

First we would like to thank the reviewer for their comments. Their time spent in critiquing the manuscript is appreciated. We believe that addressing the reviewer's concerns has led to improvements in the document. We hope the reviewer and editor agree.

Responses are in italics.

Review intro: Photochemical production of carbon monoxide is a process that is important not only as a gas flux to the atmosphere, but also to the reworking of organic matter. The factors constraining the rate(s) of this photochemical process are not well quantified. Thus, with the changes I have outlined below this study will prove to be valuable contribution to the marine photochemical community.

There are a few issues that I would like to see resolved with this paper.

My first issue is the discussion of how the AQY is correlated to the a_{412} . Since the AQY is calculated using the a_{CDOM} , by definition this correlation should hold for all samples.

The CDOM absorption coefficient is indeed a term in the calculation of CO AQYs. However, it does not follow that the two terms should therefore be correlated. The absorbance term in the CO AQY calculation is used to calculate how many of the photons entering the irradiation cell are absorbed by CDOM. The number of photons absorbed is then used to calculate the AQY (AQY = moles product produced / moles photons absorbed). If CDOM absorbance is not used in this calculation and the photons entering the cell is used in place of the photons absorbed, then the differences in the samples' abilities to absorb light are not corrected for. In this latter case a strong correlation between sample absorbance and photoreaction rate arises (e.g. Stubbins et al. 2008). Including CDOM absorbance in the CO AQY calculation removes this bias. By doing so it reveals the efficiency of photoreaction per photon actually absorbed by CDOM, irrelevant of how colorful the DOM.

That said, the above holds true if the reactant's AQY does not change during the course of the irradiation. However, it is known that CO AQYs decrease with increasing irradiation dose. A sample with higher initial CDOM absorbing the same amount of photons as one of lower CDOM would be expected to experience lower % bleaching. Therefore at the end of the irradiation a sample with lower starting CDOM would be expected to have a lower CO AQY – as it would have lost a higher percentage of its most photoreactive components. This is a problem when trying to measure environmentally relevant photochemical rates. Determining instantaneous rates is impossible due to limitations in the sensitivity of product detection (in this case CO). In this and other studies short irradiations are used (in this case 30 minutes) at light doses consistent or lower than those experienced by surface waters.

Second, the introduction of particle photochemistry in the last third of the paper seems like an afterthought.

Particle photochemistry included in the introduction and methods.

My specific comments related to the above points are as follows:

- Please reorder your methods section to follow the logical progression of data collection and analysis. i.e. irradiation, absorption, CO photoproduction, AQY determinations.

Reordered.

- End of Section 2.2

Please elaborate on how your AQY spectra were calculated.

AQY spectra were calculated as detailed in previous publications. Inclusion of additional text to detail the calculation seems redundant, although can be added at the editor's request.

- Section 3.1 "Measured apparent quantum yields"

One does not measure an AQY. One measures the photochemical production of CO and calculates the AQY. Please edit this section title to reflect what was actually done/observed.

Edited.

- Figure 3: An AQY is a function of wavelength.

Please edit the figure caption to reflect the wavelength of AQY being reported in Fig 3.

Also, AQY is a unit-less. Please correct this throughout the manuscript.

Fig. and text corrected.

- The "particulate a_{412} " is introduced for the first time in Section 3.4

Please elaborate either in this section, or the methods, how these values were obtained.

- Including particulate absorption data into your photochemical rate equation (eqn 3) also introduces a scattering term. Please indicate what assumptions were made about scattering.

Text added.

- Is the "particulate a_{412} " on page 7432 the same as the coloured particulate matter?
Please clarify.

Yes. Clarified.

Other comments:

- Section 3.2: discussion of estuarine variability of CDOM and AQY

There has been some interesting FT-ICR-MS work on the chemical changes induced by photochemical fading (i.e. Kujawinski et al 2004, Gonsior et al, ES&T 2009 or Dittmar et al, Mar. Chem. 2007). The decrease in DBE will undoubtedly lower the CDOM absorption and contribute to a lower AQY. Please add elaborate your discussion of the factors contribution to the lower AQY to include a study such as one of the above in your discussion.

The reviewer is right to highlight the above studies and the advent of FT-ICR MS as a major advance in the characterization of DOM. We are well aware of the manuscripts mentioned

and have ourselves used FT-ICR MS to define the various pools of DOM based upon their photoreactivity (Stubbins et al. 2010). However, we choose not to make reference to this work as the relevance is not apparent. It is clear that aromatics are the main photoreactants in CDOM and that these are lost during irradiation. The FT-ICR MS studies confirm this, but add little further information about how the quality of the remaining chromophores differ from those present at the start of an irradiation. This stems from the inability to determine structure with a sufficient degree of precision based solely upon the elemental formulae that constitute that data set resultant from FT-ICR MS analysis. Each molecular formula identified has many possible isomeric structures, some aromatic, some not. Determining the substituent chemistry is even harder than getting at the core/general molecular structure (i.e., assigning a molecule as aromatic, condensed aromatic, or aliphatic is possible, but saying it has a carbonyl or carboxyl substituent is nigh on impossible for most formulas identified). This is the critical issue, as many aromatic structures can absorb sunlight, yet, depending upon their substituent (Stubbins et al. 2008), and presumably, macro-molecular qualities (number of aromatic rings, charge transfer capacity etc.) the efficiency with which absorbed light is converted to the production of CO differs. We have now added reference to Stubbins et al. 2008, as this manuscript clearly shows that changes in substituent chemistry alter the CO production efficiency per photon absorbed for a suite of model aromatic chromophores. We feel this finding is of more direct relevance to the current manuscript than the FT-ICR MS literature, including our own publication in that field.

- Please update your Ziolkowski (2000) citation to Ziolkowski and Miller (2007) throughout the manuscript.

Updated.

- It appears in the AQY vs salinity plots (Figure 4) that Tamar River is characteristically different than the other AQYs presented. Please comment on what may contribute to this difference (i.e. river runoff difference due to storms, different watersheds, etc).

Comment added. Both the S. Tyne and Tamar lie above the regression line and are from moorland catchments. However, the Tay is also from a moorland system and has an AQY that falls right on the line with the rest of the data. We therefore suggest in the manuscript that no conclusions can be drawn about how source might cause minor variation in AQYs due to the limited types of catchments included in the data set.