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Prof. Gerhard Herndl Associate Editor, Biogeosciences, c/o Natascha Töpfer Copernicus Publications Editorial Support

Attn: Review of the manuscript by A. N. Loginova, C. Borchard, J. Meyer, H. Hauss, R. Kiko, and A. Engel entitled "Effects of nitrate and phosphate supply on chromophoric and fluorescent dissolved organic matter in the Eastern Tropical North Atlantic: a mesocosm study." submitted to Biogeosciences and coded bg-2015-181.

Dear Prof. Herndl,

After reading the manuscript by Loginova et al., submitted to Biogeosciences and coded bg-2015-181, I recommend **to consider** this manuscript for publication in this journal after **moderate revision.** 

## General opinion

This study presents very well documented, presented and discussed results of mesocosm experiment in the Eastern Tropical Atlantic (Cape Verde) that was designed to test influence of inorganic nutrients concentrations and mutual concentrations proportions on the production of chromophoric and fluorescent DOM and DOC as consequence of the phytoplankton growth and microbial processing. This study was very well though conducted. Collected results are novel and very well analyzed statistically. In my opinion achieved results have provided new insights on autochthonous production of DOM by phytoplankton. Author have been testing the kinetics of this process with limiting supply of inorganic phosphorus and inorganic nitrogen in different proportions. Authors have found that dissolved inorganic nitrogen has the largest impact on accumulation of DOC and chromophoric and fluorescent fraction of DOM.

I have very high regard on results achieved and documented by Authors. Although there were some inconsistencies and repetitions and minor misunderstandings that hampered the overall positive perception of this very interesting manuscript.

I will point this weak points in detailed section of the review.

Page 7210 – Abstract.

Abstract should be shorted and more consistent.

The general sentences starting from line 5:

"The quantitative and qualitative changes in DOM are often estimated by its optical ..." and ending on line 14:

"....of physical and biogeochemical processes, influencing DOM." should be removed from abstract as Authors repeated almost the same phrases in the introduction

# **Page 7212 – Introduction**

#### Line 12

"...Therefore, oceanic DOM is a complex mixture of organic compounds with different characteristics ..."

This is not true, marine, estuarine and fresh water CDOM is as well a complex heterogeneous mixture of water soluble organic compounds, that have property of light absorption. So it is much better to say more generally "aquatic DOM". Please rephrase.

#### Line 16

"absorption of light in the UV and visible wavelength ranges..." Absorption of light in the UV and visible wavelengths - is good enough. Please delete "ranges".

#### Line 19

"....its abilities to absorb in a wide wavelength range, ..."

It is better to say: "..its abilities to absorb in a wide spectral range ...:

#### Lines 21 - 21

" ...but may also reduce photosyntetically active radiation as it absorbs at chlorophyll absorption maxima ..."

Please be more specific and precise. Chlorophyll a has two absorption maxima: primary absorption maximum centered at 443 nm, and secondary absorption maximum centered at 676 nm. The "blue wavelengths" maximum could be affected by the CDOM absorption due to absorption spectra overlap, but the "red wavelengths" maximum would be very affected very unlikely. In the red part of light spectrum CDOM absorption is negligible even in the Baltic Sea, which is well known for its high CDOM concentration. In open ocean specially in the subtropical gyres the CDOM absorption is its global minimum and would not impact phytoplankton pigments absorption significantly.

#### Page 7213

## Line 16

Citation to: .... (Nelson and Siegel, 2013; Jorgensen et al., 2011), - use chronological citation order – swap cited references.

Line 24

"... affect freshly produced marine FDOM pools in an Arctic fjord system."

Stedmon and Markager have performed their mesocosm experiment in the Raunefjord near Bergen, Norway – this is not Arctic fjord, as south-western Norwegian coast is still in temperate zone.

# Page 7214

Lines 1-2,

As the Eastern Tropical North Atlantic (ETNA) is an open ocean region with, supposedly, little terrestrial DOM input, DOM has to be mainly produced by pelagic production

Reference needed to support this statement.

Line 6

Abbreviation OMZ – please define when first used.

Line 16

Abbreviation DIN – definition missing - please define when first used.

Page 17

"....on DOM "quality" by..." accumulation process is determined during quantitative analysis - so you did evaluated both CDOM?FDOM quality and quantity during experiment. Please correct.

Page 26

"...CDOM absorption and CDOM properties (S275–295 and SR), ."

Please CDOM spectral indices or CDOM spectral properties instead of just "CDOM properties". Please correct.

## Page 7217 – Methods

Lines 25 - 28

"Absorption of chromophoric dissolved organic matter (CDOM) was detected using a 100cm path length liquid waveguide cell ..."

Please give the spectral range of measurements and spectral resolution.

#### Page 7219

#### Line 2 onward

Author are inconsistent in using optical symbol. There is the missus of symbols notation according to convention proposed by Morel and Smyth (1982) severely hampers the perception of the manuscript message. Authors use notation Abs as a symbol of CDOM absorption. The symbol convention that has been applied in the field of ocean optics, see the reference: Morel and Smith, 1982; (and generally in physics) is that wavelength marked in symbolic way with small Greek letter "lambda" is written in the parenthesis after the symbol that mark the optical parameter. Neither " $\lambda$ " is not written as the subscript nor the numerical notation of wavelength. According to the same convention the absorption is marked with the letter "a", (in italics) the wavelength is at which this quantity is measured or referred is given in parenthesis immediately after the absorption symbol. The absorption due to specific optically significant water constituent such as pure water, CDOM, phytoplankton pigments, non-algal particles should be marked in the subscript after the absorption symbol but before the wavelength given in parenthesis. Therefore the symbol for absorption coefficient due to CDOM at wavelength 325 should be properly noted as  $a_{\text{CDOM}}(325)$ . The same notation shall be used by authors if they refer to CDOM absorption coefficient at any other wavelength. As reviewer I must say that, there is increasing numbers of manuscript submission which authors tends to completely ignore the symbolic convention in the field of their studies, and in physics in general. Please change all your symbols in the text figures legends and figures caption accordingly.

Please use proper symbols in the equations. Also use proper form of these equations:

$$a_{\text{CDOM}}(\lambda) = 2.303 \cdot A(\lambda)/L,$$
 (1)

where L is the optical path length and the factor 2.303 is the natural logarithm of 10.

Lines 17 - 23

The whole paragraph starting with

"No universal wavelength range or method is used in the literature for calculation of CDOM spectral slopes (S). ..."

# Page 7225

Lines 5 - 7

The sentence starting with

"Derived from 5 measured parameters, the ratio (SR) of S275–295 and spectral slopes, calculated within 350–400nm wavelength range (S350–400), had .."

Repetition. The  $S_R$  has been defined already. Please remove.

## Page 7231 – Discussion

Line 21

"CDOM absorptions were in the range of those previously reported for open waters of the Atlantic Ocean at the beginning of the experiment, while the final CDOM absorptions were twice as high (Fig. S1c, d; Nelson et al., 2009; Nelson and Siegel, 2012; Swan et al., 2013)."

I have remark on this citations – some of them do not present data in Atlantic Ocean in the proximity of the study area: e.g. Swan et al., present only on data set from temperate North Altalntic – transect A16N from Azores to Iceland,

There are also mistakes in citation – Nelson et al., 2009 – there is Nelson at al., 2007 in the reference list. If authors meant this paper (Nelson et al., 2007), presents data from Caribbean to Cape Hatteras -transect A20 and from French Guyana to Newfoundland– transect A22, and already mentioned transect A16. None of them close to Cape Verde.

Authors cite Nelson and Siegel 2012, but in the reference list there is Nelson and Siegel, 2013, Annu. Rev. Mar. Sci. Please correct. This citation is appropriate.

I would recommend to read and include in the revised reference list following papers: Kitidis et al., 2006, Deep-Sea Res. II 53, 1666–1684; Kowalczuk et al., 2013, Mar Chem. 157, 170–184; Andrew et al., 2013, Mar Chem., 148, 33-43. Papers listed above present data on CDOM optical properties in Equatorial Atlantic Ocean and sampling transect were located much closer to Cape Verde that data presented by Nelson et al., 2007 and Swan et al., 2013.

# Page 7234

Line 10

Citation to IDRISI. If want you want to cite basin text on ocean color remote sensing principle it is much better to cite classic text books e.g. Robinson I.S., 2004. (Measuring the Oceans from Space The principles and methods of satellite oceanography. Springer) than software manual. Alternatively you can cite Robinson I.S., 2010. Discovering the Ocean from Space, Springer.

Line 17

"... A-like peak fluorescence intensities for the open ocean area (Jorgensen et al., 2011) ..."

Paper by Kowalczuk et al., 2013 presents more detailed information about distribution of humic-like and protein like components in different biogeographical provinces of Atlantic Ocean.

Lines 25 - 26

Discuss your results with those presented in the papers by Jørgensen et al., 2011;Kowalczuk et al., Nelson and Siegel, 2013; Álvarez- Salgado et al., 2013: De La Fuente et al., 2014, that present evidence and empirical relationship between microbial metabolism expressed by Apparent Oxygen Utilization and fluorescence intensity of the humic-like FDOM fraction.

### **Page 7238**

Lines 1-5

"When comparing our data to the empirical model, developed by Stedmon and Markager (2001) for discrimination ..."

This is quite obvious statement, because Stedmon and Markager (2001) model was based on the mixing of different water masses in the North Atlantic and Greenland Sea with different CDOM optical characteristics. Model is very sensitive to CDOM optical characteristics in the end members. You do not have any mixing in the mesocosm, so by definition you will get different results. Please rephrase this sentence and link together with following paragraph.

Lines 10 - 12

"Thus, all data, which lie on the model curve and do not exceed the model limits (Fig. 3), are considered as in situ-produced marine CDOM. Those CDOM absorptions vs. spectral slope values, which do not fit to model limits, are considered as allochthonous or riverine CDOM."

Yes this is true, but Stedmon and Markager have compared their data set form Greenland Sea with data from Skagerak. Each data set had different end member characteristics, therefore the two hyperbolic curves did not overlapped., and showed clear discrimination between in suit produced DOM in the North Atlantic and terrestrial CDOM exported from Baltic Sea through Skagerrak. You may read studies by Stedmon and Markager 2003, and Kowalczuk et al., 2006 to understand model development and its effect on explaining CDOM optical properties and its use to explain the CDOM distribution in the Baltic Sea.

## Page 7239 – Conclusions

Line 19

" ... affect predictions of DOC concentration based on CDOM absorbance ..."

Delete absorbance and replace with absorption. Absorbance is the measurements parameter used in spectroscopy and absorption is physical process, quantified by absorption coefficients.

## **Figures**

As there are only 5 figures in the manuscript, maybe authors would consider figure with their FDOM components spectra identified by PARAFAC model.

Best regards,

Piotr Kowalczuk