We greatly appreciate the referee's thorough and constructive comments. Our responses follow the referee's comments and are *italicized*.

Responses to referee#1

1. 16163.9-25: This sentence is too long, and it's unnecessary to list 8 separate categories of CDOM photoprocesses in introduction to a paper about particulate CO photoproduction—a brief mention of important processes, explanation of why they are important, and reference to one or two reviews should suffice. The rest of the Introduction is much more relevant to your topic.
2. 16163.25-27: You first state that chlorophyll and lipid degradation are the only particulate photoprocesses receiving significant study to date, but then you go on to list a number of studies that, in fact, focus on other particulate photoprocesses. Please update your text, so it's self-consistent.
3. 16164.4-7: The word choice is quite similar to that of Zafiriou (2002)-please paraphrase further.
4. 16164.12: Mayer et al. (2006) should be included here.
5. Very recently, Estapa et al. (2012) published AQY spectra for DOC photoproduction from POC.

Comments 1-5 all relate to the Introduction. We agree with the reviewer's comments and substantially revised the Introduction.

6. 16168.12-13, 19: Consider listing cutoff-wavelength instead of model numbers (or at least confirm that the digits in the model numbers are the wavelengths, for readers unfamiliar with these filters)

The numeric value in each model number signifies the nominal 50% transmittance cutoff wavelength in nanometers. This is now explicitly stated in the text (page9.line1-2).

7. 16168.18-21: Was the CO production rate constant through every irradiation regardless of cutoff wavelength or sample absorption coefficient? Did you measure absorption coefficients of samples after irradiation to determine photobleaching extent? If so, please include this information; if not, please address how you accounted for any dose-dependence effects, particularly for the longer irradiations.

Note that there is an error in reporting the irradiation times in the original version. The longest irradiation times (8 hours for short wavelength cutoffs and 21.2 hours for long wavelength cutoffs) were for an open-ocean deep water (1000 m) sample with very low CDOM, which is ***NOT*** *reported in this paper. The actual irradiation durations were < 3 h (mostly < 2 h) for short wavelength cutoffs and <12 h for long wavelength cutoffs (****only low or no UV present****). For near-shore samples, irradiation only lasted 10 to 40 minutes under all cutoff filters. We measured CDOM absorbance spectra after irradiation for certain samples with or without particles and found no significant differences as compared with those before irradiation (see Fig. S1 in supplementary material). No particle's absorbance spectra after irradiation were determined due to technic restrictions. Because of short irradiations and lack of significant photobleaching (at least for CDOM), it was assumed that CO production rate was constant within the irradiation times, although this was not explicitly tested* *(practically this was difficult to do without compromising the AYQ irradiations, since there was only one solar simulator available). A statement concerning this point is now added to the Method-Irradiation section (page9.line8-15).*

8. 16171.9-16 and 16168.5-6: You use the b_b:K_d ratio at 300-400 nm to justify neglecting scattering in your light absorption rate calculation. However, this only shows that scattering through angles greater than 90° was negligible. Unless the sides of the irradiation cells were reflective, you need to also account for losses of side-scattered light through angles greater than ~8.5° (computed from the cell dimensions), which may more easily be affected by multiple-scattering. Also, the b_b:K_d ratio at visible wavelengths (which are still important to CO photoproduction from particles) is probably larger than at 300-400 nm. Please discuss these scattering losses, the wavelength dependence of your assumptions, and possible bias (if any) in your derived Φ spectra.

   A very good point. A Monte Carlo simulation has now been conducted to estimate the effect of particle scattering. This simulation also took into account of the multiple reflections between the bottom and upper quartz window of the irradiation cell. This latter effect also applies to the filtered (i.e. particle-free) samples. Eq. 3 in the paper is now modified to account for this reflection effect. All CDOM AQYs have been re-calculated according to this modified equation, though the effect is only a few percentages. Details of the Monte Carlo simulation are given in the paper's Supplementary Material. The results indicate the particle scattering effect is significant only for three innermost stations in the Mackenzie estuary. All data derived from AQYs have been re-calculated. The corrections for the scattering and reflection effects do not change any of the conclusions in the original paper. Please refer to page11.line23-page12.line23 in the new version for revisions made to address this scattering issue.

9. 16168.5-6: If the irradiation cells' sides were transparent, were neighboring cells in the solar simulator shielded from one another? If not, can you estimate the extra irradiance received from the sides due to "leakage" of light from scattering samples in neighboring cells?

   The side walls of our cells were wrapped with black electric tape to make sure there was no lateral light interference between the cells. This is now explicitly stated in the text (page8.line17-18).

10. 16171. Eq3 and 16174.4: At Sta. 697, at least (and perhaps others?) I suspect your irradiation samples were "optically thick" at UV wavelengths-that is, all or nearly all the irradiance was absorbed within the 0.114 m cell path. Were cells stirred during irradiation 1) to limit kinetic transport effects, and 2) in unfiltered samples, to keep particles in suspension?

    Right, samples from Sta. 695, 697 were optically thick at the UV wavelengths. The cells were not stirred. However, because the irradiation was very short for these two samples (10 min for Sta. 697 and 15 min for Sta. 695), significant photobleaching is not expected to occur in the UV-hit upper layer in the cell. Therefore, the effect of kinetic transport, if any, should be minimal. To minimize the effect of particle settling, *the cells were adequately shaken immediately before irradiation, few particles were seen on the bottom of the cell after irradiation again due to the very short irradiation durations. Several lines concerning these two issues are now added to the Method section in the new version (page9.line8-15). It is worth mentioning that one of the most important advantages of studying CO is the extremely high analytical sensitivity and precision of the CO analyzer (Xie et al., 2002), which greatly reduces the irradiation time required to produce well measurable signals and thus minimize the effects of self-shading, photobleaching, and particle settling (for particle studies).*

11. What was the uncertainty of the CO measurement and approximate, propagated uncertainty in spectrally-averaged Φ values?

    The uncertainty of CO measurement is within ±2% (Xie et al., 2002) at typical CO concentrations encountered during our study (0.2-10 nM) and the uncertainty of light measurement was within ±4% (already reported in the original version). As AQY is defined as the moles of CO produced per mole of photons absorbed, the uncertainty of the derived AQY is estimated to be within ±4.5% according to propagation of random errors. The uncertainties of CO measurement (page10.line3-4) and AQY (Table 3) are now added to the new version.

12. 16172. Eq. 5, 7, 8: Can you condense these a bit? The arithmetic is not complex, and you defined $Q_{a,\lambda}$ earlier, so perhaps you only need to write the generic equation (e.g., $P_{x,\lambda} = \Phi_{x,\lambda} \times Q_{x,a,\lambda}$).

    Yes, we now condensed these equations.

13. 16173.20 and Section 3.5: Your stations span quite a large temperature range, and temperature dependence for DOC photoproduction from POC appears to be larger than for many dissolved-phase photoreactions (Espapa et al., 2012). While a direct comparison between temperature dependence of CO photoproduction from particles and from CDOM (e.g. Zhang et al., 2006) would have been even more illustrative, you could still use the temperature dependence of the CDOM reaction measured by Zhang et al. 2006 to estimate the effect of temperature on your modeled rates. This might cause non-negligible changes in your model results since in situ temperatures were in some cases quite different than your 4°C irradiation temperature.

    We agree. Surface water temperature spanned from -0.8 to 10.3 ℃. The temperature effect is now evaluated according to Zhang et al. (2006) while a statement is added to caution the reader that the temperature dependence of particles is likely different (probably stronger than) from that for CDOM (page25.line6-19).

14. 16174.20-26: These lines are not well justified. Any spectral features in $\Phi_{p,\lambda}$ as determined here are due solely to the measured spectral shape of particulate absorption and the assumed form (Eq. 3) of the spectral shapes of $\Phi_{cdom,\lambda}$ and $\Phi_{t,\lambda}$. Only if you'd measured $\Phi_{p,\lambda}$ during a series of monochromatic irradiations would you able to infer increased photoreactivity in pigment wavebands.

    We agree. This statement is now rephrased as "Unlike the rather smooth spectral shape of $\Phi_{p,\lambda}$ for the estuarine sample (Sta. 697), the spectral patterns of $\Phi_{p,\lambda}$ for the more marine samples, particularly those from the DCM, were characterized by *conspicuous shoulders over the 500–600 nm band. This attribute might be linked to specific compounds with high photoreactivity in the DCM samples. However, as the spectral pattern of* $\Phi_{p,\lambda}$ *determined in the present study was primarily defined by the assumed spectral shapes of* $\Phi_{cdom,\lambda}$ *and* $\Phi_{t,\lambda}$ *(Eqs. (4) and (9)), more studies using monochromatic irradiations are needed to confirm or further resolve these fine spectral features."*

15. 16175.20-27, 16177.3 and Figure 4b: I would suggest removing these lines and Figure 4b. Even within the grouped subsets, the variability of both Φ_p and $a_{phy,412}$: $a_{p,412}$ is so large that you can not make a strong conclusion regarding reactivity of phytoplankton-derived organic matter. On the other hand, your statement that "more complex mechanisms" control the efficiency of particulate CO photoproduction is entirely reasonable, especially when you consider that living phytoplankton undoubtedly have evolved a variety of strategies to avoid photochemical degradation. A more useful comparison might be against $\Phi_{non\text{-}phy}$ for residual, non-pigmented particles in shelf and offshore stations (as you derive later or non-mineral POM in estuarine samples).

    We carefully re-assessed the relationship between Φ_p *and* a_p *and found that* Φ_p *actually decreased with* a_p *in the estuary and shelf. This relationship is now discussed in relation to the POC:SPM ratio (page17.line12-page18.line5). Fig. 4b is changed to* Φ_p *vs.* $a_{p,412}$*.*

16. 16177.8-16179.17: This section (on derivation and analysis of Φ_{pom}) is based on the assumption that light absorption by inorganic particulate matter does not initiate or catalyze CO photoproduction. However, the CDOM literature (e.g., Gao and Zepp, 1998) suggests a role for iron in CO photoproduction, and iron-oxide minerals are the primary contributor to a_M (e.g., Stramski et al., 2007). So I'm not sure it's justifiable at present to normalize the CO production rate solely to the organic component of the light absorption (a0, Fig 6B) is very small, and somewhat uncertain- except for a dip at 375 nm (due to spectrophotometer lamp change?) it is noisy and flat except at wavelengths below about 325 nm, and the original a_{nap} data between 250-290 nm were extrapolated from longer wavelengths (16170.5-7). Since $a_{pom} = a_{phy} + a_0$, this implies that most of a_{pom} is due to a_{phy}, which is associated with living organisms. The lack of clear trend vs. salinity (Fig 7A) underscores the uncertainty in the derived Φ_{pom} values. This section should be rewritten and shortened with more attention paid to the uncertainties in derived a_0 and a_{pom} spectra, and toward justifying the assumption that POM absorption derives all observed, particulate CO production. If uncertainties in a_{pom} are large, then this discussion will be mostly speculative in nature and Figures 6 and 7 may be unnecessary.

    We agree that a role of iron oxides cannot be excluded. This section is substantially shortened and Figs. 6-7 are removed. We now only briefly mentioned that a correction for mineral absorption could increase the AQY in the estuary by many folds while at the same time cautioning that iron oxides could have been implicated in CO photoproduction (page19.line16-page20.line14). The procedure for deriving the mineral absorption coefficient is moved to the Supplementary Material.
    The seemingly low a_0 *values are partly caused by the large y-axis scale of* a^* *in Fig. 6B (now a separate y-axis is assigned to* a_0 *in the Supplementary Material). In fact,* a_0 *on average accounted for 64% (but with a large range of 7-90%) of* a_{pom} *across the*

280-600 nm range. Re-scaling the y-axis of a_0 *clearly shows that the "dip" in the blue in the old figure actually follows the general decreasing trend but that there is a broad elevation in the visible. This elevation could be caused by certain specific compounds with high absorption in the visible. The good correlation between* a_{nap} *and M and the agreement of the derived* a^*_M *with those reported in the literature suggest that the approach for deriving* a^*_M *and* a_0 *is generally reliable.*
Although living cells may have developed strategies to mitigate photooxidation in general, currently it is not certain whether living cells are less efficient than detrital materials at CO photoproduction. For example, Xie and Zafiriou (2009) determined the relative importance of CDOM- and particle-based CO photoproduction in fresh, non-poisoned samples from the St. Lawrence estuary and the Vineyard Sound in Mass. and found similar fractions of particle-based to total CO production to those observed in the present study. Our lab currently is measuring CO photoproduction by actively growing algal cells. Preliminary results show that those living cells photo-produced CO at surprisingly high efficiencies.

17. 16185.1-2: Extrapolation to other regions is only feasible if you assume that relative photoreactivity of particles and CDOM depends only on their relative absorption coefficients. As composition probably plays a large role, you should qualify this statement.

    We agree. This statement is removed.

18. 16185.11-16: These statements are not well supported by the data, as discussed above.

    These statements are changed to accommodate the revisions made in the relevant sections.

19. Figures, general: Please make sure all text on all figures is large enough to be legible at printed size.

    Small fonts are enlarged.

20. Technical comments

    Many thanks. All technical issues are addressed following the reviewer's comments except for the URL reference, which we will yield to the suggestion from the editorial staff.

References cited in responses to reviews:

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Gao, H., and Zepp, R. G.: Factors influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States, Environ. Sci. Technol, 32, 2940–2946, 1998.

Xie, H., and Zafiriou, O. C.: Evidence for significant photochemical production of *carbon monoxide by particles in coastal and oligotrophic marine waters, Geophy. Res. Lett, 36, L23606, doi: 10.1029/2009GL041158, 2009.*

Xie, H., Andrews, S. S., Martin, W. R., Miller, J., Ziolkowski, L., Taylor, C. D., Zafiriou, O. C.: Walidated methods for sampling and headspace analysis of carbon monoxide in seawater, Mar. Chem., 77, 93-108, 2002.

Zhang, Y., Xie, H., and Chen, G.: Factors affecting the efficiency of carbon monoxide photoproduction in the St. Lawrence Estuarine system (Canada), Environ. Sci. Technol., 40, 7771-7777, 2006.