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Biogeosciences Discussions



# *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 #2**

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

GENERAL COMMENT

This manuscript reports the occurrence of a shoulder at 410-415 nm in the absorption spectra of both DOM and POM in subsurface waters of a basin scale transect along the Eastern Atlantic Ocean. The authors also found this absorption shoulder in a few samples from Santa Barbara Basin and New Caledonia in the Pacific Ocean. Breves et al. (Ocean Dynamics 53, 86-97, 2003) have already described the presence of this shoulder in subsurface waters of the Indian Ocean and hypothesised that it was linked

to a pronounced fluorescence emission of the samples at about 660 nm when excited at 420 nm. This would mean that the absorption shoulder at 410-415 nm and the red fluorescence maxima recurrently found in previous works (e.g. Broenkow et al., Journal of Marine Research 43, 875-891, 1985) belong together and that it should be a pigment degradation product.

The innovation of this manuscript is the concentration of CDOM by solid phase extraction. However, the authors use the isolates just to study its absorption and fluorescence properties to link the absorption at 410-415 nm to the fluorescence emission at about 650-670 nm because they do not performed direct fluorescence measurements of the water samples. Unfortunately, the authors do not explore state-of-the-art high resolution molecular magnetic resonance or mass spectroscopy techniques that would probably allow testing their hypothesis that cytochrome c is behind the absorption shoulder.

In the present form, the manuscript looks just like a confirmation that the absorption shoulder at 410-415 nm also appears in more places than those reported by Breves et al. (2003), reinforcing the hypothesis, already posed by those authors, that it is an ubiquitous feature of the global ocean. To represent a significant advance in knowledge, this manuscript should either:

i) relate the shape and intensity of the absorption shoulder to the salinity (S), temperature (T) and apparent oxygen utilization (AOU) of the samples. If the absorption shoulder is a respiratory pigment, a significant correlation should be observed with AOU once the effect of water mass mixing is eliminated. Maybe the authors should try a multiple linear correlation with S, T and AOU. The manuscript by Carlson et al. (Deep-Sea Research II 57, 1433–1445, 2010) is a good example on how to proceed with this. In addition, the fluorescence maxima at Ex/Em 370 nm/420 nm that the authors found in their matrices are related to bacterial respiration (Romera-Castillo et al., Applied and Environmental Microbiology, 77: 7490–7498). Therefore, a significant linear relationship should also be observed with the fluorophore peaking at Ex/Em 410-415 nm/650-670 nm.



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or ii) expand the observations by considering the extensive dataset produced by Nelson et al. (Geophysical Research Letters 37, L03610, 2010) using a WPI UltraPath liquid waveguide spectrophotometer;

or iii) resolving the chemical structure of the chromophore absorbing at 410-415 nm.

SPECIFIC AND MINOR COMMENTS

Page 10699, lines 14-19. I do not agree with the statement that absorption measurements are mostly performed in the UV region of the spectrum and in the surface layer. Normally, absorption spectra are recorded from 250-300 nm to 600-700 nm and there are recent studies measuring CDOM in subsurface waters (e.g. Nelson et al., Marine Chemistry 89, 273– 287, 2004; Geophysical Research Letters 37, L03610, 2010).

Page 10701. A map showing the location of the sampling stations would be quite useful.

Page 10703. Fluorescence spectra should be corrected for inner filter effects, which usually produce wavelength shifts of the Ex/Em maxima.

Page 10717. Please, replace “absolute absorption at 370 nm” by “absorption coefficient at 370 nm”.

Page 10720. The absorption spectra presented in Figure 5 are not normalised to the absorption coefficient at 380 nm. Note that the units of the Y-axis are 1/m. The efficiency of the PPL cartridges to isolate the CDOM absorbing in the visible should be tested and compared with the efficiency to isolate DOC and DON. The amount of CDOM absorbing in the visible could be estimated by integrating the absorption coefficient between 380 and 600 nm.

Page 10721. The contour lines of the EEMs should be labelled.

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