Reviewer #1:

We thank reviewer #1 for their praise of the data and topic, and the thorough review. We have considered each of the comments, responding to each in turn below. In most cases we have incorporated the recommendations and believe this has led to a stronger manuscript. The reviewer's comments and our responses are as follows:

Request in general comments: The reviewer asks for more discussion of how our findings impact the global black carbon budget.

Action: The data presented apply only to dissolved black carbon defined as dissolved condensed aromatics. The data have been used to constrain the global oceanic sink for dissolved black carbon. This is already a major extrapolation with considerable error associated. We think that any further discussion would not be sufficiently supported by the data collected in this study and would be too speculative. Therefore, no further discussion of how our results apply to other pools of black carbon or of DBC in other environments has been added.

"Specific comments"

Request: P 487: is it necessary to use both DOM and DOC?

Response: Yes. DOM defines the total pool of dissolved organics. DOC is used to denote the fraction quantified as C. A line to this effect is added to the methods section 2.4.

p. 487, lines 12-19: What is the purpose of referring to "polycyclic aromatics" as PCA, when they are most commonly known as PAHs? This may only lead to confusion for your readers. Consider removing the acronym PCA, as you never refer to it later.

Response: To avoid confusion the term "PCA" is deleted. In a strict sense, PAHs do not contain heteroatoms. DBC is highly functionalized (mainly carboxyl groups), so the term "polycyclic aromatics" is more appropriate than PAHs.

p. 487, bottom of page: Update this paragraph to include the more recent citation from Kaiser and Benner (2012) that found hydrolysable amino acids to be 5 to 18 % of DOC.

Response: Kaiser and Benner 2012 found the sum of total hydrolysable amino acids + neutral sugars + amino sugars to be 5-18% of the labile fraction of DOC, not 5-18% of the total DOC. Their concentrations of quantifiable compounds in the 2012 paper equate to the same % fractions of total DOC as reported in 2009. No edit made.

p. 488, first paragraph: what about atmospheric sources of dissolved BC? There may not be papers demonstrating the direct contribution of aerosols to the DBC pool, but open ocean sediments contain terrestrial sources of aerosol black carbon (i.e. work by Lohmann). Please add aerosol deposition as a potential source of BC to the ocean either here or later on page 488 (see comment re: p488 line 20).

Response: Edit made to include reference to likely deposition of DBC to the ocean.

p. 488, line 10: The Ruiz-Morales and Mullins reference is very interesting, but I do not understand its context here. What does this paper have to do with recalcitrance of aromatic material in the environment? Perhaps you meant to cite it elsewhere in the paper. Are there any citations of the BPCA distributions (or oxidation products) of asphaltenes?

Response: Reference removed.

p. 488 line 15: At about this point in the paper, I was surprised that the relative molecularweight of the DBC you are quantifying had not yet been mentioned. To me, referring toDBC as polycyclic aromatics communicates to your readers that you have measuredPAHs such as pyrene, perylene or coronene in seawater. Since you have high resolutionMS data on the structure of the compounds (i.e. the conversion of BPCAs to BC, Dittmar2008), why not mention the size of the molecule? Please clarify and report either here orearlier in the paper that your assume an average molecular weight of the DBC and statethis value so your readers will understand the size of molecule you are quantifying asDBC.

Response: MW added to third paragraph.

p. 488 line 18: using the term “radiocarbon dating” implies that there was a one-time modern source of carbon that has been stored away from other carbon inputs and aged fora some period of time. As you are well aware, the marine black carbon is a dynamic poolwith a wide variety of sources that have significantly different contributions of 14C. Sinceit is clear that some forms DBC may contain fossil carbon that is free or depleted of 14C(i.e. a sea floor source of carbon: Dittmar and Paeng, 2009; fossil fuel influence samplesin aerosols: Gustafsson et al, 2009), it is more accurate to say that Ziolkowski and Druffeldetermined the 14C content of DBC. The latter acknowledges the fact that not all sourcesof DBC are enriched in 14C (i.e.: modern), while “radiocarbon dated” does not. Pleasereplace “radiocarbon dated” with “determined the 14C content” both here and on p. 496line 8.

Response: “Radio-carbon dated” has been removed

p. 488 line 20: Again, what about aerosol deposition? Do we know it is insignificant? Aerosol deposition of fossil fuel derived BC (i.e. burning of coal or oil that is 14C depleted) will likely contribution to 14C depleted DBC in the ocean. Could that not also be a source of DBC? Asian brown cloud black carbon was depleted radiocarbon (Gustafsson et al 2009). Please mention that this could be a potential source of BC to the marine DBC pool.

Response: The line quoted talks about compounds distributed throughout the oceans. It is not clear how the reference mentioned by the reviewer pertains to molecules occurring everywhere in the ocean. However, that deposition is a possible source of aged DBC to the surface ocean has been added in response to a previous comment.

p. 490, line 11: Please state the duration of irradiation of the test samples.

Response: It is stated in line 12.

p. 490, line 15: So, would your 28 day irradiation effectively be equal to 28*1.27 = 35 twelve hour days of irradiation? Why not say so somewhere within the text?

Response: No edit as such a statement would require many caveats and we did not want to imply the light received was equivalent to a certain number of solar days as: 1) the light field and flux from the solar simulator was not quantified directly via actinometry, 2) sunlight levels per day change with latitude and season, and 3) reporting such a number is of no value for modeling work. It is however easy to calculate, as the reviewer has done, from the data presented.

p. 493, line 1: Using this analytical method (the BPCA method), aren't there typically more isomers of B4CA formed during the oxidation of black carbon? Why was only one B4CA isomer quantified? Because only one isomer of B4CA is reported here, the reported relative proportions of B4CA to B5CA and B6CA are significantly different than that report by Dittmar, 2008. How does your reader know that the 1,2,4,5-B4CA reported here has a similar photochemical response to the other B4CAs that are not reported? The fact that you are reporting only a portion of the signal is worthy of discussion either here or when in Section 3.3. Please state what assumptions you are making by only reporting one of the three isomers of the B4CA.Also, do you not quantify B3CAs, as was done in Dittmar (2008)? Please state
why not.Other BPCA users (including Glaser et al 1998) acknowledge the formation of nitrated BPCA during the oxidation of BC to BPCAs. Theoretically, there would be nitrated B4CA formed during the oxidation of BC in DOM. Thus, you may be only quantifying a portion of the DBC oxidation products by only quantifying one of six of more forms of B4CA. It could be that the portion of the DBC oxidation products that you are not quantifying (the nitrated BPCAs, other B4CA, as well as B3CA) are more stable upon exposure to simulated sunlight than those compounds that you can quantify. Thus, the strength of your photo-lability signal is enhanced as a function of what data is presented here. Please comment on how not quantifying the nitrated BPCA and B3CAs may be affecting your interpretation of the photochemical loss of BC.
Was the formula in Dittmar (2008) used for all of these samples or were the samples measured via FT-ICR-MS before and after irradiation? Please comment on howaccurate would the formula in Dittmar (2008) be considering the structural formula of theDBC changed over the course of the irradiation. If you measured the samples via FTICR-MS before and after irradiation, including that data would complement your BPCAdata very nicely.

Response: We have tried to address the above comments in the text, without adding excessive and redundant text to the manuscript. The edits and rationale for them are presented below:

The BPCA method section (2.6) has been edited to address the use of one isomer of B4CA, the lack of B3CA data and the rationale for calculation of total DBC concentrations from B5CA and B6CA.

That only one B4CA isomer was quantified is now also noted twice in section 3.3.

Nitrated BPCAs – any production of nitrated B4CA during oxidation would result in an underestimate in the concentrations of B4CA. This is addressed via the assumption that oxidation is not 100% efficient added to the methods section.

It is our understanding that for nitrated BPCAs to be considered dissolved black carbon, they were nitrated during nitric acid oxidation, not in the water sample prior to extraction and analysis. As such they should have similar photo-reactivity to the B4CA isomer quantified. Nitrated BPCAs for which the N derived from the DOM (i.e. they were N containing in the original seawater sample) would not be considered condensed aromatics. As these compounds do not fall under our definition of DBC the possibility that they may exist in our samples is not addressed. To do so would simply add statements of conjecture with no discernable value, thus diverting from the focus of the paper, the latter being praised by reviewer #2.

Reactivity of B3CAs – a note is added to suggest that B3CAs, which were not analysed here, should be less photoreactive than their more condensed analogues (Section 3.3).

The calculation of DBC was based upon Dittmar 2008 and modifications now added to the methods section. No FT-ICR MS data exists for this sample set.

p. 493, line 12-16: Does the time period of photo-exposure matter for these other studies?

Response: The second paragraph of the methods now includes a caveat about the potential differences in optical conditions between studies. It does not provide an in depth review of each of the other studies which are readily available to the reader.

p. 494, line 23: Please comment on how quantitative the DBC concentration numbers areif not all of the oxidation products of the black carbon were quantified?

Response: Errors for total DBC are believed to be an underestimate (due to incomplete PPL recovery and/or less than 100% efficient conversion of DBC to BPCAs). Precision is ~2%. See methods addition.

p. 495, line 3: Gonsior et al (2009) would also be a very appropriate reference to cite here.

Response: References added.

p. 496, line 25 or so: Do you think the photochemical removal of DBC is a primary or secondary photochemical reaction? It would be useful for you to comment on whether ornot the CDOM quality will ultimately influence the rate photochemical removal of DBC and if you would expect to see different rates of photochemical loss under different conditions.

Response: The presented experiments offerinsufficient insight into the mechanism of DBC photodegradation to make a discussion of possible mechanisms meaningful. However, it is now noted that other studies have shown that CO2 is produced from aromatic rings during irradiation (2nd paragraph Section 3.2). This does not offer insight into whether the reaction is primary or secondary, just that aromatic carbon can be a source of the carbon in photoproduced CO2.

Without more quantitative assessments of DBC photodegradation rates (apparent quantum yields) it is hard to determine how the rates will vary in natural waters. This is discussed in section 3.4.We have not expanded upon this subject in the paper.

Reviewer #2

We thank reviewer #2 for the positive review and constructive comments. Each of their comments was addressed as detailed below:

Response to minor revisions:

The reviewer suggested reference to Vahatalo et al. 1999 to note that aromatic cores can be the source of photoproduced CO2 and therefore photo-mineralization of DOC. This edit has been made in section 3.2.

Request: Remove the "the" in the fragment: On the 20th of September

Action: None. The inclusions of the "the" is grammatically correct in British English. I believe British English is accepted by the journal. If not, then this edit and uses of English spelling and grammar will be altered to US spelling.

Request: add limit of detection and volume analyzed to section 2.4 DOC

Action: The limit of detection and precision of DOC analyses as calculated during method development in our laboratories is reported in Stubbins and Dittmar (2012 – in minor revision at L&O Methods). The values calculated and reported in that paper are now added to the current paper's methods section at the end of the paragraph in section 2.4. The volumes analyzed have also been added.

Comment: p493. Ln 12: The comparison amongst these different samples is fine, but I wonder if it is entirely accurate with respect to irradiation regime. Were all samples optically thin? Are these DOC changes based on similar irradiance exposures (eg, approximating natural sunlight)?

Action: Edited beginning of paragraph #2 in section 3.1 to mention that the various literature cited used irradiation sources, flasks (pathlengths) and CDOM concentrations (absorption coefficients) that differed from those used in our current dataset, therefore the quality and quantity of light "seen" by our chromophores differed from that seen by the literature CDOM. Edit reads: The previous irradiations noted above were conducted under various light sources, in irradiation vessels of varying pathlength and include samples with varying absorption coefficients. As such, the quantity and quality of light received by CDOM chromophores varied between those studies and the work presented here. Nevertheless, it is apparent that in terms of its photo-lability, NADW DOC has more in common with the terrestrially influenced samples than those freshly derived from phytoplankton.

Request: p493,L19: It is worth noting that these are C18 extracts and not whole DOC. It is an important subtlety that should be acknowledged
Edit: Now reads: Lignin in solid phase extracts and the d13C of high molecular weight DOM, both signatures of DOM source, indicate that terrestrial DOM is exported to NADW from the Arctic Ocean (Hernes and Benner, 2006).

Request: p494,L27: Why not write "a 95% loss in DBC" to keep consistent with DOC and CDOM?

Edit: "20-fold" is replaced with 95% as requested.

Request: Replace fall with decrease

Action: Done

Request: p496,L27: "In the current irradiations DBC tracked CDOM..."; please re-word, this is confusing.

Edited to read: In the current irradiations, the photo-degradation of DBC and CDOM light absorption were well correlated, unfortunately there is no estimate of the global oceanic photo-chemical CDOM sink for use in scaling DBC photo-degradation to the global ocean.

Comment: p497: These paragraphs seem more more like Discussion rather than Conclusions. I recommend moving them up to the Discussion section.

The discussion and conclusions have been redrafted with the majority of the old conclusions moved to the discussion.