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Title: Photo-lability of deep ocean dissolved black carbon

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General comments:

Black carbon is a reduced form of carbon that is produced by the thermal alteration of carbon. This could occur through burning or other high temperature processes. It is thought that black carbon may be an important long-term carbon sink due to the supposed recalcitrance of this aromatic carbon. Marine chemists have been interested in black carbon due to it potential to be a recalcitrant portion of the dissolved organic carbon pool. This study suggests that black carbon in the deep ocean, which may originate from hydrothermal sources on the sea floor, is susceptible to photochemical breakdown and that these highly aromatic compounds are much more labile than we have previously thought.

In this study, the authors have exposed dissolved organic carbon sampled from 3000 m depth in the Atlantic Ocean to the equivalent of a month's worth of sunshine and subsequently quantified the loss of BC at four time points during that month. The black carbon in this study was measuring using chemical marker molecules, benzene polycarboxylic acids, formed during the oxidation of black carbon. While this study presents a very limited amount of data, only four time points on one water sample, this is the first dataset of its kind. These results are important for two reasons: 1) these findings dissuade the hypothesis that aromatic in the deep sea is resistant to breakdown and 2) the authors have identified a black carbon loss process that has yet to be considered in context of the currently unbalanced global black carbon budget. In my opinion, as currently written this paper has not yet reached its full potential. The authors have focused primary on the lability of this material. I would have like to see more discuss on the how these finding may impact the global black carbon budget. Global sources of black carbon far outweigh the known sinks. But since we are not knee deep in black carbon, there must be loss processes that have yet to be indentified. This study identifies a loss process of black carbon that has never been quantified before: the photo-oxidation of black carbon in marine dissolved organic carbon. I think the authors have a wonderful opportunity to discuss the implications of these findings beyond the marine DOC pool and specifically discuss how these findings may impact the global black carbon budget. Expanding the focus of the discussion will enable the paper to have a much broader impact on the scientific community.

Specific comments:

p. 487: Is it necessary to use both DOM and DOC? Please either distinguish how DOM is different from DOC or edit the document so that only one form of organic carbon is referred to.

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.

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.

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).

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?

p. 488 line 15: At about this point in the paper, I was surprised that the relative molecular weight of the DBC you are quantifying had not yet been mentioned. To me, referring to DBC as polycyclic aromatics communicates to your readers that you have measured PAHs such as pyrene, perylene or coronene in seawater. Since you have high resolution MS data on the structure of the compounds (i.e. the conversion of BPCAs to BC, Dittmar 2008), why not mention the size of the molecule? Please clarify and report either here or earlier in the paper that your assume an average molecular weight of the DBC and state this value so your readers will understand the size of molecule you are quantifying as DBC.

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 for a some period of time. As you are well aware, the marine black carbon is a dynamic pool with a wide variety of sources that have significantly different contributions of ^{14}C. Since it is clear that some forms DBC may contain fossil carbon that is free or depleted of ^{14}C (i.e. a sea floor source of carbon: Dittmar and Paeng, 2009; fossil fuel influence samples in aerosols: Gustafsson et al, 2009), it is more accurate to say that Ziolkowski and Druffel determined the ^{14}C content of DBC. The latter acknowledges the fact that not all sources of DBC are enriched in ^{14}C (i.e.: modern), while "radiocarbon dated" does not. Please replace "radiocarbon dated" with "determined the ^{14}C content" both here and on p. 496 line 8.

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 ^{14}C depleted) will likely contribution to ^{14}C 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.

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

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?

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 how accurate would the formula in Dittmar (2008) be considering the structural formula of the DBC changed over the course of the irradiation. If you measured the samples via FT-ICR-MS before and after irradiation, including that data would complement your BPCA data very nicely.

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

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

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

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 or not 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.

p. 497, lines 13-17: From what I understand of your discussion here, you are saying that the photochemical turn over of black carbon is faster than the “apparent age” of DBC as determined by Ziolkowski and Druffel. But doesn’t your comparison of rates here also assume that there is one source of DBC to the ocean and it is ^{14}C modern? I do not believe that is an accurate assumption based on what we know about the non-sea surface sources of DBC, which are likely to be depleted in ^{14}C (i.e. Dittmar and Koch, 2006; Dittmar and Paeng, 2009). To remedy this issue, please expand this discussion point to (a) also relate this loss term to potential inputs of BC (i.e. is there accumulation over time or is this loss larger than potential input terms) and (b) edit this section to further clarify what assumptions you are making, and how realistic these assumption are, when comparing this loss term to the ^{14}C data of Ziolkowski and Druffel (2010).

It is worth keeping in mind that ^{14}C values can only be used for turnover time calculations when the system has a modern source, a single loss term and is in steady state. See Trumbore and Druffel (1995) for a discussion for limitations of the use of turnover time and ^{14}C, as well as the differences between turnover time and residence time. You might be interested to know that according to the residence time model outlined in Trumbore and Druffel (1995), Ziolkowski and Druffel’s reported ^{14}C DBC values have a residence time close to 50,000 years.

p. 497, line 15: The rate of BC loss that you are reporting is pretty significant! I think you can take the discussion of your findings a step or two further. For example, what does this loss rate mean for (a) the global black carbon budget and (b) the fate of the carbon that is being photo-oxidized? Does this new loss term help balance the global black carbon budget? If this material is photo-oxidized, does it reside in the seawater as dissolved inorganic carbon, or does could it ultimately be emitted to the atmosphere as CO_2? Please expand upon your discussion here to consider some of the above points.

How do these results translate to BC that is not in the deep sea? Based you’re your results, I would have liked to see some sort of discussion of the physical relevance of exposing deep water to sunlight for this duration. How likely is this to occur? How long does water typically reside in the mixed layer? Would these results be different if you had used surface DOC? If so, why?

p. 497, line 18-21: Note: if the recalcitrance of the molecule is being implied via the ^{14}C content, it is worth noting that a DBC source with old ^{14}C would also make the compounds appear more recalcitrant, thus supporting the hypothesis of a fossil source of DBC on the sea floor (Dittmar and Paeng, 2009, Dittmar and Koch, 2006).

Knowing that DBC is photo-labile, please comment/speculate on why the observed concentration (Dittmar and Paeng, 2009) and ^{14}C content (Ziolkowski and Druffel, 2010) of DBC fairly constant in the world’s oceans.

p. 497 line 26: again Gonsior et al (2009) would be a very appropriate reference to cite here.

p. 498, line 18: I like the long term vision here, but I wonder if this analytical method is still in its infancy with regard to assembling a budget of marine BPCA data. Can you speculate on if there would be different BPCAs observed if different DOC isolation techniques were used (SPE, RO/ED, ultra-filtration)? Is there any interlab variability with respect to quantifying BPCAs? How useful will the dataset be if users cannot report all the BPCA (i.e. no all B4CAs being reported, some users report nitrated BPCAs while others do not)? Perhaps you can make technical recommendations of what developments would enable building a robust BPCA budget.

p. 503 table 1: (a) Please include a description here or in the methods of how the DBC was calculated from the BPCA concentrations. Also, is this a minimum BC concentration if there was only one B4CA isomer and no B3CAs quantified? (b) Please describe either here or in the methods section how the errors of the DBC concentration were determined. Was this replicate samples or some other method of error estimation? (b) B6CA (nM) after 28 days: You had no absolutely no error associated with this measurement? Is that reasonable?

Technical comments:

-p 489, line 5: I found this sentence is awkward; consider editing it for clarity.

-p. 497, line 17: Check the spelling of the citation.

-p. 505, figure 2: I tried plotting the data in Table 1 to reproduce Figure 2. My slope did not agree. Check if your numbers in Table 1 can reproduce the reported slope in Figure 2.

Additional references:

Glaser et al (1998). Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Organic Geochemistry, vol. 29 (4) pp. 811-819

Gonsior et al. (2009). Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution fourier transform ion cyclotron resonance mass spectrometry. Environmental Science and Technology, 43, 698-703.

Gustafsson et al (2009). Brown Clouds over South Asia: Biomass or Fossil Fuel Combustion?. Science, vol. 323 (5913) pp. 495-498

Kaiser, K., and R. Benner (2012), Organic matter transformations in the upper mesopelagic zone of the North Pacific: Chemical composition and linkages to microbial community structure, *J. Geophys. Res.*, 117, C01023, doi:10.1029/2011JC007141.

Trumbore, S. E. and E. R. M. Druffel, (1995), Carbon isotopes for characterizing sources and turnover of non-living organic matter, in, Zepp, R. G. and Ch. Sonntag, (eds) Role of Non-Living Organic Matter in the Earth's Carbon Cycle, John Wiley and Sons, p. 7-22.