Summary:

This paper makes significant new progress in quantifying the efficiency of photochemical carbon monoxide production by particles. The authors use their efficiency spectra to drive a model of coupled (dissolved + particulate) CO photoproduction in the southeastern Beaufort Sea. The photochemical contribution to the carbon cycle in this region is likely to undergo significant change as ice cover decreases so the model results are timely with respect to the warming climate. Measurements of particulate, photochemical reaction efficiencies require more stringent optical assumptions and experimental controls than are necessary in the absence of particles, and while the authors address some of these issues, there are a few missing details which I have identified below. Also unlike dissolved-phase photoreactions, particulate reactions may involve organic matter, inorganic minerals, or some combination of both. I would like to see stronger justification for the authors' assumptions in this respect. To date, however, there are few measurements of particulate photoreaction efficiencies, so this work represents an important contribution to the growing literature on this subject.

Comments refer to "page.line"

General comments

- 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.
- 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.
- 16164.4-7: The word choice is quite similar to that of Zafiriou (2002)—please paraphrase further.
- 16164.12: Mayer et al. (2006) should be included here
- 16165.1-3: Very recently, Estapa et al. (2012) published AQY spectra for DOC photoproduction from POC.
- 16168.12-13, 19: Consider listing cutoff-wavelengths instead of model numbers (or at least confirm that the digits in the model numbers are the wavelengths, for readers unfamiliar with these filters)
- 16168.18-21: Was the CO production rate constant throughout 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.

- 16171.9-16 and 16168.5-6: You use the b_b:K_d ratio at 300-400nm 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 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.
- 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?
- 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?
- 16169.4 – What was the uncertainty of the CO measurement and approximate, propagated uncertainty in spectrally-averaged Φ values?
- 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., $P_{x,\lambda} = \Phi_{x,\lambda} \times Q_{x,a,\lambda}$)
- 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 (Estapa 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.
- 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 be able to infer increased photoreactivity in pigment wavebands.

- 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 cannot 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 for non-mineral POM in estuarine samples).
- 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 rate. Second, the "organic, non-pigment" component of spectral absorption (a_0, 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 250-299nm 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 drives 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.
- 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.
- 16185.11-16: These statements are not well-supported by the data, as discussed above.
- Figures, general: Please make sure all text on all figures is large enough to be legible at printed size.

Technical comments

- 16162.27: change “no” to “not”
- 16164.26: change “affect” to “impact”
- 16165.3-4: sentence beginning “we modeled” – change to present tense to match the first sentence of the paragraph
- 16166.26-27: I believe the URL for a reference cited should be listed in the bibliography but not in the text.
- 16167.12: change “gravity-pushed” to “gravity-filtered”
- 16173.6-7: change “equivalent to the solar insolation-normalized production of CO” to “of CO production”
- 16175.9: change “DCM’s” to “At the DCM,”
- 16175.15-17: change to read, “…from the MS and CB corresponded to a narrow range of low a_{cdom} (…) and were scattered with respect to a_{cdom}.”
- 16175.18: change “DCM’s” to “at the DCM, the”
- 16176.24: change “displaying” to “display”
- 16178.13: change “surge” to “steeper increase”
- 16178.24: change “lied above” to “was larger than”
- 16178.25: change “interested” to “these”
- 16178.29: change “thereby disabling us to” to “and we could not”
- 16181.13-14: change “…increased for both CDOM and particles but the one for particles went up far more.” to “…increased for CDOM and especially for particles.”

References

Estapa, M. L., Mayer, L. M. and Boss, E.: Rate and apparent quantum yield of photodissolution of sedimentary organic matter, Limnology and Oceanography, 57(6), 1743–1756, 2012.

Gao, H. and Zepp, R. G.: Factors influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States, Environmental Science & Technology, 32(19), 2940 – 2946, 1998.

Mayer, L. M., Schick, L. L., Skorko, K. and Boss, E.: Photodissolution of particulate organic matter from sediments, Limnology and Oceanography, 51(2), 1064 – 1071, 2006.

Stramski, D., Babin, M. and Wozniak, S.: Variations in the optical properties of terrigenous mineral-rich particulate matter suspended in seawater, Limnology and Oceanography, 52(6), 2418 – 2433, 2007.

Zafiriou, O. C.: Sunburnt organic matter: Biogeochemistry of light-altered substrates, Limnology and Oceanography Bulletin, 11(4), 69–71, 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(24), 7771–7777, doi:10.1021/es0615268, 2006.