Reply to Reviewer #1 (RC C6270)

We thank the reviewer very much for his/her encouragement and positive opinions on our work. Our responses are italicized.

General comments

1) The DOC loss could partially be due to CO photoproduction yet this was not discussed. I think the authors need to correct their estimates (or provide bounds) considering some loss as CO.

We added the following text at the beginning of Section 3.2 for clarification: "Note that photochemical DOC loss leads to production of CO_2 (in the form of dissolved inorganic carbon, DIC) and carbon monoxide (CO), with DIC being the main product (Miller and Zepp, 1995). As photomineralization rates reported in this study were equated to DOC loss rates, the former also included the CO component. Based on our unpublished AQY spectrum for CO photoproduction from CDOM in Saguenay River surface water ($AQY_{CO}(\lambda) = 3.07 \times 10^{-10} \exp(5661 / (149.1 + \lambda)$), where λ is wavelength in nanometers), we estimated that the ratio of DIC to CO photoproduction was 31. Photomineralization was thus overwhelmingly dominated by DIC production in our study."

2) p14312 L12: Might it be better to just describe this as an oxygen gradient (supersaturated, saturated, depleted) after describing how the oxygen conditions were achieved. I know there is the problem of some reoxygenation during sample transfer and I think the authors do a good job of making that caveat clear, but reference to O2-, air-, N2-purging is cumbersome.

"O2-saturated" and "O2-supersaturated" are a bit confusing when they refer to [O2] at equilibrium with air and close to saturation with pure O2, respectively, since "O2-saturated" is usually understood as "saturated with pure O2", and "supersaturated" can cover wide, unspecified ranges. Although the [O2]s in the O2- and N2-purged samples somewhat deviated from those expected from equilibrium with O2 and N2, respectively, they in fact are close to the equilibrium concentrations. For simplicity and approaching conformity to the practice of previous studies (Gao and Zepp, 1998; Xie et al., 2004; Lou and Xie, 2006), we now refer to the air-, O2-, and N2-purging as air-, O2-, and N2-treatment, respectively. As we have reported the initial [O2]s for each of these treatments and explicitly stated that the [O2] for "O2-saturated" was slightly below O2-saturation and for "N2-saturated" was slightly above free of O2, we hope there will be no confusion/misunderstanding arises from using these expressions.

3) P14313: "TDOM" often is used for terrigenous (terrestrial) DOM so its use to describe transparent CDOM is confusing. Also, perhaps misleading. For example, is this meant to convey transparency at 330 nm or transparency at all wavelenghts, even

deep into the UV? If the former, this certainly is not correct as molecules may lack charge transfer for absortpion bands in the mid UV but absorb strongly at say 254 nm. If the latter, the discussion as written was purely speculative. One way forward is to perhaps show how slope values (S or SR) change during photodegradation. If slope changes all line up together over the first 50 hours of exposure (re: Fig 3) and then diverge, you may get a bit more insight to the differences between oxygen conditions.

We agree with the reviewer. We tested other wavelengths, 254 nm, 300 nm, and 400 nm, and found the ratios of the fractional DOC loss to the fractional a_{CDOM} *loss are somewhat lower compared to those at 330 nm but the patterns are similar (Fig. 1 below). The discussion of TDOM is now removed and replaced with a statement of "A closer examination of the data indicates that the ratio of the fractional DOC loss to the fractional* $a_{CDOM}(330)$ *loss decreased from 0.82 in the* N_2 *treatment to 0.64 in the air treatment to 0.54 in the* O_2 *treatment (Fig. 5C). Similar results were obtained at the wavelengths of 254 nm, 300 nm, and 400 nm (data not shown). Therefore, photochemical DOC loss proceeded more efficiently under* O_2*-deficiency than under oxic conditions on a per-*a_{CDOM}*-loss basis, opposite to the trend of the time-based DOC loss rate. In other words, higher fractions of CDOM were mineralized under* O_2*-depletion than under oxygenation."*

Accordingly, the original statement in the Summary, "Photochemical breakdown of CDOM led to a nearly complete mineralization (i.e. DIC production) under suboxic conditions but to only a partial mineralization under oxic conditions, with the rest transformed to TDOM", is modified to "Photochemical breakdown of CDOM led to a higher degree of mineralization (i.e. DIC production) under suboxic conditions than under oxic conditions".

Following the reviewer's suggestion, we also plotted the time-course variations of the spectral slope ratio (now Fig. 3C), S_R*, defined as the slope coefficient between 275-295 nm divided by the slope coefficient between 350-400 nm (Helms et al., 2008). A short discussion of* S_R *was added to Section 3.1, which is copied as follows:*

At the start of this section: "Figure 3 shows the time-course variations of $[O_2]$*, pH, the absorption coefficient at 330 nm (*$a_{CDOM}(330)$*), and the spectral slope ratio (*S_R*) defined as the ratio of the spectral slope coefficient between 275 nm and 295 nm to that between 350 nm and 400 nm.* S_R *has been used to characterize the source, molecular size, and photoprocessing of CDOM (Helms et al., 2008)."*
After describing loss of CDOM: "S_R *continuously increased over the entire irradiation period in the air- and* O_2*-treatments;* S_R *in the* N_2*-treatment increased with irradiation time up to ~120 h and became stable thereafter (Fig. 3C), suggesting a complete exhaustion of* O_2*. Notably, the changes in* S_R *for the three different* O_2 *levels nearly lined up together during the first 24 h of irradiation but started diverging at ~48 h when* $[O_2]$ *in the* N_2*-treatment dropped to a constant level (Fig. 3A)."*

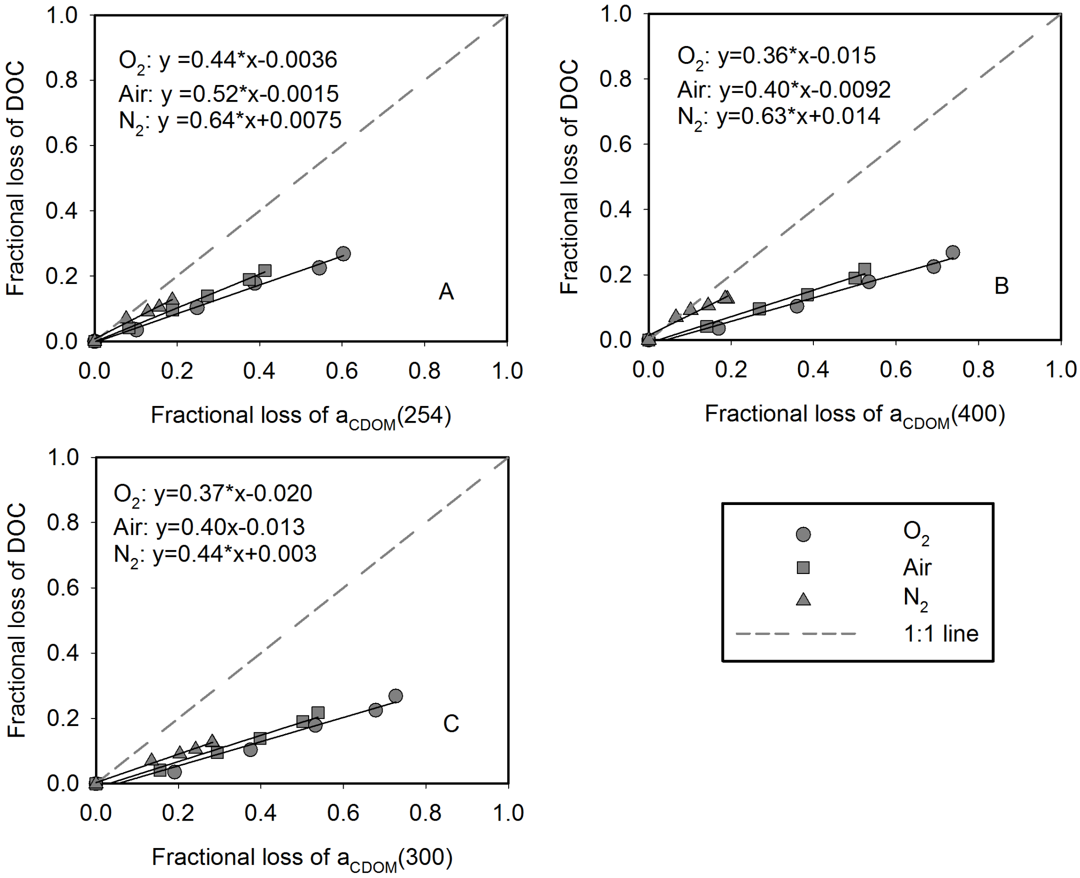

Fig. 1. Fractional DOC loss versus fractional a_{CDOM} loss at 254 nm (A), 300 nm (B), and 400 nm (C).

4) The role of lignin in explaining these results could be better emphasized. The methoxy (-OCH3) groups in dissolved lignin are good candidates for CO, CO2, and CH4. P14314, L17-21: Makes sense if the aldehydes in lignin are being oxidized to acids.

We are unable to find papers directly linking the methoxy groups in dissolved lignin to CO2 photoproduction or photochemical DOC loss. Benner and Kaiser (2011) revealed that the photodegradation rate constant of lignin phenols increases with the number of methoxy substitutions on the aryl ring. However, as the lignin and its degradation only account for minor portions of the bulk DOC and the photochemical DOC loss, respectively, the results of Benner and Kaiser (2011) do not prove that the methoxy groups play a critical role in DOC photodegradation or that they are good candidates for CO2 photochemically produced.

Methoxy groups do enhance the efficiency of CO photoproduction from model aromatic compounds (Stubbins et al., 2008). Nevertheless, the direct precursors for CO are likely other compounds, such as formaldehyde, that are produced from photodegradation of methoxy-substituted aromatic compounds (Stubbins et al., 2008).

Furthermore, the CO AQY rapidly decreases with photobleaching (Zhang et al., 2006), suggesting a quick photochemical removal of the methoxy-substituted lignin phenols if they do play a dominant role in CO photoproduction. In contrast, the DOC photomineralization AQY observed in the present study either remained stable (in the O_2*-saturated sample) or increased (in the* O_2*-supersaturated sample) with photobleaching, which appears contradictory with a methoxy-driven mechanism.*

CH_4 *production from photodegradation of methoxy-substituted lignin model compounds, such as methoxy-substituted stilbenes, under anaerobic conditions has been reported (e.g. Weir et al., 1995; 1996). The proposed mechanism involves the cleavage of the O-*CH_3 *bond, producing the* CH_3 *radical followed by H-abstraction to generate* CH_4*. A brief discussion of this* CH_4 *production pathway, as shown below, is now added to "Future work" in Section 4:*
"…and methyl ester that are naturally present in aquatic environments. For river and riverine-impacted coastal waters, particular attention should be paid to methoxy-substituted phenols in dissolved lignin, since these compounds are highly susceptible to photodegradation (Benner and Kaiser, 2011) and since the methoxy groups in certain lignin model phenols have been demonstrated to be efficient precursors of CH_4 *under anaerobic conditions (Weir et al., 1995). Moreover, anoxic microniches…"*

5) The CH3 radical may be a key intermediate in low O2 settings. I wondered, too, if nitrate photolysis is important in these photochemical pathways?

Photolysis of nitrate produces OH radicals (Zarifiou and True, 1979). The reactions of the OH radical with bromide and carbonate/bicarbonate produce the Br_2^- *and* CO_3^- *radicals (Zehavi and Rabani, 1972; True and Zafiriou, 1987), which might be involved in the photosensitized production of the* CH_3 *radical and hence* CH_4 *(Bange and Uher, 2005). However, this process can be important only in waters containing elevated nitrate concentrations. In waters having normal levels of nitrate, the dominant source of the OH radical is CDOM photooxidation (Mopper and Zhou, 1990). This topic is beyond the scope of the present paper (due to lack of relevant data, such as nitrate concentrations) but certainly warrants investigation in the future.*

Specific comments

p14310, L8: "moisturized" – better word choice here; not worried about methane's complexion! :)

The sentence is revised to "…, the dry CH_4 *standard was saturated with water vapor before injection."*

p14315, L15: "different" not "differed"

"differed" is changed to "different".

p14321, L9: This result has been observed in CDOM photobleaching; may wish to explore this result a bit more. Photomethanificiation tracks more closely with photobleaching than does photooxidation? Perhaps photomethanification is more of a primary photochemical process. No photodecarboxylation requried, for example.

In this study, photomethanification in the air-treatment tracked nicely with both photobleaching (Fig. 6B) and photomineralization (i.e. a major photooxidation pathway, Fig. 5C). This was because photobleaching and photomineralization were correlated very well (Fig. 5B). The relative contributions of UVB (16%), UVA (44%), VIS (40%) to CH_4 *photoproduction were also similar to those (UVB: 15%; UVA: 41%; VIS: 44%) for photomineralization. Therefore, based on these results, it's hard to infer whether photomethanification is a primary or secondary photochemical process. Bange and Uher (2005), however, found that photoproduction of* CH_4 *from acetone is a photosensitized process (*CH_4 *is produced in the presence of CDOM but not produced in pure water). The observed behavior of* CH_4 *production at different* O_2 *levels, is in line with the mechanism of the* CH_3 *radical as an intermediate followed by H-abstraction, as proposed by Bange and Uher (2005). The reaction of the* CH_3 *radical with* O_2 *is favored under oxic conditions, leading to lower* CH_4 *production rates. This mechanism has already been discussed in our paper.*

For these reasons, we decided not to further elaborate the mechanism but added a line to the Summary and Future Work that future work should also elucidate the mechanisms of photomethanification of organic matter in natural waters.

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