L&O, Miller & Zepp 1995 GRL, Miller et al. 2002 L&O, Belanger et al. 2006, Aarnos et al. 2012). Many earlier studies have concluded that photochemistry has a larger importance in the transformation of terrestrial DOC in coastal waters than reported in this study. For example, Aarnos et al. 2012 estimated that the photochemical transformation of DOC in the Baltic Sea equals the input of terrestrial DOC to the Baltic Sea. Why the conclusion of this study is different from many earlier studies? Do the BAPs (not measured in the present study) play a major role? Is the residence time of terrestrial DOC in SAB short? Or is there any other explanations? Scattering of photons (Eq. 11)?