

## ***Interactive comment on “Indications for a ubiquitous dissolved pigment degradation product in subsurface waters of the global ocean” by R. Röttgers and B. P. Koch***

**Anonymous Referee #1**

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Review of bg-2011-383: Köttgers Koch. Indications for a ubiquitous dissolved pigment degradation product in subsurface waters of the global ocean.

General comments This manuscript presents evidence for the occurrence of a pigment like absorption peak at around 410 nm in subsurface ocean waters, which superimposes the overall exponential shaped absorption spectrum of colored dissolved organic matter (CDOM). They find this peak to be widespread within their set of samples from the Atlantic and a few samples available to them from the Pacific and additionally can trace a similar signal in the particulate absorption from depths with low phytoplankton abundance. Fluorescence spectroscopy on DOM isolates reveal that the absorption in

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this region also results in a fluorescence at wavelengths between 650-680 nm. They conclude that these signals originate from a “bacterial respiration pigment”. I find the dataset interesting but consider the work in its current form as unfinished. Much more could be obtained from this data with some modeling of the absorption spectra and plotting of the data with other parameters (oxygen, T, or S), along the lines of what is published in Breves et al 2003. I was not originally aware of the Breves paper, but after reading it I find that this BG submission does not really provide anything new on the origins of this material, rather just shows that it can also be found in the Atlantic. If the authors expand on their data analysis and calibrate the fluorescence signals they would be able to directly compare the data they have collected with the earlier work in the Arabian Sea. Additionally it would be good to see auxiliary data. What did the water column temperature, salinity and oxygen profiles look like? At least for the stations where profile CDOM samples were taken. Finally, I like the idea that it may represent cytochrome c and am sure there is some link to redox conditions. It would be a great idea to discuss this in the Discussion rather than look at latitudinal patterns, which I do not quite know how to interpret. In its current condition I do not find the manuscript suitable for publication, but recommend that the authors expand the data analysis on what seems like an interesting phenomenon that many of us have not seen in our own datasets, possibly due to storage problems.

Some specific comments

1. I find the paper would benefit from a clearer distinction from the Breves et al 2003 paper. Rather than focusing on Broenkow et al 1992 which is quite vague. Why not present the conclusions of Breves et al 2003 and lead on to how this work will build on it? Another paper that seems to be very relevant is Broenkow et al 1985, although it does not seem that they are able to distinguish clearly between the two emission peaks you find (surface vs 200m at 650 and 670 nm).

2. I find it intriguing that some many earlier studies have not found similar peaks in the absorption spectra. One possibility is that the signal is degraded during storage

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(Breves et al 2003) and therefore may disappear below the detection limit of most standard spectrophotometers quite quickly. This should be discussed rather than just saying that all other studies have been on surface water samples (which is not true).

3. It would be good to see how the CDOM measurements compared between the two instruments used (PSICAM and the LWCC approach). It seems that some samples were measured on both (fig 3) but it is unclear which is which? I am convinced that the absorption peak is not an instrumental artifact but this could be made more convincing. Lines 164-172.

4. It is unclear how the fluorescence intensities were adjusted to compile the data from different measurements with different signal amplification into one EEM. The treatment of the fluorescence spectra in general was quite poor. There are several issues such as intensity calibration (what are the units?), instrument spectral bias correction and inner filter effects, which are basically ignored. This makes the data presented here impossible to compare with other studies using other instruments. This is especially relevant for your discussion where the position of maxima are slightly different between samples (can occur due to inner filter effects) and studies (due to instrumental effects). See Murphy et al 2010 for some of these issues *Environ. Sci. Technol.* 2010, 44, 9405–9412. For example the greatest fluorescence intensity should be from excitation below 300 nm. This is apparent once you correct for inner filter effects.

5. There is repeated use of “absolute” and “specific” which I think is incorrect and needs revising. How does the “absolute absorption” (e.g. 147) or fluorescence (e.g. line 204) differ from just the absorption values?

6. Breves et al 2003 carried out an analysis of this absorption peak by modeling the absorption spectra using an exponential and a Gaussian. I suggest that a similar approach should be used here. This would allow you to isolate the signal from this absorption peak and plot with other parameters or just look at vertical profiles. See their Figure 11. This would also help you with comparing with the particulate absorption

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data e.g. in line 187-192.

7. I suggest you try to include a spectrum of cytochrome c (absorption and fluorescence). It will make your arguments more convincing in section 4.4. In particular there might also be a dependency on whether it is oxidized or reduced which may give rise to some of the correlations with low oxygen conditions (shown in earlier work, but why not here (if you have the oxygen data from the CTD?)).

Minor details

Line 32. Include reference for “ a large proportion of is refractory”.

Line 32-34. Rephrase this sentence. Possibly expand. Try to cover too many issues in one sentence.

Line 36. “suitable” seems like the wrong word to use.

Line 39. “accessed” should this be accessed.?

Line 41. Drop “e.g.”

Line 44. “ mostly performed in UV rather than at visible”. I don't agree. The majority of studies measure CDOM absorption at least between 300 and 650 nm, so well into the visible range.

Line 46-47. I agree that many studies have focused on surface water due to remote sensing, but there are also several works covering deeper CDOM samples. E.g. Del Castillo, *Coble Deep-Sea Research II* 47 (2000) 1563-1579. Nelson et al. *Deep-Sea Research I* 45 (1998) 931-957. Stedmon Markager *Limnol. Oceanogr.*, 46(8), 2001, 2087–2093. Nelson et al. / *Marine Chemistry* 89 (2004) 273–287. These are missing from the discussion on the origins of CDOM.

Line 49. Either it degrades or it is refractory.

Line 50. Have you considered other studies on the origins of CDOM. For example

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some of the papers above discuss this. Also Steinberg et al have a range of peaks being produced by organisms Mar Ecol Prog Ser 267: 45–56, 2004, and Norman et al (Deep-Sea Research II 58 (2011) 1075–1091) show the presence of shoulders on CDOM absorption spectra.

Line 51. The last sentence on fluorescence appears as a bit of an add on. As a lead on to the next section on red fluorescence it would be worthwhile expanding on this some explaining that a fraction of CDOM also fluoresces.

Line 54. Start with “Previous studies have shown that”.

Line 67-68 What wavelengths was Broenkow measuring at. I could not find the ones for fluorescence or light attenuation.

Line 119. How about reporting the efficiency of the CDOM extraction? In fig 5 legend you mention normalized spectra, but in the figure the absorption coefficient is plotted. Is this right? Could the procedure really extract everything apart from a little at around 450 nm, and did it add absorption at 370 nm?

Line 153. “Linear deflection” what do you mean? Breves et al 2003 refer to it as a Gauss addition which seems easier to follow.

Line 178. DO you have a reference for the heterotroph/detritus absorption spectra from deep ocean?

Line 198. This also shows no dependency on instrument right?

Line 217-220. Or inner filter effects could cause this difference.

Line 245-247. This sentence seems too speculative.

Line 259. The absorption spectrum of cytochrome c also has peaks just above 500 nm which would also fit with your excitation spectra Fig 7b.

Line 276. Could also be explained by the lack of instrumental and inner filter correction.

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Line 282. What is the “absorption efficiency”?

Line 341-343. This sentence seems strange. Consider rephrasing.

Line 386-389. This is pushing it a little. Seems too ambitious and I am not quite sure how this can be related to rates.

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Interactive comment on Biogeosciences Discuss., 8, 10697, 2011.

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