Point-by-point response to reviewers:

In the following: **RC:** reviewer's comment

AC: Autor's comment

REVIEW 1:

Autor comments to : *Review by Piotr Kowatczuk on*

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.

Page 7210 – Abstract.

RC: 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.

AC: This sentence will be removed. We will revise the abstract to make it more concise.

Page 7212 – Introduction

Line 12

RC: "...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.

AC: Here we emphasize *"oceanic* DOM" in order to bring reader to understanding that it is "*oceanic"* DOM that will be examined in the study. We will remove "*oceanic"* as all DOM, we meet in nature, is a complex mixture of organic compounds.

Line 16

RC: " 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".

AC: The **"***ranges"* will be deleted.

Line 19

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

AC: The "*wavelength"* will be changed to "*spectral".*

Lines 21-21

RC: " …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.

AC: The "*absorbs at chlorophyll absorption maxima ..." will be* changed to …"*absorbs at the first chlorophyll absorption maximum (at 443nm)".*

Page 7213

Line 16

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

AC: Those references will be changed to chronological order.

Line 24

RC: "… 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.

AC: The "… affect freshly produced marine FDOM pools in an Arctic fjord system" will be changed to "… affect freshly produced marine FDOM pools in *temperate climate conditions (Raunefjord, Norway)* ".

Page 7214

Lines 1- 2

RC: 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.

AC: The sentence will be modified to: "The Eastern Tropical North Atlantic (ETNA) is an Open Ocean region, and in the Open Ocean pelagic production of DOM is, supposedly, of greater importance, rather than terrestrial DOM input (e.g. Coble et al., 2007)".

Line 6

RC: Abbreviation OMZ – please define when first used.

AC: The definition will be added, when the abbreviation is used first (Page 7214 Line 6).

Line 16

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

AC: The DIN abbreviation will be defined, when is used first (Page 7214 Line 16).

Page 7217

RC: "….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.

AC: The "*DOM "quality"* will be changed to "*DOM quantity and quality"*

Page 26

RC: "…CDOM absorption and CDOM properties (S275–295 and SR), ." Please CDOM spectral indices or CDOM spectral properties instead of just "CDOM properties". Please correct.

AC: The "*CDOM properties"* will be corrected to "*CDOM spectral properties".*

Page 7217 – Methods

Lines 25 -28

RC: "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.

AC: The absorption of chromophoric dissolved organic matter (CDOM) was detected using a 100cm path length liquid waveguide cell in the range from 178.23 to 885.21 nm over 0.22nm interval. This information will be added to the method section.

Page 7219

Line 2 onward

RC: Authors 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 "· " 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 $a_{CDOM}(325)$. 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:

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

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

AC: Indeed, we met many ways for marking CDOM absorption coefficients in the literature. Many authors used similar symbols as we use in our manuscript. Taking into account the convention, mentioned by the referee, our symbol will be changed according to the accepted system. The consistency of the symbol mark will be traced.

Lines 17 – 23

RC: The whole paragraph starting with "No universal wavelength range or method is used in the literature for calculation of CDOM spectral slopes (S). …"

AC: It is not quite clear what the referee suggestion is regarding this paragraph.

Page 7225

Lines 5 – 7

RC: 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.

AC: This part of the sentence will be removed.

Page 7231 – Discussion

Line 21

RC: "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.

AC: The reference to Nelson et al., 2007 and Swan et al., 2013 will be removed. Andrew et al. (2013) will be used for comparison of CDOM absorption in our experiment. Kowalczuk et al. (2013) and Kitidis et al. (2006), however, are using different wavelength, than we do and in order to avoid making our paper even wordier, those papers will not be used for direct comparison.

Page 7234

Line 10

RC: 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.

AC: Robinson I.S. (2010) will be cited here.

Line 17

RC: " … AA-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.

AC: The paper by Kowalczuk et al. (2013) indeed contains more detailed information about optically active DOM distribution in Atlantic. However, the fluorescence intensities of all amino acid-like and humic-like compounds were summed within groups. Our purpose was to compare our parameters to ones with the closest spectral properties. Therefore, we used

Jorgensen et al. (2011), where the global distributions are reported for the separate components.

Lines 25 – 26

RC: 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.

AC: We agree that link between humic-like substances and microbial reworking has to be better discussed. We will improve this part.

Page 7238

Lines 1 – 5

RC: "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.

AC: The comparison to mixing model will be removed, parameters, used for this relationship, will be changed to $S_{275\text{-}295}$ and $a_{CDOM}(325)$ and this sentence will be rephrased or deleted.

Lines 10 – 12

RC: "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.

AC: The comparison to mixing model will be removed, parameters, used for this relationship, will be changed to $S_{275\text{-}295}$ and $a_{CDOM}(325)$. The equation that used will be reparametrized and stay in the manuscript.

Page 7239 – Conclusions

Line 19

RC: " … 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.

AC: "*absorbance"* will be changed to "*absorption"*

Figures

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

AC: The figures in the current manuscript are rather numerous, therefore it was decided that the figure with the fingerprints and spectral loadings of modelled components went to the attachments of the manuscript. However, we understand the importance of including it to the text body and will include the figure now.

REVIEW 2:

Autor comments to : *Review by anonymous reviewer2 on*

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.

General comments:

I think the authors should focus the goals of the manuscript better. Is the goal to test the nutrient influence on CDOM optical properties through stimulation of phytoplankton and/or bacterioplankton? Or by contrast is the goal to compare different models (relationships) with different optical parameters with the mesocosms data?

I think that the setup of the mesocosms etc was designed to test specifically the nutrient effects on DOM optical properties. Therefore, I think the comparisons with other models seems to be secondary and I have doubts about if their inclusion in this manuscript have any sense or just makes the paper wordy. For instance, I cannot see the relevance for the comparison with the relationship between a375 and the 320-500 nm spectral slope proposed by Stedmon and Markager (2001) obtained for the Greenland Sea. It is hard to see the usefulness of this comparison that makes the paper longer unnecessary. The comparison, any case, it should be in a natural nutrient gradient in the oceanic waters but not in a particular sea without any reference to mineral nutrients. That is, they can obtain more data from literature covering a wide gradient of nutrients or the authors should just reconsider to include this part of the manuscript. More or less the same comment for the comparison with the Fichot and Benner (2012) ´s model. This model was proposed to related terrigenous DOM with the spectral slope from 275 to 295nm for its use as terrestrial tracer, but not with mineral nutrients, then what is the point of that.

AC: The mineral nutrients influence is indeed the main focus of this paper. The comparison part to models will, therefore, be removed. However, we will keep the equations, found during this study.

Specific comments:

Introduction

Page 6 (line 138)

RC: Please introduce the meaning of OMZ the first time you use these acronyms

AC: The acronym OMZ will be introduced (Page 6 Line 138).

Materials and Methods

Page 8 (lines 163-178)

RC: This paragraph includes too many details and I think could be shortened.

AC: This paragraph will be shortened. **!!!** This paragraph was not shortened, as the information presented here is needed for understanding of the experimental setup.

Page 10 (line 229)

RC: The CDOM and FDOM samples were stored at 4ºC during 6 months. That is a lot of time storage!!!. Despite the low temperature of conservation and that the 0.45μm filtration will prevent some bacterial growth. It is well known that there are bacteria crossing this filter pore size and, of course, bacteria growth at 4ºC particularly under nutrient enrichments. I have my reservations about the time since the samples were collected and analyzed. I recommend including a note on that issue or any kind of control about potential errors.

AC: We agree that 6 month is a long time of storage, therefore we emphasized this duration in the manuscript. However, we agree to the referee that we did not discuss it appropriately.

Swan et al. (2009) made tests on open ocean CDOM storage. They demonstrated that the CDOM changes are unappreciable, when the storage of prefiltered CDOM samples at 4°C does not exceed one year.

An although, in our study, CDOM and FDOM samples were passed through filers with larger pore size, than those, used in Swan et al. (2009), the concentrations of all optically active parameters were very similar between treatments up to day 4 of both experiments (e.g. after setting up of the nutrient amendments). Therefore, we believe, if CDOM and FDOM would undergo considerable changes during storage under effect of nutrients, the difference between samples at the beginning stage of experiment, where nutrients were already added would be bigger and significant. Therefore, the error, that could occur, would be systematic and would not influence the CDOM and FDOM development patterns during the study.

The note on storage, however, must have been added. Therefore, we will add it to the discussion.

Page 11 (line 271-272)

RC: In the mesocosms, authors have calculated the absorption coefficients at

325 nm (line 267) because is the most common wavelength in the literature. Then, they also calculated coefficients at 355 nm and at 375 nm only for comparative reasons. The information provides by the spectral slopes encompasses the changes among wavelengths within a band. I think the coefficients at 355nm and 375 nm are redundant and I have many concerns about the relevance of the comparisons with the models of this paper (please see the previous comments) that is the 2 ultimate reason for these calculations. I suggest deleting the comparisons and these two absorption coefficients. The paper will be better focused.

AC: The CDOM coefficients at other wavelengths than 325nm will be removed. $a_{CDOM}(325)$ will be used for the model development. The comparison with models of Stedmon and Markager and Fichot and Benner will be removed as well.

Page 11 (line 279-285)

RC: Again, It has no sense for me two calculate three spectral slopes; $S_{275-295}$; $S_{350-400}$; $S_{320-500}$ (S_{SEMO}). Helms et al. (2008) showed that the wavelength band more sensitive to changes is from 275 to 295. Therefore, the calculation of S_{SEMO} is redundant and less precise that $S_{275-295}$. I suggest deleting these calculations to simplify the paper without losing information.

AC: As comparison to Stedmon and Markager will be removed, S_{SEMO} will also be removed. However, $S_{350-400}$ is needed for S_R calculation.

Page 12 (lines 308-309)

RC: Delete this last sentence of the paragraph.

AC: It will be deleted.

Page 13 (line 324)

RC: Delete "(see Table 1, Fig. 1,2)".

AC: It will be deleted.

Page 13 (line 329)

RC: Delete "(see Fig. 3,4,5)".

AC: It will be deleted.

Results

Page 14 (line 363)

RC: Change "abundance" for "concentration"

AC: It will be replaced.

Figure 3

RC: I suggest deleting this figure and the associated results

AC: As comparison to model of Stedmon and Markager (2001) will be removed from the manuscript, figure 3 will be changed. The S_{SEMO} and $a_{CDOM}(375)$ will be replaced with $S_{275\text{-}295}$ and $a_{CDOM}(325)$. The fit to the data will be reparametrized. The figure will stay in the manuscript, but with no link to the mentioned model.

Figure 5

RC: I suggest deleting the figure e. Even although the molar absorption coefficient at 355 nm (a355/DOC) could be considered as a surrogate of terrigenous DOM (dissolved lignin), the parameter determined in the Fichot and Benner (2012) in river-influenced oceanic waters, I cannot see the connection between the influence of mineral nutrients (N and P) using waters from the Eastern Tropical North Atlantic with this molar absorption coefficient at 355 nm and the spectral slopes $S_{275\text{-}295}$ in the mesocosms. Sorry, but I cannot see the meaning of this figure.

AC: As comparison to model of Fichot and Benner (2012) will be removed from the manuscript, figure 3 will be changed. The $a_{CDOM}(355)$ will be replaced with $a_{CDOM}(325)$. The fit to the data will be reparametrized. The figure will stay in the manuscript, but with no link to the mentioned model.

Table 2

RC: Units of the spectral slopes are wrong just nm^{-1} not $d^{-1}nm^{-1}$

AC: Units $d^{-1}nm^{-1}$ will be changed to nm^{-1} d^{-1}. These units were used, as they refer to the linear trend in change of *S* over time. We agree that symbol we used in the table is confusing; therefore, *S* will be changed to d*S*.

Page 18 (line 489)

RC: Change “In order to access” for ” to assess”

AC: It will be changed.

Discussion

Page 21 (lines 534-548)

RC: This first paragraph seems an introduction. Please delete from line 546 to 548, these are the goals that should appear at the end of the introduction section.

AC: This paragraph will be removed.

RC: In general, discussion section needs to be polished and I missed references to key papers on this topic. It needs more focus and structure.

For instance, some missing (not all) references.

Biers et al. 2007. The role of nitrogen in chromophoric and fluorescent dissolved organic matter formation. Mar. Chem. 103: 46–60.

Kramer & Herndl. 2004. Photo- and bioreactivity of chromophoric dissolved organic matter produced by marine bacterioplankton. Aquat. Microb. Ecol. 36: 239–246.

Ortega-Retuerta, E., et al. 2009. Biogeneration of chromophoric disolved organic matter by bacteria and krill in the Southern Ocean. Limnol. Oceanogr. 54:1941–1950.

Romera-Castillo et al. 2011. Net Production and Consumption of Fluorescent Colored Dissolved Organic Matter by Natural Bacterial Assemblages Growing on Marine Phytoplankton Exudates. AEM doi:10.1128/AEM.00200-11

AC: The suggested papers were reviewed, Biers et al. (2007) and Kramer & Herndl (2004) will be added to both introduction and discussion and Romera-Castillo et al. (2011) will be added to discussion. We will revise the discussion in order to gain it better focused and structured.

INTERACTIVE COMMENT:

Autor comments to : *Interactive comment by M. Mostofa on*

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.

1. DIN and DIP should be fully abbreviated

AC: DIN and DIP will be defined, when first used (Abstract: Page7210 Line 3, Introduction: Page7214 Line 16). Afterwards, abbreviations will be used.

2. "Fluorescence properties of CDOM (FDOM) allow discriminating between different structural CDOM properties" Here, "Fluorescence properties of CDOM (FDOM)" should be replaced by "Fluorescent DOM (FDOM)".

AC: It will be replaced.

3. "where effects of DIP ("Varied P") and DIN ("Varied N") supply" is confusing

that should be revised

AC: This sentence will be changed to: "Here we present results from two mesocosm experiments ("Varied P" and "Varied N") conducted with a natural plankton community of the ETNA, where effects of DIP and DIN supply on DOM optical properties were studied".

4. "The bound-to-protein amino acid-like FDOM component" should be replaced as "protein-like or aromatic amino acid-like"

AC: The *bound-to-protein* will be changed to *protein-like.*

5. Page 7225, Lines 15 to 20: This study should more properly explain about FDOM components. Each component (aromatic amino acids or protein, fulvic acids or humic acids) are mostly composed of two peaks, one at shorter wavelength region and another is longer wavelength region. That discussion should be properly written. Another most important issue of this study is that authors should not use the Raman Unit that make changes the component excitation and emission wavelengths and changes fluorescence intensity. I strongly recommend, not to use Raman Unit, Author can use the arbitrary unit (a.u.) or standard Quinine sulphate unit (QSU). Such effect causes a lot of differences in excitation emission wavelengths in Table 3 from other references that mentioned in the Table. Authors can find the differences from the following reference how does differ with other peaks and wavelengths and EEM spectra too. [Reference: Mostofa KMG, Liu CQ, Yoshioka T, Vione D, Zhang YL, Sakugawa H (2013) Fluorescent dissolved organic matter in natural waters. In:

Mostofa KMG, Yoshioka T, Mottaleb A, Vione D (Eds), Photobiogeochemistry of Organic Matter: Principles and Practices in Water Environments, Springer, New York, Chapter 6, pp 429-559].

AC: The description of secondary peaks will be added to results.

Raman Units are widely used for measurements in open ocean and, therefore, using RU in our study was crucial for comparison of data from ETNA with general open ocean FDOM levels. As well, Stedmon and Markager (2005) appeared to be very important for motivation and discussion of our results, as they used mesocosm and nutrient amedments. They also used RU.

We believe that the units, in which FDOM is measured, do not change the relative location of peaks. As taking QS calibration line is laborious procedure, it is time-demanding; therefore, the QS calibration curve is often taken in different day than the actual measurements. Thence, when QSU are used, both, samples and QS solutions are calibrated by Raman Spectrum first.

The shifts in peak locations, compared to the literature in the table 3, would be rather caused by different packaging status (such as molecular composition, isomeric structure, condensation etc.) as result of different pH, salinity, temperature, light conditions between different studies etc.

6. Author then rewrite the next paragraph and the related explanation regarding FDOM.

AC: Please, see previous comment.

7. Authors did not show the three fluorescent components as an EEM Figure that should be needed to show in the manuscript.

AC: The figures in the current manuscript are rather numerous, therefore it was decided that the figure with the fingerprints and spectral loadings of modelled components goes to the attachments of the manuscript. However, we understand the importance of including it to the text body and will include the figure now.

A list of all relevant changes that are made in manuscript

REWIEW1:

Page 7210 – Abstract.

RC: 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.

AC: these sentences were deleted. Abstract was shortened, the first and seventh sentences were rephrased. We hope it can be red better now.

Page7212 - Introduction

Line 12

RC: "...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.

AC: The *"oceanic*" was changed to "*natural"*

Line 16

RC: " 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".

AC: The **"***ranges"* was deleted.

Line 19

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

AC: The "*wavelength"* was changed to "*spectral".*

Lines 21-21

RC: " …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.

AC: The sentence was changed into:" *Due to its abilities to absorb in a wide wavelength range, CDOM may protect primary producers from harmful UV irradiation in the water column, but may also reduce photosyntetically active radiation, as it absorbs* ***at similar wavelength as the first chlorophyll absorption maximum (~443 nm)*** *(Zepp et al., 2008)*".

Page 7213

Line 16

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

AC: Those references were changed to chronological order.

Line 24

RC: "… 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.

AC: The sentence was changed to: "*Stedmon and Markager (2005) have reported that nutrients affect freshly produced marine FDOM pools in* ***temperate climate conditions (Raunefjord, Norway)***".

Page 7214

Lines 1- 2

RC: 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.

AC: The sentence was modified to: "*In the open ocean regions, as is the Eastern Tropical North Atlantic (ETNA), pelagic production of DOM is, supposedly, of greater importance than terrestrial DOM input (e.g. Coble et al., 2007)*".

Line 6

RC: Abbreviation OMZ – please define when first used.

AC: (Page 7214 Line 6) the definition was added to sentence: "*It features a shallow* ***Oxygen Minimum Zone (OMZ)*** *at about 100 m depth with oxygen concentrations about 60 µmol* O_2 kg^{-1} *(Brandt et al., 2015) and a deeper OMZ at approximately 300-600 m depth with oxygen concentrations up to 40* O_2 *µmol* kg^{-1} *(Karstensen et al., 2008)*".

Line 16

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

AC: (Page 7214 Line 16) The definition of DIN abbreviation was added to sentence: "*Here we investigated the effects of different* ***dissolved inorganic nitrogen*** *(DIN) and dissolved inorganic phosphorous (DIP) concentrations and of their supply ratio (DIN:DIP) on DOM quantity and quality by using spectroscopic methods of DOM analysis (e.g. accumulation and*

properties of CDOM and FDOM) during mesocosm study with natural pelagic community off the Cape Verdean Archipelago, an area, affected by low oxygen-core eddies".

Page 7217

RC: "….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.

AC: The "*DOM "quality"* was changed to "*DOM quantity and quality"* in the same sentence: "*Here we investigated the effects of different dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP) concentrations and of their supply ratio (DIN:DIP) on DOM* ***quantity and quality*** *by using spectroscopic methods of DOM analysis (e.g. accumulation and properties of CDOM and FDOM) during mesocosm study with natural pelagic community off the Cape Verdean Archipelago, an area, affected by low oxygen-core eddies*".

Page 26

RC: "…CDOM absorption and CDOM properties (S275–295 and SR), ." Please CDOM spectral indices or CDOM spectral properties instead of just "CDOM properties". Please correct.

AC: The "*CDOM properties"* was corrected to "*CDOM spectral properties"* in the sentence: "*To do so, DOC concentrations, CDOM absorption and* ***CDOM spectral properties*** *($S_{275-295}$ and S_R), FDOM fluorescence, as well as chlorophyll a (chl a), and bacterial abundance, were analyzed during the course of two mesocosm experiments, conducted as a part of the Collaborative Research Centre 754 (SFB754) "Climate-Biogeochemistry Interactions in the Tropical Ocean" (www.sfb754.de)*".

Page 7217 – Methods

Lines 25 -28

RC: "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.

AC: The information was added to sentence: "*The measurements were done over spectral* ***range of 178.23 to 885.21 nm at 0.22 nm interval***".

Page 7219

Line 2 onward

RC: Authors 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 "· " 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 $a_{CDOM}(325)$. 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:

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

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

AC: All symbols (including figures and tables) for CDOM absorption were changed from "a_{325}" to "$a_{CDOM}(325)$"

Page 7225

Lines 5 – 7

RC: 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.

AC: This part of the sentence was removed.

Page 7231 – Discussion

Line 21

RC: "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.

AC: The reference to Nelson et al., 2007 and Swan et al., 2013 were removed. Andrew et al. (2013) was added for comparison of CDOM absorption in our experiment: "*At the beginning of the experiment, CDOM absorption coefficients were in the range of those previously reported for open waters of the Atlantic Ocean, while the final CDOM absorptions were twice as high (Fig.S1c, d;* ***Andrew et al., 2013, Nelson and Siegel, 2013)***".

Page 7234

Line 10

RC: 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.

AC: Robinson I.S. (2010) was cited here: "*Our data suggest, that the stable* $S_{275\text{-}295}$ *to* $a_{CDOM}(325)$*/DOC relationship could be used for DOC estimation in the open ocean, when* $S_{275\text{-}295}$ *and* $a_{CDOM}(325)$ *are known, as, for instance, in field studies, where optical sensors are used. For remote sensing, however, an application of this relationship would be rather difficult, since ocean color remote sensing measurements are limited to an "optical window" of visible to near-infrared wavelength range (****Robinson, 2010****)*".

Lines 25 – 26

RC: 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.

AC: For that purpose the subparagraph was added: "*Marine humic substances were previously assigned to bacterially derived substances due to significant covariance of their concentrations to apparent oxygen utilization in deep open ocean waters (****Swan et al., 2009, Kowalczuk et al., 2013, Nelson and Siegel, 2013****). As well, previous studies of Stedmon and Markager (2005), Kowalczuk et al. (2009) and Zhang et al. (2009) showed that humic-like components, similar by spectral properties to Comp.1, were produced via microbial DOM reworking (Table 3)*".

Page 7238

Lines 1 – 5

RC: "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.

AC: The sentence was deleted, as no comparisons to models of Stedmon and Markager (2001) and Fichot and Benner (2012) is done any more.

Lines 10 – 12

RC: "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.

AC: The comparison to mixing model will be removed, parameters, used for this relationship, was changed to $S_{275\text{-}295}$ and $a_{CDOM}(325)$. The equation that used was reparametrized.

Page 7239 – Conclusions

Line 19

RC: " … 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.

AC: "*absorbance"* was changed to "*absorption"* in sentence: "*An input of humic substances can increase the CDOM/DOC ratio and therewith affect predictions of DOC concentration based on CDOM* ***absorption***".

Figures

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

AC: The figure was added (as Fig.4).

REVIEW 2:

General comments:

I think the authors should focus the goals of the manuscript better. Is the goal to test the nutrient influence on CDOM optical properties through stimulation of phytoplankton and/or bacterioplankton? Or by contrast is the goal to compare different models (relationships) with different optical parameters with the mesocosms data?

I think that the setup of the mesocosms etc was designed to test specifically the nutrient effects on DOM optical properties. Therefore, I think the comparisons with other models seems to be secondary and I have doubts about if their inclusion in this manuscript have any sense or just makes the paper wordy. For instance, I cannot see the relevance for the comparison with the relationship between a375 and the 320-500 nm spectral slope proposed by Stedmon and Markager (2001) obtained for the Greenland Sea. It is hard to see the usefulness of this comparison that makes the paper longer unnecessary. The comparison, any case, it should be in a natural nutrient gradient in the oceanic waters but not in a particular sea without any reference to mineral nutrients. That is, they can obtain more data from literature covering a wide gradient of nutrients or the authors should just reconsider to include this part of the manuscript. More or less the same comment for the comparison with the Fichot and Benner (2012) ´s model. This model was proposed to related terrigenous DOM with the spectral slope from 275 to 295nm for its use as terrestrial tracer, but not with mineral nutrients, then what is the point of that.

AC: The comparison part to models was removed (pp27-28, lines: 750-783). However, the equations were reparametrized and kept in (eq.(2), eq.(3)).

Specific comments:

Introduction

Page 6 (line 138)

RC: Please introduce the meaning of OMZ the first time you use these acronyms

AC: (Page 6 Line 138) the definition was added to sentence: ”*It features a shallow **Oxygen Minimum Zone (OMZ)** at about 100 m depth with oxygen concentrations about 60 µmol* O_2 kg^{-1} *(Brandt et al., 2015) and a deeper OMZ at approximately 300-600 m depth with oxygen concentrations up to 40* O_2 *µmol* kg^{-1} *(Karstensen et al., 2008)*”.

Materials and Methods

Page 10 (line 229)

RC: The CDOM and FDOM samples were stored at 4ºC during 6 months. That is a lot of time storage!!!. Despite the low temperature of conservation and that the 0.45µm filtration will prevent some bacterial growth. It is well known that there are bacteria crossing this filter pore size and, of course, bacteria growth at 4ºC particularly under nutrient enrichments. I have

my reservations about the time since the samples were collected and analyzed. I recommend including a note on that issue or any kind of control about potential errors.

AC: The subparagraph was added to the discussion concerning the length of sample storage on page 26 (lines 736-751).

Page 11 (line 271-272)

RC: In the mesocosms, authors have calculated the absorption coefficients at

325 nm (line 267) because is the most common wavelength in the literature. Then, they also calculated coefficients at 355 nm and at 375 nm only for comparative reasons. The information provides by the spectral slopes encompasses the changes among wavelengths within a band. I think the coefficients at 355nm and 375 nm are redundant and I have many concerns about the relevance of the comparisons with the models of this paper (please see the previous comments) that is the 2 ultimate reason for these calculations. I suggest deleting the comparisons and these two absorption coefficients. The paper will be better focused.

AC: The CDOM coefficients at other wavelengths than 325nm were removed. $a_{CDOM}(325)$ was used for the model development. The comparison with models of Stedmon and Markager and Fichot and Benner was removed as well (pp27-28, lines: 750-783). The absorption coefficients in Fig.3 and Fig.6e were changed to $a_{CDOM}(325)$, eq.(2) and eq.(3) were reparametrized.

Page 11 (line 279-285)

RC: Again, It has no sense for me two calculate three spectral slopes; $S_{275-295}$; $S_{350-400}$; $S_{320-500}$ (S_{SEMO}). Helms et al. (2008) showed that the wavelength band more sensitive to changes is from 275 to 295. Therefore, the calculation of S_{SEMO} is redundant and less precise that $S_{275-295}$. I suggest deleting these calculations to simplify the paper without losing information.

AC: S_{SEMO} calculation was removed.

Page 12 (lines 308-309)

RC: Delete this last sentence of the paragraph.

AC: The sentence: "*The spectral characteristics of these components are described in Table 3*" was removed.

Page 13 (line 324)

RC: Delete "(see Table 1, Fig. 1,2)".

AC: The "*(see Table 1, Fig. 1,2)"* was deleted.

Page 13 (line 329)

RC: Delete "(see Fig. 3,4,5)".

AC: The "(see Fig. 3,4,5)" was deleted.

Results

Page 14 (line 363)

RC: Change "abundance" for "concentration"

AC: It was replaced.

Figure 3

RC: I suggest deleting this figure and the associated results

AC: The S_{SEMO} and $a_{CDOM}(375)$ were replaced with $S_{275\text{-}295}$ and $a_{CDOM}(325)$. A comparison to model of Stedmon and Markager (2001) was removed.

Figure 5

RC: I suggest deleting the figure e. Even although the molar absorption coefficient at 355 nm (a355/DOC) could be considered as a surrogate of terrigenous DOM (dissolved lignin), the parameter determined in the Fichot and Benner (2012) in river-influenced oceanic waters, I cannot see the connection between the influence of mineral nutrients (N and P) using waters from the Eastern Tropical North Atlantic with this molar absorption coefficient at 355 nm and the spectral slopes $S_{275\text{-}295}$ in the mesocosms. Sorry, but I cannot see the meaning of this figure.

AC: The $a_{CDOM}(355)$ was replaced with $a_{CDOM}(325)$. The fit to the data was reparametrized. A comparison to model of Fichot and Benner (2012) was removed from the manuscript.

Table 2

RC: Units of the spectral slopes are wrong just nm^{-1} not $d^{-1}nm^{-1}$

AC: Units $d^{-1}nm^{-1}$ were changed to nm^{-1} d^{-1}. *S* was changed to d*S*.

Page 18 (line 489)

RC: Change "In order to access" for " to assess"

AC: It was changed.

Discussion

Page 21 (lines 534-548)

RC: This first paragraph seems an introduction. Please delete from line 546 to 548, these are the goals that should appear at the end of the introduction section.

AC: This paragraph was removed copletely.

RC: In general, discussion section needs to be polished and I missed references to key papers on this topic. It needs more focus and structure.

For instance, some missing (not all) references.

Biers et al. 2007. The role of nitrogen in chromophoric and fluorescent dissolved organic matter formation. Mar. Chem. 103: 46–60.

Kramer & Herndl. 2004. Photo- and bioreactivity of chromophoric dissolved organic matter produced by marine bacterioplankton. Aquat. Microb. Ecol. 36: 239–246.

Ortega-Retuerta, E., et al. 2009. Biogeneration of chromophoric disolved organic matter by bacteria and krill in the Southern Ocean. Limnol. Oceanogr. 54:1941–1950.

Romera-Castillo et al. 2011. Net Production and Consumption of Fluorescent Colored Dissolved Organic Matter by Natural Bacterial Assemblages Growing on Marine Phytoplankton Exudates. AEM doi:10.1128/AEM.00200-11

AC: The citations of Biers et al. (2007) and Kramer & Herndl (2004) were added to introduction (page 5, lines 120-137 of new version). The citations of Biers et al. (2007) and Kramer & Herndl (2004) were added to discussion (pp21-22, lines 584-590 and p23 lines 640-648) and citation to Romera-Castillo et al. (2011) was added to discussion (p21, lines(562-567). Discussion was also revised.

INTERACTIVE COMMENT:

1. DIN and DIP should be fully abbreviated

AC: DIN and DIP were defined, when first used (Abstract: in the first sentence:"*In open ocean regions, as is the Eastern Tropical North Atlantic (ETNA), pelagic production is the main source of dissolved organic matter (DOM) and is affected by* ***dissolved inorganic nitrogen (DIN) and phosphorus (DIP)*** *concentrations*".; Introduction: Page7214 Line 16: in the sentence: "*Here we investigated the effects of different* ***dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP)*** *concentrations and of their supply ratio (DIN:DIP) on DOM quantity and quality by using spectroscopic methods of DOM analysis (e.g. accumulation and properties of CDOM and FDOM) during mesocosm study with natural pelagic community off the Cape Verdean Archipelago, an area, affected by low oxygen-core eddies*"). Afterwards, abbreviations were used.

2. "Fluorescence properties of CDOM (FDOM) allow discriminating between different structural CDOM properties" Here, "Fluorescence properties of CDOM (FDOM)" should be replaced by "Fluorescent DOM (FDOM)".

AC: This was replaced.

3. "where effects of DIP ("Varied P") and DIN ("Varied N") supply" is confusing

that should be revised

AC: The sentence was revised into: "*Here we present results from two mesocosm experiments ("Varied P" and "Varied N") conducted with a natural plankton community from the ETNA, where the effects of DIP and DIN supply on DOM optical properties were studied*".

4. "The bound-to-protein amino acid-like FDOM component" should be replaced as "protein-like or aromatic amino acid-like"

AC: The *bound-to-protein* was changed to *protein-like* (Abstract, Page 2, line 21 of new version).

5. Page 7225, Lines 15 to 20: This study should more properly explain about FDOM components. Each component (aromatic amino acids or protein, fulvic acids or humic acids) are mostly composed of two peaks, one at shorter wavelength region and another is longer wavelength region. That discussion should be properly written. Another most important issue of this study is that authors should not use the Raman Unit that make changes the component excitation and emission wavelengths and changes fluorescence intensity. I strongly

recommend, not to use Raman Unit, Author can use the arbitrary unit (a.u.) or standard Quinine sulphate unit (QSU). Such effect causes a lot of differences in excitation emission wavelengths in Table 3 from other references that mentioned in the Table. Authors can find the differences from the following reference how does differ with other peaks and wavelengths and EEM spectra too. [Reference: Mostofa KMG, Liu CQ, Yoshioka T, Vione D, Zhang YL, Sakugawa H (2013) Fluorescent dissolved organic matter in natural waters. In: Mostofa KMG, Yoshioka T, Mottaleb A, Vione D (Eds), Photobiogeochemistry of Organic Matter: Principles and Practices in Water Environments, Springer, New York, Chapter 6, pp 429-559].

AC: The remark on secondary peaks for protein-like components was added (Results: Page 15, Line 416 of new version).

7. Authors did not show the three fluorescent components as an EEM Figure that should be needed to show in the manuscript.

AC: The figure was added as Fig.4.

A marked up MS version: **Effects of nitrate and phosphate supply on chromophoric and fluorescent dissolved organic matter in the Eastern Tropical North Atlantic: a mesocosm study**

A.N. Loginova~~*~~,*[1], C. ~~Borchard~~Borchard[1], J. ~~Meyer~~Meyer[1], H. ~~Hauss~~Hauss[1], R. ~~Kiko~~Kiko[1], and A. ~~Engel~~Engel[1]

~~GEOMAR~~[1]GEOMAR Helmholtz-Centre for Ocean Research Kiel, Düsternbrooker Weg 20, 24105 Kiel, Germany

*Correspondence should be addressed to: aloginova@geomar.de

Key words: Dissolved Organic Carbon (DOC), humic-like fluorescence, tyrosine-like fluorescence, tryptophan-like fluorescence

Formatiert: Hochgestellt

Abstract

~~The~~ In open ocean regions, as is the Eastern Tropical North Atlantic (ETNA~~) is an open ocean region with little input of terrestrial dissolved organic matter (DOM), suggesting that~~), pelagic production ~~has to be~~is the main source of ~~DOM. Inorganic~~dissolved organic matter (DOM) and is affected by dissolved inorganic nitrogen (DIN) and phosphorus (DIP) concentrations ~~affect~~. Changes in pelagic production~~, leading to DOM modifications. The quantitative and qualitative changes in DOM are often estimated by its optical properties. Colored DOM (CDOM) is often used to estimate dissolved organic carbon (DOC) concentrations by applied techniques, e.g. through remote sensing, whereas DOM properties, such as molecular weight, can be estimated from the slopes of the CDOM absorption spectra (*S*). Fluorescence properties of CDOM (FDOM) allow discriminating between different structural CDOM properties. The investigation of distribution~~ under nutrient amendments were shown to also modify DOM quantity and ~~cycling of CDOM and FDOM was recognized to be important for understanding of physical and biogeochemical processes, influencing DOM.~~quality. However, little information is available about the effects of nutrient variability on chromophoric (CDOM) and fluorescent (FDOM) DOM dynamics. Here we present results from two mesocosm experiments ("Varied P" and "Varied N") conducted with a natural plankton community ~~of~~from the ETNA, where the effects of DIP ~~(*varied P*)~~ and DIN ~~(*varied N*)~~ supply on DOM optical properties~~ of DOM~~ were studied. CDOM accumulated proportionally to phytoplankton biomass during the experiments. ~~*S*~~Spectral slope (*S*) decreased over time indicating accumulation of high molecular weight DOM. In ~~*varied*~~Varied N, an additional CDOM portion, as a result of bacterial DOM reworking, was determined. It increased the CDOM fraction in DOC proportionally to the supplied DIN. The humic-like FDOM component (Comp.1) was ~~derived~~produced by bacteria proportionally to DIN supply. The ~~bound-to-~~protein~~-amino acid~~-like FDOM component (Comp.2) was released irrespectively to phytoplankton or bacterial biomass, but depending on DIP and DIN concentrations~~, as a part of an *overflow* mechanism.~~. Under high DIN supply, Comp.2 was removed by bacterial reworking~~ processes~~, leading to an accumulation of humic-like Comp.1. No influence of nutrient availability on amino acid-like FDOM component in peptide form (Comp.3) was observed. Comp.3 potentially acted as an intermediate product during formation or degradation Comp.2. Our findings suggest that changes in nutrient concentrations may lead to substantial responses in the quantity and ~~'quality'~~quality of optically active DOM and, therefore, might bias results of the applied *in situ* optical techniques ~~for an estimation~~ of DOC estimations concentrations in open ocean regions.

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Introduction

Dissolved organic matter (DOM) is the largest dynamic pool of organic carbon in the ocean. Its global inventory constitutes of approximately 662 pentagrams of carbon (PgC) (Hansell et al., 2009). Labile and semi-labile high molecular weight (HMW) DOM is released primarily by phytoplankton (Carlson and Hansell, 2015). It is used as substrate by ~~the~~ heterotrophic communities, which, in turn, release less bioavailable semi-refractory or even refractory DOM, thereby modifying the quantity and quality of the DOM pool (Azam et al., 1983, Ogawa et al., 2001, Jiao et al., 2010). Therefore, ~~oceanic~~natural DOM is a complex mixture of organic compounds with different characteristics, such as molecular structure and molecular weight, resulting in different optical properties (Stedmon and Nelson, 2015).

For instance, the presence of conjugated double bonds (polyenes) results in the absorption of light in the UV and visible ~~wavelength ranges~~wavelengths (Stedmon and Álvarez-Salgado, 2011). The light absorbing DOM fraction is referred to as 'chromophoric' or 'colored' DOM (CDOM) (Coble, 2007). Due to its abilities to absorb in a wide wavelength range, CDOM may protect primary producers from harmful UV irradiation in the water column, but may also reduce photosyntetically active radiation, as it absorbs at similar wavelength as the first chlorophyll absorption ~~maxima~~maximum (~443 nm) (Zepp et al., 2008). Photons, absorbed by CDOM, may induce the formation of free radicals, which by colliding with other molecules or other radicals produce new organic molecules, reducing metals or introducing short inorganic and organic substances as byproducts (Sulzberger and Durisch-Kaiser, 2008). Modified by photoreactions, CDOM may serve, as biological substrates for auto- and heterotrophic communities, by releasing nutrients and low molecular weight (LMW) organic compounds, as well as a source of trace gases (e.g. CO, CO_2) (Kieber et al., 1990, Moran and Zepp, 1997, Kieber et al., 1999).

CDOM absorption has often been used as an indicator for dissolved organic carbon (DOC) concentrations in the Ocean (Fichot and Benner, 2011, 2012, Rochelle-Newall et al., 2014). For example, DOC concentration in estuarine surface waters can be derived from CDOM absorption by remote sensing techniques, assuming a direct relationship between CDOM absorption and DOC concentrations (Del Castillo, 2005, 2007). In the open ocean, however, this relationship varies throughout the water column (Nelson and Siegel, 2013), and factors affecting it are poorly understood.

A better knowledge on factors influencing the CDOM/DOC relationship could improve our understanding of DOM cycling, as well as of the regulation of light attenuation in the ocean.

Furthermore, the knowledge of the factors, influencing the open ocean CDOM/DOC relationship would be useful for the estimation of DOC concentrations from CDOM absorption measurements by remote sensing techniques.

As CDOM embodies a complex mixture of organic compounds that have overlapping absorption spectra, with, generally, no single compound dominating (Del Vecchio and Blough, 2004), CDOM absorbance spectra ~~generally~~ decrease exponentially toward longer wavelength, with no discernible peaks. Therefore, the CDOM concentration is commonly expressed as absorption coefficient at chosen wavelength (e.g. 325, 355, 375nm) (Stedmon ~~et al.,~~and Markager, 2001, Fichot and Benner, 2012, Nelson and Siegel, 2013).

To derive information on CDOM quality, such as molecular weight and modification processes, spectral slopes (*S*) of CDOM light absorption and spectral slopes ratio (S_R) are used (Helms et al., 2008, Zhang et al., 2009).

It has been shown that ~~spectral slopes at wavelength regions 275-295 nm and 300-500 nm ($S_{275-295}$ and $S_{300-500}$)~~S decrease with increasing ~~in~~ DOM molecular weight, and, therefore, may be used as an indicator of accumulation/degradation of bioavailable HMW-DOM (De Haan and De Boer, 1987, Helms et al., 2008, Zhang et al., 2009).

The ratio of ~~$S_{275-295}$ to spectral slope~~S at wavelength region 275-295 nm ($S_{275-295}$) to *S* at 350-400 nm ($S_{350-400}$), S_R, is used to estimate CDOM ~~transformations.~~transformation processes. S_R increases as CDOM becomes involved in photoreactions and decreases as CDOM ~~is microbially reworked~~undergoes microbial reworking (Helms et al., 2008).

The presence of aromatic rings in CDOM often also results in fluorescence (Stedmon and Álvarez-Salgado, 2011).

Fluorescent DOM (FDOM) excitation/emission (Ex/Em) spectra allow discriminating between different pools of CDOM (Coble, 2007, Stedmon and Bro, 2008, Mopper et al., 2007, Yamashita et al., 2010). The substances that are excited and emit in the UV spectral range commonly correspond to labile proteinaceous DOM, and therefore are referred to as amino acid-like (tyrosine- and tryptophan-like) FDOM (e.g. Coble, 1996). The substances that are excited in the UV spectral range, but emit in the visible spectral range were identified as fulvic- and humic-like FDOM (Gueguen and Kowalczuk, 2013). Tyrosine- and Tryptophan-like substances have been used for the assessment of *in situ* primary productivity, while humic-like substances are used for the indication of allochtonous (e.g. riverine) DOM or microbial DOM transformation (Coble, 1996).

Although the CDOM and FDOM distribution and cycling has been described for many open ocean sites (Jørgensen et al., 2011, Kowalczuk et al., 2013, Nelson and Siegel, 2013~~,~~

~~Jorgensen et al., 2011~~), specific sources and factors influencing their composition and transformations are yet not well understood.

For example, CDOM accumulation is often related to nutrient remineralization (Swan et al., 2009, Nelson and Siegel, 2013). However, the effects of nutrient variability on CDOM concentration and on the relationship between CDOM and DOC are largely understudied.

Stedmon and Markager (2005) have reported that nutrients affect freshly produced marine FDOM pools in ~~an Arctic fjord system.~~temperate climate conditions (Raunefjord, Norway). In their study, the amino acid-like fluorescence was enhanced under phosphate (P) and silica limitation, but was independent from phytoplankton composition. Bacterially produced humic-like FDOM components were reported to accumulate under ~~phosphate~~P and silica limitation as well. ~~However, the authors revealed some doubts about a setup~~Later, by addition of ~~phosphorus limitation. Therefore, the influence of~~ different synthetic dissolved organic and inorganic ~~nutrients on~~nitrogen (N) substrates to microbial incubations, Biers et al. (2007) emphasized the role of N in CDOM accumulation. They showed that CDOM and FDOM ~~components remains to~~ production by bacteria, cultured in natural seawater medium, can be ~~resolved.~~affected to different degrees by the chemical composition and steric effects of the organic N source, while inorganic N sources do not contribute significantly to CDOM or FDOM accumulation. On the other hand, Kramer and Herndl (2004) demonstrated that bacteria may be able to transform about 30% of taken up inorganic N into semi-labile to refractory humic DOM.

~~As~~Stedmon and Markager (2005), however, revealed some doubts about a setup of P limitation. Besides, Kramer and Herndl (2004) and Biers et al. (2007) were based on single bacterial cultures, and phytoplankton and net-effects, associated with natural aquatic bacterial community, were excluded. Therefore, the influence of inorganic nutrients on CDOM concentration and FDOM components in natural waters remains to be resolved.

In the open ocean regions, as is the Eastern Tropical North Atlantic (ETNA~~) is an open ocean region with~~), pelagic production of DOM is, supposedly, ~~little~~of greater importance than terrestrial DOM input~~, DOM has to be mainly produced by pelagic production.~~ (e.g. Coble et al., 2007).

In classical view, the ETNA is considered ~~as~~ an "excess ~~nitrogen (~~N~~)~~"" region compared to the 'Redfield N:P ratio' of 16 (see Redfield, 1987 and Gruber and Sarmento, 1997) reflecting high rates of biological N-fixation due to Saharan dust deposition, with N:P ratios 16-25 at depth (see Fanning, 1992). It features a shallow Oxygen Minimum Zone (OMZ) at about 100

m depth with oxygen concentrations about ~~30µmol~~60 µmol O_2 kg^{-1} (Brandt et al., 2015) and a deeper OMZ at approximately 300-600 m depth with oxygen concentrations up to 40 O_2 µmol kg^{-1} (Karstensen et al., 2008). However, eddies originating in the Mauritanian upwelling regime and propagating westward can harbor much lower oxygen concentrations (~4 ~~µmolO_2~~µmol O_2 kg^{-1}; Karstensen et al., 2014), potentially enabling N-loss processes (Strous et al., 2006, Kartal et al., 2007, Jetten et al., 2009, Jayakumar et al., 2009). Those mesoscale eddies, may ~~support~~transport nutrient loaded but relatively N deficient waters to the surface (McGillicudy et al., 2003, 2007, Mathis et al., 2007). Furthermore, it has been shown that non-diazotroph primary production in the surface waters of ETNA can be N-limited (Franz et al., 2012, Hauss et al., 2013).

Here we investigated the effects of different ~~DIN~~dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP) concentrations and of their supply ratio (DIN:DIP) on DOM ~~"~~quantity and quality~~"~~ by using spectroscopic methods of DOM analysis (e.g. accumulation and properties of CDOM and FDOM) during mesocosm ~~experiments~~study with natural pelagic ~~communities of~~community off the Cape Verdean Archipelago, an area, affected by low oxygen-core eddies.

During these mesocosm experiments, we tested whether (1) pelagic production is a source of CDOM and FDOM, (2) CDOM and FDOM accumulation and composition are affected by changes in nutrient stoichiometry, and whether (3) the relationship between CDOM absorption and DOC concentrations is stable under variable nutrient concentrations.

To do so, DOC concentrations, CDOM absorption and CDOM spectral properties ($S_{275-295}$ and S_R), FDOM fluorescence, as well as chlorophyll *a* (chl *a*), and bacterial abundance, were analyzed during the course of two mesocosm experiments, conducted as a part of the Collaborative Research Centre 754 (SFB754) "Climate-Biogeochemistry Interactions in the Tropical Ocean" (www.sfb754.de).

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2. Methods

2.1 Setup of the mesocosms experiment

Two 8-day mesocosm experiments were conducted consecutively in October 2012 at the Instituto Nacional de Desenvolvimento das Pescas (INDP), Mindelo, Cape Verde. Seawater from 5 m depth was collected into four 600L tanks in the night of the ~~1~~01.10/~~2~~02.10 and 11.10/12.10 for the first and second experiment, respectively. The sampling was done with the RV *Islândia* south of São Vicente (16°44.4'N, 25°09.4'W). For each experiment, sixteen mesocosm-bags were placed floating in 4 'flow-through' cooling baths that were kept at surface seawater temperature (25.9 - 28.7°C) ~~using 'flow-through' principle~~ with the water from the Mindelo bay in front of the INDP. The mesocosms were filled alternately (about 10 seconds per filling event) and randomly from the tanks by gravity flow using submerged hose in order to achieve even distribution of the water and minimize bubble formation. A mesh to filter zooplankton was not used. The precise volume of each mesocosm was determined by addition of 1.5 mmol of silicate and subsequent measurement of the resulting silicate concentration. The water volume in the mesocosms ranged from 106 to 145L. For simulation of surface water conditions, the mesocosms were shaded with blue transparent lids to approximately 20% of sunlit irradiation (56-420 µE m^{-2} s^{-1}, depending on cloud cover).

Nutrients were manipulated by adding different amounts of phosphate (DIP) and nitrate (DIN). In the first experiment, the DIP supply was varied ~~(*varied*~~("Varied P~~)~~") at relatively constant DIN concentrations in twelve of the sixteen mesocosms, while in the second experiment the initial DIN concentrations were varied ~~(*varied*~~("Varied N~~)~~") at constant DIP supply in twelve of the sixteen mesocosms.

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In addition to this, four 'cornerpoints', where both, DIN and DIP, were varied, were chosen to be repeated during both experiments (see target DIN and DIP values in Table 1). However, during the first experiment, setting the nutrient levels in one of the 'cornerpoint' mesocosms (mesocosm 10) was not successful and it was decided to adjust the DIN- and DIP-concentrations in this mesocosm to 'Redfield N:P ratio' of 16 (Redfield, 1987) and therefore add another replicate to the treatment 12.00N/0.75P. Another 'cornerpoint' mesocosm (mesocosm 5) during the first experiment was excluded from further analyses as no algal bloom had developed.

Initial sampling for biogeochemical parameters was accomplished immediately after the mesocosms filling (day 1). Nutrients were added after the initial sampling. Daily water sampling was conducted between 9:00 and 10:30 a.m. on days 2 to 8.

The target and actual nutrient concentrations are shown in Table 1 and the corresponding treatment indications will be used in the following.

2.2 Sampling and Analyses

2.2.1 Particulate organic matter

Samples of ~~0.5 L~~500 mL for chl *a* measurements were vacuum-filtered (< 200 mbar) onto Whatman GF/F filters (25 mm, 0.7 µm), 1 ml of ultrapure water was added and the filters were frozen at -20°C for at least 24 hours. Subsequently, pigments were extracted using acetone and measured in a Trilogy® fluorometer (Turner Designs) calibrated with a chl *a* standard (*Anacystis nidulans*, Walter CMP, Kiel, Germany) dilution series (Parsons et al., 1984).

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For bacterial cell counts, samples (5 ~~ml~~mL) were fixed with 2% formaldehyde, frozen at -80°C and transported to the home laboratory. Samples were diluted 1:3, stained with SYBR-Green and measured at a flow rate of 11.0 µL min^{-1} by flow cytometry (FACScalibur, Becton Dickinson, San Jose, CA, USA).

2.2.3 Dissolved organic matter

Dissolved organic carbon (DOC) duplicate samples (20 mL) were filtered through combusted GF/F filters and collected in combusted glass ampoules. Samples were acidified with 80 µL of 85% phosphoric acid, flame sealed and stored at 4°C in the dark until analysis.

DOC samples were analysed by applying the high-temperature catalytic oxidation method (TOC -VCSH, Shimadzu) ~~after~~adapted from Sugimura and Suzuki (1998). The instrument was calibrated every 8-10 days by measuring of 6 standard solutions of 0, 500, 1000, 1500, 2500 and 5000 µgC L^{-1}, prepared using a potassium hydrogen phthalate standard (Merck 109017). Every day before each set of measurements, ultrapure (MilliQ) water was used for setting the instrument baseline, following by the measurement of the deep-sea water standard (Dennis Hansell, RSMAS, University of Miami) with known DOC concentration in order to verify result representation by the instrument. Additionally, two DOC control samples were prepared each day of measurement using a potassium hydrogen phthalate standard (Merck 109017). The control samples had dissolved carbon concentrations within the range of those in samples and were measured along the sample analyses in order to avoid mistakes due to baseline flow during measurements. The DOC concentration was determined in each sample out of 5 to 8 replicate injections.

For chromophoric dissolved organic matter (CDOM) and fluorescent dissolved organic matter (FDOM), ~~2 x 35ml~~duplicate samples of 35ml for each parameter were collected daily into combusted (450°C, 8 hours) amber-glass vials after filtering through 0.45 µm polyethersulfone syringe filters (CHROMAPHIL® Xtra PES-45/25, MACHEREY-NAGEL GmbH & Co.KG). The samples were stored at 4°C in the dark during 6 month pending analyses. All samples were brought to room temperature before analyses.

Absorption of chromophoric dissolved organic matter (CDOM) was detected using a 100 cm path length liquid waveguide cell (LWCC-2100, World Precision Instruments, Sarasota, Florida) and a UV-VIS spectrophotometer (Ocean Optics USB 4000) in conjunction with the Ocean Optics DT-MINI-CS light source. The absorbance was measured ~~relatively to~~against ultrapure water (MilliQ) by injection to the cell with a peristaltic pump. The measurements were done over spectral range of 178.23 to 885.21 nm at 0.22 nm interval.

For the determination of fluorescent dissolved organic matter (FDOM), 3D fluorescence spectroscopy - Excitation-Emission Matrix Spectroscopy (EEMs) - was performed using a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) equipped with a xenon flash lamp. The fluorescence spectra for samples were measured in a 4-optical window 1 cm Quartz SUPRASIL® precision cell (Hellma®Analytics). The blank-3D fluorescence spectra and Water Raman scans were performed daily using an Ultra-Pure Water Standard sealed cuvette (3/Q/10/WATER; Starna Scientific Ltd). The experimental wavelength range for sample and ultra-pure water scans was 230 to 455 nm in 5 nm intervals on excitation and 290 to 700 nm in 2 nm intervals on emission. Water Raman scans were recorded from 285 to 450 nm at 1 nm intervals for emission at the 275 nm excitation wavelength (Murphy et al~~.~~., 2013~~:~~ ~~Appendix 1~~). All fluorescence measurements were managed at 19°C (Cary Single Cell Peltier ~~Accessory~~Assessory, VARIAN), PMT 900V, 0.2 s integration times and 5 nm slit width on excitation and emission monochromators. The absorbance for EEMs corrections was procured simultaneously with Shimadzu® 1800 UV-VIS double-beam spectrophotometer. The absorbance was measured at the room temperature (~19°C) in 2-optical window 5 cm Quartz SUPRASIL® precision cell (Hellma®Analytics). ~~–~~The measurements were done at 1 nm wavelengths intervals from 230 to 750 nm against MilliQ water as a reference. The obtained data were converted to absorbance in a 1 cm cell.

2.3 Data evaluation

2.3.1 CDOM

The measured CDOM absorbance spectra were corrected to the refractive index of remaining particulate matter and colloids after Zhang et al. (2009) and for salinity after Nelson et al. (2007), and converted to absorption coefficients according to Bricaud et al. (1981):

(1) $a_\lambda = 2.303 A a_{CDOM}(\lambda) = 2.303 \times A(\lambda)/L;$

where $a_\lambda a_{CDOM}(\lambda)$ – is the absorption coefficient at wavelength λ (m^{-1}), $A(\lambda)$ (λ) - is the absorbance value at same wavelength and L – is the effective optical path length (m).

Commonly In rivers and the coastal waters, absorption coefficients at 355 (a_{355}) $a_{CDOM}(355)$) and 375 (a_{375}) $a_{CDOM}(375)$) nm are commonly used to express CDOM concentrations in coastal waters (Granskog et al., 2007, Stedmon et al., 2011), since CDOM concentrations there are very high, and absorption coefficient). Absorption coefficients at 440-445nm (a_{440}) is $a_{CDOM}(440)$) are used for comparison of field CDOM measurements to remote sensing (Swan et al., 2013).

Open In open ocean blue waters show only very low, absorbance at wavelengths of 400-600 nm is very low. Therefore, absorption at 325 nm (a_{325}) $a_{CDOM}(325)$) is often used for expression of the open ocean CDOM concentrations (Nelson and Siegel, 2013).

The area off Cape Verdean Archipelago, where water for mesocosms was taken, is not influenced by river inflow and is considered as the open ocean area. Thus, a_{325} $a_{CDOM}(325)$ was chosen for expression of CDOM concentration. For comparison of CDOM properties with models developed previously a_{355} and a_{375} were obtained, as well.

No universal wavelength range or method is used in the literature for calculation of CDOM spectral slopes (S). Instead, S is often calculated by nonlinear least square fitting for relatively long wavelength ranges and by log-transformed linear regression for shorter wavelength ranges (Twardowski et al., 2004, Helms et al., 2008). Both, nonlinear fitting and log-transformed linear regression, as well as several wavelength ranges, were used in this work for estimation of CDOM properties and their comparison to the literature.

The spectral slope for the interval 320-500 nm (S_{SEMO}) was determined by fitting the absorption spectra to the simple exponential model with offset (SEMO; Twardowski et al., 2004) using nonlinear least square fitting (MATLAB, The MathWorks Inc.). This model was chosen as it explained best the shape of CDOM absorption spectra, obtained in our study, in the given wavelength range from all nonlinear models tested after Twardowski et al. (2004).

Spectral slopes for the intervals 275-295nm ($S_{275\text{-}295}$) and 350-400 ($S_{350\text{-}400}$) were calculated after Helms et al. (2008) using log-transform linear regression.

The CDOM alteration indicator, slope ratio (S_R), was also calculated after Helms et al. (2008) as well, as ratio of $S_{275\text{-}295}$ to $S_{350\text{-}400}$.

To describe ~~the~~changes in CDOM spectral properties along with change in CDOM concentration, the following equation was used:

(2) $$~~S_{SRMG}~~S_{275-295} = \alpha + \beta/~~a_{375}~~a_{CDOM}(325);$$

where α and β are the regression coefficients. ~~The properties were compared to the model of Stedmon and Markager (2001) for marine CDOM developed for the Greenland Sea, in which $\alpha = 7.4$ and $\beta = 1.1$.~~

The variability of the relationship ~~a_{355}/DOC~~ $a_{CDOM}(325)/DOC$ vs $S_{275-295}$ ~~was compared with the model developed by Fichot and Benner (2012)~~, as possible tool for DOC ~~calculation~~estimation from ~~known a_{355} and $S_{275\text{-}295}$~~spectroscopic measurements, was expressed as:

(3) $$~~a_{355}/DOC~~\, a_{CDOM}(325)/DOC = e^{(\gamma-\delta S_{275-295})} + e^{(\varepsilon-\zeta S_{275-295})};$$

where ~~$\gamma = 5.679$, $\delta = 81.299$, $\varepsilon = 8.459$ and~~, $\varepsilon$and ζ ~~$= 241.052$~~ are regression coefficients ~~developed for the river estuaries (after Fichot and Benner, 2012).~~.

2.3.2 FDOM

The 3D fluorescence spectra were corrected for spectral bias, background signals and inner filter effects. Each EEM was normalized to the area of the ultra-pure water Raman peaks, measured in the same day. EEMs were combined into three-dimensional data array, analyzed by PARAFAC (Stedmon and Bro, 2008) and validated by split-half analysis using "drEEM toolbox for MATLAB" after Murphy et al. (2013).

Only up to ~~3~~ three components could be validated. For models with more than ~~3~~three components the results varied during split-half analysis (see Murphy et al., 2013), indicating the possibility of identifying the instrument noise as a signal (e.g. Stedmon and Markager, 2005). The fluorescence of each component is stated as fluorescence at excitation and emission maximums in Raman units (RU). ~~The spectral characteristics of these components are described in Table 3.~~

2.3.3 Mesocosm data treatment

Based on the nutrient component that was mainly varied, the experiments are referred to as ~~*varied*~~Varied P and ~~*varied*~~Varied N in the following.

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High variability of CDOM components (~~Appendix A~~Fig.S1) was observed on day 1 and day 2 of ~~*varied*~~Varied P and ~~day1~~day 1 of ~~*varied*~~Varied N. This variability was likely associated to the filling and manipulation of the mesocosm bags and vanished afterwards. These days were excluded from further calculations, and day 3 and day 2 were defined as "start" or "beginning" of ~~*varied*~~Varied P and ~~*varied*~~Varied N, respectively. Day 8 was defined as the "end" of both experiments. To exclude initial variability, changes of the different DOM parameters over time were calculated as the difference between sampling day and start day:

$$\Delta Ci(k) = Ci(k) - Ci(start); \quad (4)$$

where C is a concentration, absorption or fluorescence intensity, i is a mesocosm id ($i = 1 - 16$) and k is the day of experiment.

For the presentation of the development over time, POM and DOM Δ-values were averaged for each nutrient treatment ~~(see Table 1, Fig.1, 2).~~.

The 'cornerpoints' are not presented in the DOM development plots, since both DIN and DIP in them were modified. Therefore, including these treatments could bias the interpretation of effects induced by single inorganic nutrients. However, in plots and analyses where DIP or DIN influence was investigated all treatments were included to avoid ~~the~~a single nutrient effect overestimation ~~(see Fig.3, 4, 5).~~.

For an estimation of the drivers of changes in DOM optical properties, the covariance of total accumulation of DOM compounds (Δ_8DOM) with the cumulative sum of POM ($\sum_{POM}$) parameters was tested by linear regression analysis.

Mean normalized deviations (mean dev. %), calculated as:

$$mean\ dev\ \% = \frac{100}{\Delta Cn} \sum_{start}^{end} \Delta Ci(k) - \overline{\Delta C(k)}; \quad (~~6~~5)$$

where C- is a concentration, absorption or fluorescence intensity, k – is the day of experiment, n – is a total number of days ($n = end - start$) and i - is a mesocosm ID ($i = 1 - 16$); $\Delta Ci(k)$ is calculated by equation (4), $\overline{\Delta C(k)}$ – is the mean ΔC for all mesocosms at the day k, and $\overline{\Delta C}$ – is average ΔC for all mesocosms during the whole experiment. Mean dev. (%) were tested against nutrient supply (~~*varied*~~Varied P and ~~*varied*~~Varied N) and DIN:DIP supply ratio in the mesocosms at day 2 in order to estimate the nutrient and stoichiometry effect on DOM accumulation in the mesocosms.

All statistical tests in this work were performed by the use of Sigma Plot 12.0 (Systat). The significance level ~~accepted~~ was $p < 0.05$.

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3. Results

3.1 Particulate organic matter development

After nutrient addition, a phytoplankton bloom development was observed in all mesocosms during both experiments. Maximum chl *a* concentrations in ~~*varied*~~Varied P occurred at day 5 (Fig.1a), with higher concentrations in treatments with initial nutrients supplied at lower or equal to Redfield N:P ratio (12.00N/0.75P, 12.00N/1.25P, 12.00N/1.75P). However, no significant relationship of the cumulative sums of chl *a* ($\Sigma_{chl\ a}$) to DIP concentration was recognized (p>0.05, n=15). In ~~*varied*~~Varied N, chl *a* concentrations reached its maximum at day 6 (Fig.1b) and $\Sigma_{chl\ a}$ were significantly affected by the initial DIN concentrations (Wilcoxon rank test: p<0.001, n=16), indicating that DIN was ~~limiting~~regulating phytoplankton biomass buildup.

Bacterial abundance increased until day 6 (paired t-test: p>0.001, n=31) in all mesocosms and then stayed relatively constant towards the end of both experiments (paired t-test: p>0.05, n=31; Fig.1c, d). In ~~*varied*~~Varied P, cumulative sums of bacterial abundance (Σ_{bac}) were not related to the initial DIP supply (p>0.05, n=15). Highest bacterial abundance was observed at day 6, yielding 2.0±0.7x10^6 mL^{-1} averaged for all treatments (Fig.1c). In contrast, in ~~*varied*~~Varied N, Σ_{bac} ~~indicated significant covariance~~was significantly positively correlated to DIN amendments (p<0.01, n=16). The highest bacterial abundance of 2.6±0.2x10^6 mL^{-1} was observed at day 6 in the treatment with the highest initial DIN concentration (20.00N/0.75P).

3.2 Dissolved organic matter

3.2.1 Dissolved organic matter ~~abundance~~concentration

~~Initial~~The initial DOC ~~concentrations~~concentration (day 3), did not differ significantly between treatments in ~~*varied*~~Varied P (one way ANOVA: p>0.05, n=15) and was 99±5 µmol L^{-1} on average. In contrast, in ~~*varied*~~Varied N initial DOC concentrations (day 2) varied significantly among ~~mesocosms~~treatments (Holm-Sidak test: p<0.001, n=16) with 87±2 µmol L^{-1} in the treatment with second lowest initial DIN concentrations (4.00N/0.75P), 91±1 µmol L^{-1} ~~in~~on average for the Redfield DIN:DIP treatment (12.00N/0.75P) and ~~in~~for the treatment with the lowest initial DIN concentrations (2.00N/0.75P), and 95±3 µmol L^{-1} in the treatment with the highest initial DIN concentrations (20.00N/0.75P). The calculation of DOC accumulation (ΔDOC) thus allowed a better comparison of bulk DOC dynamics between treatments than absolute concentrations and will be given in the following.

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During both experiments, DOC accumulated significantly over time (paired t-test of start and end values: p<0.001, n=~~31~~15 and 16, respectively) with generally higher accumulation observed in ~~varied~~Varied N than in Varied P (Mann-Whitney rank sum test: p<0.001, n=120). On day 8, accumulation of DOC (Δ_8DOC) was highest (33±23 µmol L^{-1}) in the highest DIP treatment (12.00N/1.75P) in ~~varied~~Varied P (Fig.2a), as well as in the highest DIN treatment (20.00N/0.75P) in ~~varied~~Varied N (67±3 µmol L^{-1}) (Fig.2b).

Initial average CDOM absorption at 325 nm (~~a_{325}~~)$a_{CDOM}(325)$) was 0.17±0.03 m^{-1} and 0.15±0.01 m^{-1} for mesocosms of ~~varied~~Varied P and ~~varied~~Varied N, respectively (~~Appendix A. c~~Fig.S1c, d). ~~The~~For both experiments, the starting CDOM absorption values were not significantly different between treatments (one way ANOVA: p>0.05, n=~~31).~~15 and p>0.05, n=16). However, they differed between the two experiments (one way ANOVA: p<0.05, n=31). CDOM accumulation (~~Δa_{325}~~)$\Delta a_{CDOM}(325)$) will be given in the following, as it allows a better comparison of CDOM dynamics between experiments than absolute absorption coefficients.

CDOM accumulated over time during both experiments (paired t-test of start and end values: p<0.001, n=~~31).~~15 and p<0.001, n=16, respectively). CDOM accumulation on day 8 (~~$\Delta_8 a_{325}$~~)$\Delta_8 a_{CDOM}(325)$) was~~ the~~ highest in the medium to high DIP treatment (12.00N/0.75P, 12.00N/1.25P, 12.00N/1.75P) in ~~varied~~Varied P (0.35±0.03 m^{-1}) (Fig.2c) and in the highest DIN treatment (20.00N/0.75P) in ~~varied~~Varied N (0.48±0.13 m^{-1}) (Fig.2d).

Spectral slopes, calculated within the 275-295 nm spectral range, ($S_{275\text{-}295}$) differed between treatments in the beginning of ~~varied~~Varied N (one way ANOVA: p<0.05, n=16), whereas treatments in the beginning of ~~varied~~Varied P were not significantly different (one way ANOVA: p~~<~~>0.05, n=15). ~~In contrast, initial values of spectral slopes, calculated within the 320-500 nm spectral range (S_{SEMO}), varied between treatments at the beginning of *varied P* (one way ANOVA: p<0.05, n=15), but not at the beginning of *varied N* (one way ANOVA: p<0.05, n=16).~~ In order to avoid the influence of initial differences of spectral slopes on data analyses, daily changes in spectral slopes ($\Delta S_{275\text{-}295}$~~ and ΔS_{SEMO}~~) were calculated. More negative $\Delta S_{275\text{-}295}$ ~~and ΔS_{SEMO}~~ indicate that the spectral ~~slopes are~~slope is decreasing. As the spectral slope ~~decrease~~decreased, CDOM absorption at longer wavelengths ~~becomes~~became higher, indicating accumulation of HMW CDOM.

$S_{275\text{-}295}$ decreased over time in both experiments (paired t-test~~: p<0.001, n=31).~~ of start and end values: p<0.01, n=15 and p<0.01, n=16, for Varied P and Varied N respectively). The most negative $\Delta S_{275\text{-}295}$ values (-0.016±0.004 nm^{-1} and -0.014±0.002 nm^{-1}) were observed in

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the treatments with medium and high initial DIP concentrations (12.00N/0.75P, 12.00N/1.25P, 12.00N/1.75P) at the end (day 8) of ~~*varied*~~Varied P (Fig.2e) and in the treatment with the highest initial DIN concentrations (20.00N/0.75P) in at the end (day 8) of ~~*varied*~~Varied N (Fig.2f), respectively. ~~Values for ΔS_{SEMO} decreased on average by 7±3 µm^{-1} from the beginning (day 3 and day 2) until the end (day 8) of both experiments (*paired t-test: p<0.001, n=15, 16).*~~ In general, ~~ΔS_{SEMO} dynamics mirrored those of~~ $\Delta S_{275\text{-}295}$~~. Both~~ decreased faster in treatments with medium and high initial DIP concentrations (12.00N/0.75P, 12.00N/1.25P, 12.00N/1.75P) in ~~*varied*~~Varied P and in treatment with the highest initial DIN concentrations (20.00N/0.75P) in ~~*varied*~~Varied N (Table 2).

~~Derived from measured parameters,~~In the ~~ratio (S_R) of~~ relationship between $S_{275\text{-}295}$ and ~~spectral slopes, calculated within 350-400 nm wavelength range ($S_{350\text{-}400}$),~~$a_{CDOM}(325)$ no apparent differences between treatments were found. The relationship could be explained by equation (2) with $\alpha = 0.022$ and $\delta = 0.0035$ (Fig.3).

The S_R had much larger uncertainties within treatments than spectral slopes themselves. The initial S_R (day 3 and day 2) ~~S_R were~~was not statistically different among treatments in each experiment (one way ANOVA: p>0.05, n=~~31~~15 and 16, respectively) and between experiments (one way ANOVA: p>0.05, n=31).

S_R increased only slightly over time in almost all mesocosms of ~~*varied*~~Varied P (paired t-test of start and end values: p<0.05, n=15; Fig.2g). In ~~*varied*~~Varied N, S_R increased significantly on day 5 (paired t-test of start and day 5 values: p<0.001, n=16) and decreased again slightly on day 7 (paired t-test of day 5 and day 7 values: p<0.05, n=16) in almost all mesocosms (Fig.2h).

Three FDOM components with distinct spectral properties were identified during PARAFAC analysis of our dataset. The first FDOM component (Comp.1) was excited at 235 nm and emitted at 440-460 ~~(300)~~ nm, the second (Comp.2) and the third (Comp.3) FDOM components were excited at 275~~(<230)~~ and 265 nm and emitted at 340 and 294 nm respectively. Both also had secondary excitation peaks at wavelength less than 230 nm (Table 3, ~~Appendix B).~~ Fig.4).

The initial fluorescence of Comp.1 was 0.019±0.001 Raman Units (RU) in ~~*varied*~~Varied P and 0.0108±0.0009 RU in ~~*varied*~~Varied N. Initially, Comp.1 fluorescence was not significantly different between treatments in both, ~~*varied*~~Varied P and ~~*varied*~~Varied N (one way ANOVA: p>0.05, n=~~31~~15 and p>0.05, n=16, respectively) in contrast to initial differences between two experiments (one way ANOVA: p<0.01, n=31).

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Subtracting the initial fluorescence of Comp.1 (ΔComp.1 ~~calculating~~) allowed tracing the accumulation of freshly-produced Comp.1 during the experiments (Fig.2i, j).

ΔComp.1 indicated an accumulation of Comp.1 over time in both experiments (paired t-test of start and end values: $p<0.001$, $n=$~~31).~~15 and $p<0.001$, $n=16$). In ~~varied~~Varied P, differences in ΔComp.1 fluorescence between treatments at the end of the experiment were not significant (t-test: $p>0.05$, $n=6$) and revealed 0.014±0.004 RU on the average for all mesocosms (Fig.2i). In ~~varied~~Varied N, the highest ΔComp.1 fluorescence intensities of 0.025±0.004 RU were found in the treatment with the highest DIN supply (20.00N/0.75P) (Fig.2j). Here, clear differences were observed between treatments at the end of the experiment (one way ANOVA: $p<0.01$, $n=$~~11~~8).

The fluorescence intensities of Comp.2 were almost identical at the start of ~~varied~~Varied P and ~~varied~~Varied N, yielding 0.029±0.005 RU and 0.029±0.007 RU, respectively. No significant differences were observed between treatments (one way ANOVA: $p>0.05$, $n=$~~31~~15 and $p>0.05$, $n=16$, for Varied P and Varied N respectively) and experiments (one way ANOVA: $p>0.05$, $n=31$).

Comp.2 fluorescence increased in all mesocosms over time (paired t-test of start and end values: $p<0.001$, $n=$~~31~~15 and $p<0.001$, $n=16$) (Fig.2k, l). At the end (day 8) of ~~varied~~Varied P, the maximum ΔComp.2 fluorescence was 0.063±0.007 RU in the treatment with highest DIP addition (12.00N/1.75P) (Fig.2k). ~~It~~At day 8, it was significantly higher than that in the treatment with the lowest initial DIP concentration (12.00N/0.25P) (t-test: $p<0.05$, $n=6$~~) at day 8.~~). Differences between treatments with the highest (20.00N/0.75P) and the lowest (2.00N/0.75P) initial DIN concentrations at the end (day 8) of ~~varied~~Varied N were not significant (t-test: $p>0.05$, $n=6$) and the maximum ΔComp.2 fluorescence comprised 0.04±0.03 RU on average for all mesocosms (Fig.2l).

The Comp.3 fluorescence intensity was highly variable during both experiments (Fig.2m, n). Its starting values were not statistically different between ~~varied~~Varied P and ~~varied~~Varied N (two way ANOVA: $p>0.05$, $n=31$) and comprised 0.03±0.02 RU in both.

In ~~varied~~Varied P, Comp.3 fluorescence intensity increased from start until day 5 (paired t-test of start and day 5 values: $p<0.05$, $n=15$) and decreased after day 6 until end of experiment (paired t-test of day 5 and end values: $p<0.05$, $n=15$) (Fig.2m). In ~~varied~~Varied N, Comp.3 accumulated significantly only after day 6 (paired t-test of day 6 and end values: $p<0.05$, $n=16$) (Fig.2n).

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3.2.2 Assessing the origin of optically active dissolved organic matter

To investigate a potential influence of phytoplankton or bacteria abundances on DOC concentrations and CDOM and FDOM accumulation, cumulative sums of chl *a* ($\Sigma_{chl\ a}$) and bacterial abundance (Σ_{bac}) of each mesocosm (~~Appendix C~~Section S2) were tested against total accumulation of DOM components at day 8 (Δ_8DOM) using linear regression analysis.

Values of Δ_8DOC correlated significantly with $\Sigma_{chl\ a}$ in ~~*varied*~~Varied P (p<0.05, n=15) and in ~~*varied*~~Varied N (p<0.001, n=16), but not with Σ_{bac} (p>0.05, n=15~~,~~ and p>0.05, n=16, respectively).

~~To look at CDOM properties, the relationship between S_{SEMO} and a_{375} were compared to an equation (2) parametrization by Stedmon and Markager (2001) for marine CDOM of the Greenland Sea. In our study, no apparent differences between treatments were found and all data for S_{SEMO} versus a_{375} could be expressed by equation (2). However, our data went beyond the limits defined by Stedmon and Markager, except those in the beginning of experiment (Fig.3). Therefore, new parameterization of the equation (2) was obtained in this study by nonlinear least square fitting method (MATLAB, The MathWorks Inc.), with α = 17.5 and δ = 0.2.~~

~~Furthermore,~~ CDOM accumulation (~~$\Delta_8 a_{325}$~~$\Delta_8 a_{CDOM}(325)$) correlated significantly to $\Sigma_{chl\ a}$ in ~~*varied*~~Varied P (p<0.05, n=15) and ~~*varied*~~Varied N (p<0.001, n=16), indicating that phytoplankton biomass was regulating CDOM dynamics in both experiments. While no covariance of ~~$\Delta_8 a_{325}$~~$\Delta_8 a_{CDOM}(325)$ with Σ_{bac} was observed during ~~*varied*~~Varied P (~~*lin. regr.:* p>0.05~~, n=15), a significant correlation of ~~$\Delta_8 a_{325}$~~$\Delta_8 a_{CDOM}(325)$ with Σ_{bac} (~~*lin. regr.:* r^2=0.33,~~ p<0.05, n=16) occurred in ~~*varied*~~Varied N, indicating that bacteria may be partially responsible for CDOM dynamics under DIN stimulation.

ΔComp.1 behaved similar to ~~Δa_{325}~~$\Delta_8 a_{CDOM}(325)$ during both experiments. However, Δ_8Comp.1 was neither correlated to Σ_{bac} (p>0.05, n=15), nor to $\Sigma_{chl\ a}$ concentration (p>0.05, n=15) in ~~*varied*~~Varied P. In contrast Δ_8Comp.1 was significantly correlated to both, $\Sigma_{chl\ a}$ (p<0.001, n=16) and Σ_{bac} (p<0.05, n=16) in ~~*varied*~~Varied N.

Similar to Δ_8Comp.1, in ~~*varied*~~Varied P, Δ_8Comp.2 did not reveal a significant relationship to $\Sigma_{chl\ a}$ (p>0.05, n=15) concentration or to Σ_{bac} (p>0.05, n=15). In ~~*varied*~~Varied N, Δ_8Comp.2 also did not correlate to $\Sigma_{chl\ a}$ concentration (p>0.05, n=16), but it covariate significantly to Σ_{bac} (p<0.01, n=16), supporting a potential influence of bacterial abundance on fluorescence intensities of Comp.2.

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In contrast to Δ_8Comp.1 and Δ_8Comp.2, Δ_8Comp.3 did not covariate, neither with Σ_{bac} (p>0.05, n=15, and p>0.05, n=16), nor with $\Sigma_{chl\ a}$ concentration (p>0.05, n=15, and p>0.05, n=16) in both experiments.

3.2.3 Effect of inorganic nutrients on optically active DOM

To assess the nutrient influence on DOM accumulation, mean normalized deviations (mean dev. %) of ΔDOC, ΔCDOM ($\Delta a_{CDOM}(325)$) and ΔFDOM were calculated for each mesocosm (including "corner" points) and tested against initial DIP supply in Varied P, and against initial DIN supply in Varied N using linear regression analysis (Fig. 5), and also against DIN:DIP ratio combining both experiments.

DOC accumulation was related to the initial inorganic nutrient supply in both experiments. Higher ΔDOC (mean dev. %) corresponded to higher DIP supply (p<0.05, n=15) in Varied P (Fig. 5a) and to higher DIN supply (p<0.05, n=16) in Varied N (Fig. 5b). However, no overall effect of DIN:DIP ratios was revealed when data from both experiments were combined (p>0.05, n=31). Therefore, accumulation of DOC, in general, was dependent rather on total initial amount of macronutrients, than on the relative concentration of DIN to DIP.

ΔCDOM (mean dev. %) correlated significantly to DIN supply (p<0.001, n=14) (Fig.4c), but not to DIP supply (p>0.05, n=15) (Fig.5d). Similar to ΔDOC (mean dev. %), no effect of initial DIN:DIP ratios on ΔCDOM (mean dev. %) was determined (p>0.05, n=31).

ΔComp.1 (mean dev. %) did not exhibit a significant relationship to the initial DIP supply (p>0.05, n=15) (Fig.5e), but correlated significantly to the initial DIN concentrations (p<0.001, n=12) (Fig.5f).

Oppositely, ΔComp.2 (mean dev. %) increased with initial DIP supply (p<0.05, n=14) (Fig.5g), but not with initial DIN supply (p>0.05, n=12) (Fig.5h). Thus, Comp.2 accumulation was higher under the higher DIP concentrations.

In contrast to both previous FDOM components, ΔComp.3 (mean dev. %) did not reveal covariance neither to DIP (p>0.05, n=15) (Fig.5i), nor to DIN (p>0.05, n=12) initial supply (Fig.5n).

No overall effect of DIN:DIP ratios on ΔComp.1, ΔComp.2 and ΔComp.3 (mean dev. %) was determined when data from both experiments were combined (p>0.05, n=27, p>0.05, n=27 and p>0.05, n=27, respectively).

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Hence, accumulation of Comp.1 was dependent on the initial DIN concentrations, accumulation of Comp.2 increased with increase of initial DIP concentrations and Comp.3 was unaffected by nutrient treatments.

3.2.4 Nutrients effects on the relationship between CDOM and DOC

To investigate the relationship between CDOM absorption and DOC concentrations during the course of the experiments, daily DOM accumulation (ΔDOC) was tested against daily accumulation of CDOM at 325 nm (~~Δa_{325}~~)$\Delta a_{CDOM}(325)$) by linear regression analysis for each mesocosm and for all data combined (Fig.~~5a~~6a, b). Direct overall relationships were observed between ΔDOC and ~~Δa_{325}~~$\Delta a_{CDOM}(325)$ in both, ~~*varied*~~Varied P (p<0.001, n=75) and ~~*varied*~~Varied N (p<0.001, n=95).

The estimated slopes of ~~those~~ linear regressions, determined for each mesocosm for ~~Δa_{325}~~$\Delta a_{CDOM}(325)$ vs ΔDOC~~,~~ ($d\Delta a_{CDOM}(325)/d\Delta DOC$), were tested for correlation with the initial DIP (Fig.~~5c~~6c) and DIN (Fig.~~5d~~6d) concentration~~. Estimated slope values~~, in Varied P and Varied N, respectively. The $d\Delta a_{CDOM}(325)/d\Delta DOC$ significantly increased with an increase of initial DIN supply (p<0.01, n=16), indicating that the ~~CDOM~~colored fraction of DOC was affected by nutrient availability ~~and~~, specifically by DIN supply.

Although the relationship between CDOM and DOC revealed a dependency on initial DIN supply, the values of ~~CDOM at 355 nm (a_{355}~~$a_{CDOM}(325)$ to DOC ratio (~~a_{355}~~/$a_{CDOM}(325)$/DOC) did not reveal a significant nutrient effect, when plotted against $S_{275\text{-}295}$ (Fig.~~5e~~6e).

All data of $S_{275\text{-}295}$ and ~~a_{355}~~/$a_{CDOM}(325)$/DOC of our study ~~can~~could be described by the equation (3~~)~~), with coefficients~~, derived by Fichot~~ γ, δ, ε and ~~Benner (2012) for calculations of DOC concentrations. All our data points were fitting~~ζ equal to ~~8% uncertainty interval of estimation of DOC concentrations, defined by Fichot~~5.67, 81.23, 3.18 and ~~Benner (2012)~~23.03, respectively (Fig.~~5e).~~ 6e).

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4. Discussion

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~~Optically active DOM and its properties are often used for estimation of DOC concentrations and processes, influencing DOM. CDOM was previously shown to accumulate along with the remineralization of inorganic nutrients (Zhang et al., 2009) and therefore, was assumed as an indicator of bacterial DOM reworking (Swan et al., 2009, Nelson and Siegel, 2013). However, CDOM was also shown to be consumed during dark incubations (Zhang et al., 2009), and therefore characterized as containing fresh and labile DOM. For discrimination between freshly released by phytoplankton and microbially altered CDOM pools, specific properties of the CDOM spectrum are commonly used. Spectral slopes, for instance, can indicate a relative changes in HMW CDOM proportion in CDOM (Helms et al., 2008). Spectral slope ratios were used before to discriminate between biogeochemical processes influencing CDOM (Helms et al., 2008). Fluorescent fraction of CDOM (FDOM) is used for better characterization and discrimination between DOM pools with different spectral and therefore structural properties (Coble, 1996, Gueguen and Kowalczuk, 2013). Here, we investigated nutrient effects on the production, accumulation and cycling of CDOM and FDOM, as well as nutrient effects on relationship between CDOM absorption and DOC concentrations.~~

4.1 Nutrient effects on the production and cycling of optically active DOM

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Our results ~~indicated~~indicate that chl *a* accumulation and bacterial growth were stimulated by DIN supply. Along with the response of POM production to inorganic nutrient amendments, changes in the optically active DOM fractions were observed.

Initial DOC concentrations, measured in both experiments (~~Appendix Aa~~Fig.S1a, b), were in the range or slightly higher of those previously reported and modelled for the upper 30 m of the ~~ETNA~~Tropical Atlantic Ocean watercolumn (Hansell et al., 2009).

In both experiments, DOC accumulated over time (Fig. 2a, b) and seemed to be produced mainly ~~by~~through phytoplankton release. The highest DOC accumulation was observed on the moment of rapid transition from nutrient replete to nutrient depleted conditions (see also Engel et al., 2015). That is in line with previous studies (Engel et al., 2002, Conan et al., 2007, Carlson and Hansell, 2015) showing DOM accumulation after the onset of nutrient limitation, while the chl *a* signal decreased.

~~An~~The effect of initial nutrient ~~concentration~~concentrations on DOC accumulation (Fig. ~~4a~~5a, b), observed in our study, was shown previously. In a mesocosm study with ETNA waters, Franz et al. (2012) observed that higher DOC concentrations developed when the initial

inorganic nitrogen supply was high. As well, DOC concentrations in their study were even higher when high DIN concentrations were combined with high DIP supply. In their mesocosm experiment in ~~Arctic~~Raunefjord, Conan et al. (2007) and Stedmon and Markager (2005) observed that at silicate-replete conditions, DOC concentrations under high initial DIN supply did not vary significantly from those under high initial DIP concentrations. In our study, silicate was also not limiting phytoplankton growth and higher DOC concentrations occurred at higher DIP as well as at higher DIN concentrations, supporting earlier findings.

Bacterial turnover may have influenced the composition of DOM (as it is seen by changes in spectral slope ratios and FDOM components) while DOC concentrations seemed to be not related to bacterial abundances. This observation may be explained by rapid bacterial consumption of labile DOM accompanied by the bacterial release of altered humic-like DOM (Azam et al., 1983, Ogawa et al., 2001), which are therefore not influencing measured DOC concentrations (e.g. Kirchman, 1991).

At the beginning of the experiment, CDOM ~~absorptions~~absorption coefficients 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 (~~Appendix Ac~~Fig.S1c, d; ~~Nelson~~Andrew et al., ~~2009~~2013, Nelson and Siegel, ~~2012, Swan et al., ~~2013). Similar to our experiments, CDOM absorption was previously shown to accumulate by factor of 2 ~~to 3 ~~during mesocosm studies ~~(Zhang et al., 2009,~~, such as study by Pavlov et al~~., ~~. (2014~~).~~), where nutrient levels for DIN were kept at 5 µmol L^{-1} and 0.32 µmol L^{-1} for DIP.

In our experiments, the accumulation of CDOM during the phytoplankton bloom (Fig. 2c, d) as well as significant covariance to phytoplankton pigment – chl *a* - concentration suggests that phytoplankton was the major source of CDOM. This is consistent with previous studies that show CDOM to be produced by extracellular release from phytoplankton (Romera-Castillo et al., 2010) or by phytoplankton degradation or lysis (Hu et al., 2006, Zhang et al., 2009, Organelli et al., 2014).

~~Changes in CDOM spectral properties, such as the ~~The decrease of CDOM spectral slopes over time (Fig. 2e, f~~),~~) along with the increase in CDOM concentrations (Fig.3) indicated that absorption in the visible wavelength range increased relatively to the UV wavelength range. As the absorption at longer wavelength is corresponding to larger molecules, we may assume that HMW-CDOM accumulated during both experiments. HMW-DOM was previously shown to be more labile for bacterial consumption than low molecular weight DOM (at molecular weight cutoff of 1 kDa) (Benner and Amon, 2015), as bacterial activity was higher,

when incubating with HMW-DOM (Amon and Benner, 1996). Furthermore HMW-DOM is typically accounting ~~to~~for 30 to 60 % of the total DOM released via phytoplankton (Biddanda and Benner, 1997, Engel et al., 2011). Therefore, we consider the spectral slope decrease over time as an indication of labile CDOM production via phytoplankton release.

In treatments with high initial DIN concentrations, bacterial abundance was significantly higher than in those ~~at~~with lower initial DIN concentrations. Furthermore, bacterial abundances in Varied N correlated significantly to CDOM concentrations. We therefore suggest that higher bacterial abundance may have been responsible for an additional production of CDOM in mesocosms, particularly in those~~, where~~ with high initial DIN supply ~~was high~~.

This suggestion is made also based on changes in optical properties during our study. ~~As~~As Helms et al (2008) and Zhang et al. (2009) showed before, the spectral slope ratio (S_R) decreases, when bacterial modification of CDOM takes place. A slight decrease of S_R towards the end of ~~*varied*~~Varied N (Fig.2 h), most likely indicated that CDOM was reworked by bacteria. ~~The idea~~Our conclusion of ~~an~~ additional CDOM production by bacteria in this experiment is also in agreement with previous studies, where DOM bacterial reworking was indicated as CDOM source (Rochelle-Newall and Fisher, 2002, ~~Nelson et al.,~~ Kramer and Herndl, 2004, Nelson ~~and Siegel, 2013~~et al., 2004, Biers et al., 2007, Swan et al., 2009~~),~~ Nelson and Siegel, 2013).

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However, due to its large uncertainties within treatments, S_R was not sufficient to estimate the degree of bacterial CDOM production, most likely due to screening of the effect by simultaneous high HMW-DOM production via phytoplankton release. Therefore, CDOM production via phytoplankton release, which occurred proportionally to phytoplankton biomass, was likely more pronounced than CDOM production via bacterial reworking of labile DOM.

The CDOM to DOC ratio was also affected by variable initial DIN concentrations. A significant positive correlation of CDOM accumulation over time with DOC concentration was found in both experiments (Fig.~~5a~~6a, b), indicating that DOC and CDOM had been affected by the same processes. Estimated slopes of ΔCDOM against ΔDOC (Fig. ~~5d)~~6d), in Varied N, were highest at highest initial DIN concentrations ~~in *varied N*~~, indicating that relative proportion of CDOM in bulk DOM may be regulated by the presence of DIN.

Factors, influencing the ratio between CDOM absorption and DOC concentrations are little understood so far. It is known that CDOM absorption often co-varies with DOC concentration

in river estuaries and coastal seas, which are influenced to a high degree by conservative mixing of riverine and marine waters (Nelson and Siegel, 2013, Rochelle-Newall et al., 2014). However, in the open ocean, the relation is losing its consistency (Nelson and Siegel, 2013). We suggest that under higher initial DIN concentrations bacterial abundance is higher and such is the bacterial reworking of DOM. Higher bacterial reworking, in its turn, causes an increase in the proportion of the colored fraction in DOM. Our results suggest that an increase of initial DIN concentrations by 10 µmol L^{-1} would cause an increase in CDOM accumulation ($\Delta a_{CDOM}(325)$) by 1.4 x 10^{-3} m^{-1} μmol^{-1} L (see Fig.6d) relative to accumulation of DOC (ΔDOC). The change, however, is small, compared to those, caused by other factors, as, for instance, mixing and photochemical oxidation (Stedmon and Nelson, 2015). Nonetheless, the effect may be important in regimes or at times, where or when changes of DIN concentrations are high.

~~We suggest that, under higher initial DIN concentrations, higher bacterial abundance and hence higher bacterial reworking of DOM, the proportion of the colored fraction in DOM increases. Our results suggest that an increase of initial DIN concentrations by 10 µmol L^{-1} would increase CDOM accumulation (Δa_{325}) relative to DOC concentrations (ΔDOC) by 1.4 x 10^{-3} m^{-1} μmol^{-1} L^{-} (see Fig.5d). The change however is small, compared to those, caused by other factors, as, for instance, mixing and photochemical oxidation (Stedmon and Nelson, 2015). However, the effect may be important in regimes or at times of large changes in DIN concentrations.~~

When CDOM properties, such as spectral slopes $S_{275\text{-}295}$, were also taken into account, the variance of relationship between CDOM ~~(a_{355})~~ and DOC between treatments was not as apparent (Fig.~~5e~~6e). We found a good correspondence between $S_{275\text{-}295}$ and ~~a_{355}~~/$a_{CDOM}(325)$/DOC ratio during our study, which could be explained by ~~the model of Fichot and Benner (2012).~~

~~Although the model was developed for DOC calculation from CDOM absorption and the spectral slope in river estuaries, our~~equation (3). Our data ~~fitted to the model limits. Therefore our data support the findings of Fichot and Benner (2012) of a~~ suggest, that the stable $S_{275\text{-}295}$ to ~~a_{355}~~/$a_{CDOM}(325)$/DOC relationship~~.~~

~~The model assumption is that changes in relative molecular weight and CDOM absorption~~ could be used for DOC estimation in the open ocean, when $S_{275\text{-}295}$ and $a_{CDOM}(325)$ are ~~proportional to changes in DOC concentrations. This relation, therefore, may be useful~~known, as, for instance, in field studies, where optical ~~measurements~~sensors are ~~available only~~used.

For remote sensing, however, an application of this relationship would be rather difficult, since ocean color remote sensing measurements are limited to an "optical window" of visible to near-infrared wavelength range (~~IDRISI Guide to GIS and Image Processing~~Robinson, 2010).

~~More~~Besides absorption, FDOM fractions were more sensitive to nutrient amendments ~~were FDOM fractions, of which~~. During our study, three different fluorescent components could be identified ~~during this study (Appendix B~~(Fig.4).

The characteristics of the first component, Comp.1 (Table 3), were similar to those of the humic-like peak 'A' described by Coble et al. (1996). The Comp.1 fluorescence was within the reported range of A-like peak fluorescence intensities for the open ocean area (~~Jorgensen~~Jørgensen et al., 2011) or slightly higher towards the end of experiments depending on mesocosm treatment~~.~~ (Fig.S1i, j).

~~Previous~~Marine humic substances were previously assigned to bacterially derived substances due to significant covariance of their concentrations to apparent oxygen utilization in deep open ocean waters (Swan et al., 2009, Kowalczuk et al., 2013, Nelson and Siegel, 2013). As well, previous studies of Stedmon and Markager (2005), Kowalczuk et al. (2009) and Zhang et al. (2009) showed that humic-like components, similar by spectral properties to Comp.1, ~~are~~were produced via microbial DOM reworking (Table 3~~, Appendix Ai, j).~~).

In our study, in ~~*varied*~~Varied N, Comp.1 was strongly correlated to initial DIN concentrations, as the final Comp.1 fluorescence intensity was almost three fold higher at the highest initial DIN supply than that in the treatments with lowest DIN supply. Thus, since bacterial abundance was DIN dependent in this experiment and Comp.1 fluorescence intensities correlated significantly to bacterial abundances, the bacteria were likely responsible for Comp.1 occurrence during our experiments. ~~In *varied P*, *Comp.*1 was not related to bacterial abundance. Similar initial DIN concentrations in all mesocosms may be a reason of the absence of covariance of *Comp.*1 with bacteria, since no significant differences between treatments were noticed for bacterial abundance and also only a little difference was noticed for *Comp.*1. Therefore, bacterial abundance may still be responsible for *Comp.*1 accumulation in this experiment. Also, if *Comp.*1 is bacterially mediated, its higher abundances in the end of our experiments compared to those in the open ocean may be explained by higher substrate availability in the mesocosms than that in the North Atlantic~~The proportional to DIN bacterial production of humic-like Comp.1 in our study is in agreement with Kramer and Herndl (2004) and Biers et al. (2007), where DIN and its organic derivatives

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were considered to be the primary drivers of humic-like DOM accumulation via bacterial reworking.

In Varied P, however, Comp.1 was not related to bacterial abundance. No significant differences between treatments were noticed for bacterial abundance and only little differences occured for Comp.1 at similar initial DIN supply concentrations. Thus, under equal initial DIN concentrations bacterial reworking of DOM could occur at similar degree, causing the absence of covariance of Comp.1 with bacterial abundance.

The higher concentrations of Comp.1 at the end of our experiments compared to concentrations measured in open ocean (Jørgensen et al., 2011) may be explained by slightly higher substrate availability in the mesocosms than that in the North Atlantic.

The fluorescence properties of the second FDOM component, Comp.2 (Table 3~~, Appendix Ak, l~~), were similar to that of the previously defined amino acid-like fluorescence (Mopper and Schulz, 1993, Coble et al., 1996, Stedmon and Markager, 2005): tryptophan-like peak 'T' (Coble et al., 1996). The fluorescence intensities of this component were in the range of that previously reported for open ocean area (~~Jorgensen~~Jørgensen et al., 2011) for the whole experimental period~~.~~ (Fig.S1k, l).

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Similar by spectral properties to Comp.2, amino acid-like compounds were previously hypothesized to represent the fluorescence of the bound-to-protein matrix amino acids tryptophan and tyrosine (Stedmon and Markager, 2005) and were assumed to be produced by phytoplankton (Mopper and Schulz, 1993, Coble et al., 1996). We, therefore, consider Comp.2 as an indicator of phytoplankton-produced proteinaceous DOM and as possible precursor for humic-like FDOM.

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In ~~*varied*~~Varied P, Comp.2 accumulated proportionally to initial DIP concentrations and its ~~abundances were~~concentration was not corresponding to chl *a* ~~concentrations~~concentration. This might indicate that proteinaceous DOM release by phytoplankton is controlled by nutrient availability, rather than by phytoplankton biomass itself, i.e. proteinaceous DOM is produced as a part of an "overflow mechanism~~ (Carlson~~" (Wood and ~~Hansell, 2015~~Van Valen, 1990) of extracellular release.

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In ~~*varied*~~Varied N, again no covariance of Comp.2 to chl *a* was determined. However, a covariance of Comp.2 with initial DIN concentrations did not occur as well. As bacteria were more abundant in treatments with higher initial DIN supply and also Comp.2 intensities revealed significant correspondence to bacteria, we suggest that ~~bacteria abundance~~bacterial

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reworking may have regulated Comp.2 fluorescence intensities, particularly under high initial DIN concentrations.

Previously, Stedmon and Markager (2005) showed an accumulation of a FDOM component, with spectral properties similar to Comp.2, during their mesocosm study treatments of high DIN and high DIP concentrations. This component was also shown to be consumed during dark and light incubations, when bacteria were added. Kirchman et al. (1991) showed that DOM uptake can be accompanied by a decrease in DIN concentrations, indicating the importance of DIN presence during bacterial reworking of labile DOM.

Therefore, Comp.2 production might be dependent on initial DIP and DIN availability, similarly to the increase of DOC concentrations. As well as at high initial DIN concentrations, Comp.2 may serve a substrate for developing bacteria, i.e. it can be ~~reworked~~consumed by bacteria ~~to~~that, in their turn, release humic-like Comp.1.

The spectral properties of the third fluorescent component (Comp.3) were similar to that of amino acid-like fluorescence (Table 3) (Mopper and Schulz, 1993, Coble et al., 1996, Stedmon and Markager, 2005): tyrosine-like peak 'B' (Coble et al., 1996) and were in the range of those previously reported for open ocean area (~~Jorgensen~~Jørgensen et al., 2011; Fig.S1m, n).

The development patterns as well as no clear response towards nutrient amendments of Comp.3 made it very difficult ~~for interpretation~~to interpret.

In Varied P, Comp.3 fluorescence intensities ~~increased~~were highest at the day of chl *a* maximum ~~in *varied P* ~~(Fig. 2m~~), suggesting that~~). Thus, Comp.3 could be released by phytoplankton ~~during its growth. Rapid~~at the growth phase, while after the chl *a* maximum, rapid bacterial reworking of ~~amino acid-like material may have occurred as well in this experiment and therefore, *Comp.*3 may have been consumed by bacteria after the chl *a* maximum. However, it could also be modified~~DOM or abiotic aggregation to Comp.2 ~~in *varied P*~~could remove Comp.3 from the mesocosms.

In ~~*varied*~~Varied N, Comp.3 fluorescence intensities were ~~significantly higher only~~generally low, but increased at the end of experiment (Fig. 2n). ~~*Comp.*3 accumulation at~~Therefore, the ~~end~~process of ~~this experiment could indicate~~ bacterial Comp.2 reworking ~~of the higher in molecular weight~~could lead to Comp.~~2 with~~3 release ~~of *Comp.*3~~ as byproduct~~.~~ at the final stage of Varied N. On the other hand, Comp.3 accumulation towards the end of this experiment could be a result of extracellular release of higher amounts of amino ~~acids~~acid-

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like substances, which accumulated under high DIN concentrations within ~~degrading~~ phytoplankton tissues~~, which were still released, after chl *a* concentration had decreased.~~ during its growth.

A fluorescent substance, similar by spectral properties to Comp.3, was previously hypothesized to represent the tryptophan and tyrosine in peptides ~~(~~by Stedmon and Markager~~,~~ (2005), ~~and~~as it ~~was also~~had been previously found accumulating during the denaturation of proteins (Determann et al., 1998). ~~No~~In their study, Stedmon and Markager (2005) found no effect of microbial ~~degradation was found~~ reworking on the abundance of this fluorescence substance in the dark and light incubations with bacteria ~~(Stedmon and Markager, 2005).~~. However, as this substance was removed during thier mesocosm experiment, they hypothesized spontaneous abiotic aggregation or photochemically induced flocculation ~~were hypothesized~~ as possible removal mechanisms.

~~For our study, we~~We, therefore ~~assume~~, conclude that~~,~~ Comp.3 potentially acted as an intermediate product during the formation or degradation of proteinaceous Comp.2 in our study. Still, the interpretation of the Comp.3 development remains speculative.

It was hypothesized previously that phosphorus limitation leads to accumulation of DOM more resistant to microbial degradation (Kragh and Sondergaard, 2009), e.g. due to phytoplankton extracellular release of this 'poor quality' DOM or limitation of bacterial DOM consumption (Carlson and Hansell, 2015). Based on changes in optical DOM properties (S_R, Comp.1, Comp.2) in our study, we suggest that labile DOM in the ETNA accumulates proportionally to either ~~high~~ DIN or ~~high~~ DIP concentrations. However, the 'poor quality' DOM accumulates more under high DIN concentrations (i.e. phosphorus limitation), due to bacterial DOM reworking. And even though bacterial activity per cell might have been limited by phosphorus availability, higher bacterial abundance in treatments with higher initial DIN supply would lead to more pronounced net accumulation of more resistant to microbial degradation DOM.

Overall, ~~during both of our experiments, the variance~~ the variances of CDOM ~~absorption values~~ and FDOM ~~components within~~ concentrations in the treatment with ~~Redfield ratio of~~ DIN:DIP of 16 (12.00N/0.75P) ~~of~~for each experiment ~~was~~were higher than the variance in this treatment between experiments. Therefore, the ~~nutrient~~ effects ~~for~~ of nutrients on CDOM and FDOM ~~components~~concentrations were considered much stronger, than possible effects, caused by ~~other factors.~~differences in initial sensitivity to nutrient additions. However, due to the ~~difference~~divergence in development pattern for some of optically active parameters (S_R,

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Comp.3~~) suggests that influence by additional factors may have influenced results and),~~ we cannot ~~be excluded.~~

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~~**4.2 Can marine CDOM in Tropical Ocean be predicted?**~~

~~When comparing our data to the empirical model, developed by Stedmon and Markager (2001) for discrimination between marine and riverine CDOM, the data from our mesocosms experiments did not fit to the model limits.~~

~~This model was developed for Arctic seas and was used successfully for separation of terrestrially originated CDOM from marine CDOM in the Arctic during mesocosm (Pavlov et al., 2014) and field studies (Granskog et al., 2012).~~

~~The model represents a parametrized equation (2), where $\alpha = 7.4$ and $\beta = 1.1$ with model limits, defined by authors as 4 standard deviations, which were calculated from results of dilution series (*see* Stedmon and Markager, 2001). 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.~~

~~Although our data did not fit the model limits, other origin than *in situ* production is hard to imagine for CDOM produced during our mesocosm study. Other factors, such as strong differences in environmental conditions, e.g. temperature, salinity, light availability, DOM background concentrations, DOM availability, as well as differences in microbial~~exclude the difference in pelagic communities ~~of Arctic compared to ETNA waters,~~ during Varied P and Varied N from the aspects that can ~~be responsible for this inconsistency~~cause an additional CDOM and FDOM variability during our study.

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~~The difference between our data and the Stedmon and Markager (2001) model prediction is caused mainly by higher spectral slope values (S_{SEMO}) of CDOM spectra. Insolation differences, between the region where the model was developed and the ETNA may be responsible for changes of CDOM spectral slope properties, as CDOM enters photoreactions (Sulzberger and Durisch Kaiser, 2008). Those photoreactions are primarily affecting the absorption in the visible wavelength range of light spectra producing uncolored and biologically available or refractory DOM (Benner and Amon, 2015). This could result in the reduction of CDOM absorption at higher wavelength and therefore explain an increase of spectral slope values.~~

~~We therefore suggest that care needs to be taken when using empirically derived models from different regions. Based on data from our mesocosm experiments, we give a new parametrization for surface waters of ETNA, that is:~~

$$~~S_{SLMD} = 17.5 + 0.2/a_{375}.~~$$

~~However, because this parametrization is based solely on our mesocosm experiments, affected by high nutrient input and phytoplankton bloom conditions, as well as absence of mixing, it needs to be reexamined in field studies in Tropical Ocean.~~

Another important aspect that could cause an additional CDOM and FDOM variability, and, therefore, bias the interpretation of obtained results during the mesocosm experiments, is the length of the sample storage. In our study, CDOM and FDOM samples were filtered through 0.45 µm pore-size filters and stored in the dark and cold (+4°C) for approximately 6 month pending analyses due to logistical reasons. This time-period is long and CDOM and FDOM concentrations could be affected by remained bacteria during storage. The long-term storage of open ocean CDOM samples has been tested previously by Swan et al. (2009). They demonstrated that the CDOM changes are unappreciable, when the storage of pre-filtered CDOM samples at 4°C does not exceed one year. Furthermore, during our study, FDOM samples from all the mesocosms were measured for day 4 of each experiment (31 samples in total) in approximately 3 month after main set of measurements has been accomplished. No drastic or appreciable changes in FDOM components concentrations have been noticed as they developed, e.g. neither between replicates, nor between treatments. Therefore, despite, the pore-sizes of our filters were larger, than those, used by Swan et al. (2009), we believe, that due to generally low CDOM and FDOM concentrations the error that could occur, would not majorly influence the CDOM and FDOM development patterns during our observations.

5. Conclusions

Our study shows that during phytoplankton blooms DOM is largely derived from phytoplankton, while its optical properties undergo considerable changes due to bacterial reworking. Thus, optically active proteinaceous substances are freshly produced by phytoplankton release. They are, however, consumed and reworked by bacteria, leading to accumulation of less-bioavailable optically active humic substances.

Our experiments indicate that DIN is the major macronutrient regulating the accumulation of bacterially originated optically active humic substances, while the accumulation of labile proteinaceous substances via phytoplankton is rather regulated by DIN and DIP. An input of humic substances can increase the CDOM/DOC ratio and therewith affect predictions of DOC concentration based on CDOM ~~absorbance.~~ absorption. Still, a relationship between CDOM spectral properties and CDOM and DOC concentrations can be derived, which is not influenced by nutrient differences.

~~Furthermore, our study contributes to the validation of the model developed by Fichot and Benner (2012). Our data suggest that this model could be used for an estimation of DOC concentrations in open waters of ETNA.~~

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All data will be available at www.pangaea.de upon publication of the manuscript.

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Table1. ~~varied~~Varied P and ~~varied~~Varied N: target concentrations and measured concentrations of DIN and DIN and treatment identifications according to target nutrients concentrations.

Mesocosm ID	~~varied~~Varied P					~~varied~~Varied N				
	target		Measured		Treatment	target		measured		Treatment
	DIN	DIP	DIN	DIP		DIN	DIP	DIN	DIP	
1	12.00	0.75	11.52	0.73	12.00N/0.75P	12.00	0.75	12.58	0.47	12.00N/0.75P
2	12.00	0.75	10.97	0.68	12.00N/0.75P	12.00	0.75	12.36	0.51	12.00N/0.75P
3	12.00	0.75	10.63	0.52	12.00N/0.75P	12.00	0.75	12.61	0.51	12.00N/0.75P
4	6.35	1.10	5.65	1.00	6.35N/1.10P	6.35	0.40	6.91	0.18	6.35N/0.40P
5	-	-	-	-	-	17.65	1.10	18.43	0.79	17.65N/1.10P
6	12.00	1.25	10.74	1.14	12.00N/1.25P	20.00	0.75	20.56	0.47	20.00N/0.75P
7	12.00	1.25	11.16	1.12	12.00N/1.25P	20.00	0.75	20.60	0.45	20.00N/0.75P
8	12.00	1.25	10.89	1.09	12.00N/1.25P	20.00	0.75	21.90	0.45	20.00N/0.75P
9	12.00	1.75	10.55	1.56	12.00N/1.75P	4.00	0.75	4.62	0.44	4.00N/0.75P
10	12.00	0.75	10.82	0.61	12.00N/0.75P	17.65	0.40	18.47	0.22	17.65N/0.40P
11	12.00	1.75	10.82	1.58	12.00N/1.75P	4.00	0.75	4.49	0.47	4.00N/0.75P
12	12.00	1.75	11.07	1.53	12.00N/1.75P	4.00	0.75	3.99	0.49	4.00N/0.75P
13	12.00	0.25	11.16	0.14	12.00N/0.25P	2.00	0.75	2.06	0.46	2.00N/0.75P
14	12.00	0.25	11.18	0.16	12.00N/0.25P	6.35	1.10	6.69	0.78	6.35N/1.10P
15	17.65	1.10	16.90	1.01	17.65N/1.10P	2.00	0.75	1.87	0.56	2.00N/0.75P
16	12.00	0.25	11.33	0.15	12.00N/0.25P	2.00	0.75	2.71	0.~~484148~~	2.00N/0.75P

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Table 2. Estimated linear ~~trends for~~change (per day) ($dS_{275-295}$) of spectral slope parameters for replicated treatments.

Parameter	~~varied~~Varied P				~~varied~~Varied N			
	12.00N/0.25P	12.00N/0.75P	12.00N/1.25P	12.00N/1.75P	2.00N/0.75P	4.00N/0.75P	12.00N/0.75P	20.00N/0.75P
~~S_{275}~~$dS_{275-295}$ (d^{-1}-nm^{-1} d^{-1})	-2.3×10^{-3}	-3.2×10^{-3}	-4.0×10^{-3}	-3.0×10^{-3}	-1.4×10^{-3}	-2.3×10^{-3}	-3.2×10^{-3}	-3.3×10^{-3}
~~S_{SEMO} (d^{-1}-nm^{-1})~~	~~$-0.7*10^{-3}$~~	~~$-1.1*10^{-3}$~~	~~$-1.5*10^{-3}$~~	~~$-1.4*10^{-3}$~~	~~$-1.1*10^{-3}$~~	~~$-1.5*10^{-3}$~~	~~$-2.0*10^{-3}$~~	~~$-2.0*10^{-3}$~~

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Table 3 Spectral characteristics of excitation and emission ~~maxima~~maximums and range of intensities (Fmax range) of the three fluorescent components identified by PARAFAC modelling in this study and their comparison with previously reported ones

this study				Literature		
Peak (region)	Excitation max	Emission max	Fmax range (RU)	Peak (region)	Autor	Properties
Comp.1	235	440-460 (300)	0.0090-0.0450	1 (<240(355)/476)	Stedmon and Markager 2005	Humic-like; Accumulated in P- and Si- limited bags *Source*: Microbial degradation, *Sink*: Photodegradation
				A (230-260/380-460)	Coble 1996	humic-, fulvik-like; *Sourse*: autochtonous, allochtonous; terrestrial
				C3 (250 (310)/400)	Kowalczuk et al. 2009	*Source*: Bacterial reworking
				C3 (255(330)/412)	Zhang et al. 2009	Terrestrial and marine humic-like; *Source*: microbial activity
				1(<230-260/400-500)	Ishii et al. 2012	Small-sized molecules, Photoresistant, biologically unavailible, conservative tracer; *Source*: Photodegradation
Comp.2	<230(275)	340	0.0200-0.1305	6 (280/338)	Stedmon and Markager 2005	Protein-like; Tryptophan-like fluorescence of protenacious material *Source*: algae at the growth; *Sink*: UV, microbial reworking
				T (275/340)	Coble 2007	Tryptophan-like, protein-like; autochtonous
				peak-T (275/358)	Romera-Castillo et al. 2010	protein-like; *Source*: sterile algae
Comp.3	265	290-300	0.0004-0.2105	4(275/306(338))	Stedmon and Markager 2005	Protein-like: fluorescence of tryptophan and tyrosine in peptides Higher production rates during establishing algal bloom *Source*: growing algae *Sink*: aggregation or microbial uptake
				B (275/305)	Coble 2007	Tyrosine-like, protein-like; *Source*: autochtonous
				C2 (275/<300)	Zhang et al. 2009	Tyrosine-like, protein-like; *Source*: autochtonous
				7 (270/299)	Yamashita et al. 2008	Tyrosine-like, protein-like; *Source*: autochtonous

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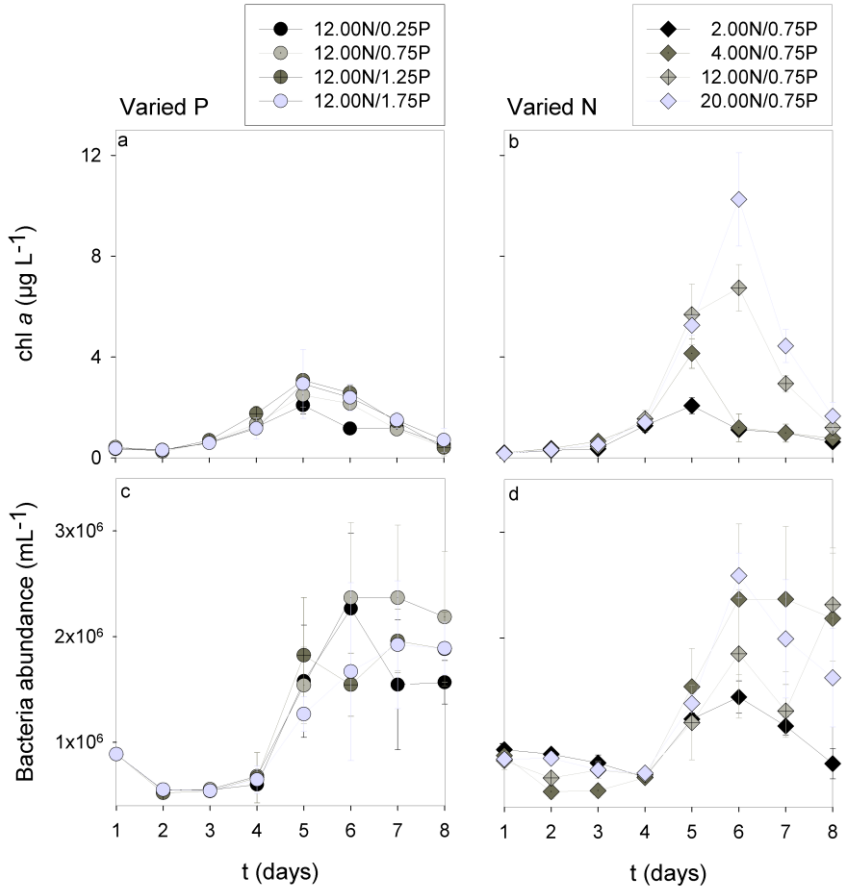

Fig.1 ~~The mean~~Mean development of chl *a* (a), bacterial abundance (c) in replicated treatments during ~~*varied*~~Varied P; and chl *a* (b), bacterial abundance (d) in replicated treatments during ~~*varied*~~Varied N~~.~~

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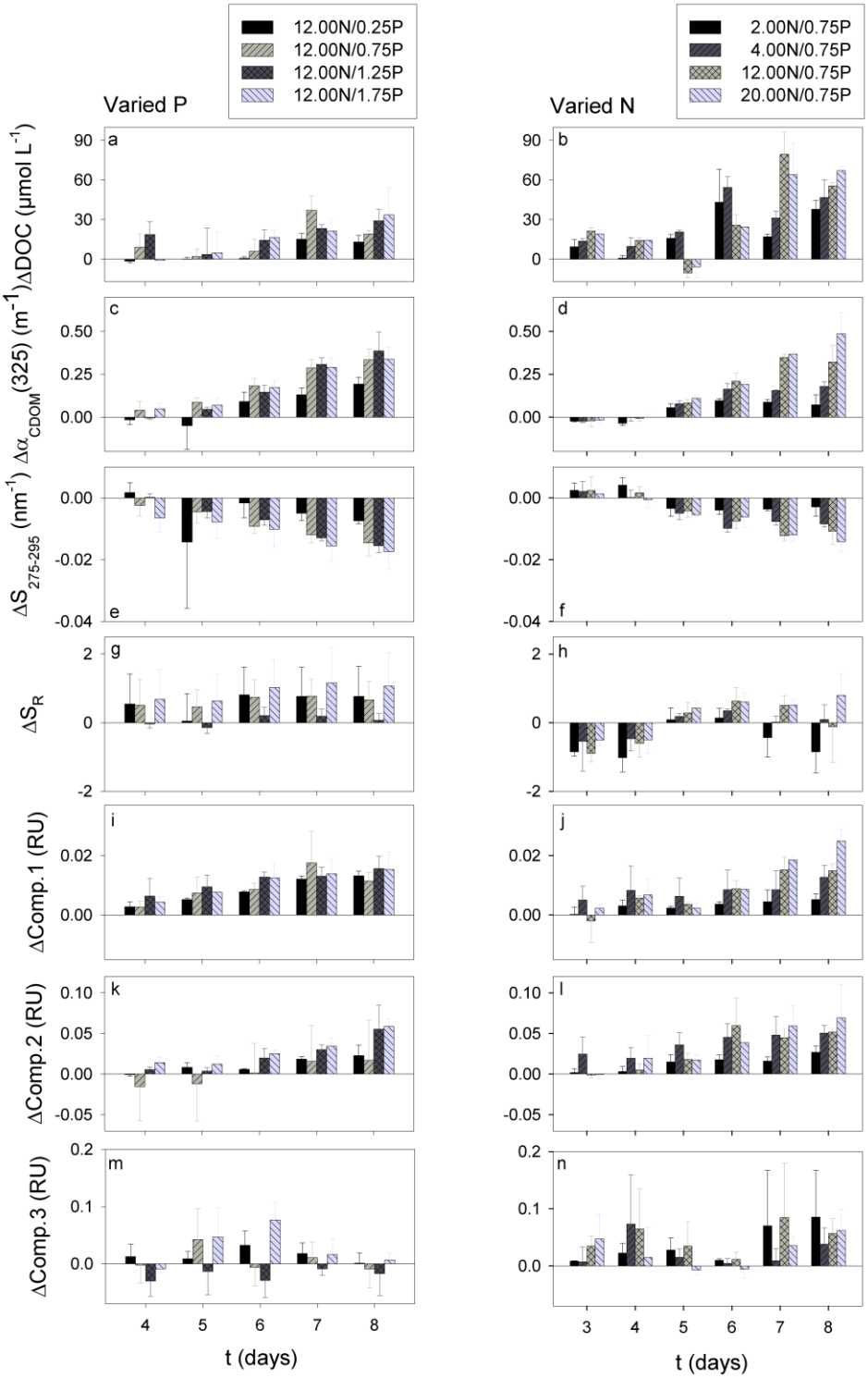

Fig.2 ~~The accumulation~~Accumulation over time: of DOC (ΔDOC) (a) during the ~~*varied*~~Varied P and (b) ~~during the *varied*~~Varied N, of CDOM ~~at 325nm (Δa_{325})~~($\Delta a_{CDOM}(325)$) (c) during the ~~*varied*~~Varied

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P and (d) ~~during the *varied*~~Varied N, of Spectral Slope ~~within 275-295 nm spectral range~~ ($\Delta S_{275\text{-}295}$) (e) during the ~~*varied*~~Varied P and (f) ~~during the *varied*~~Varied N, of spectral slope ratio (~~$S_{275\text{-}295}$/ $S_{350\text{-}400}$~~) ΔS_R) (g) during the ~~*varied*~~Varied P and (h) ~~during the *varied*~~Varied N, of first FDOM component fluorescence intensity (ΔComp.1) (i) during the ~~*varied*~~Varied P and (j) ~~during the *varied*~~Varied N, of second FDOM component fluorescence intensity (ΔComp.2) (k) during the ~~*varied*~~Varied P and (l) ~~during the *varied*~~Varied N, of third FDOM component fluorescence intensity (ΔComp.3) (m) during the ~~*varied*~~Varied P and (n) ~~during the *varied*~~Varied N~~.~~

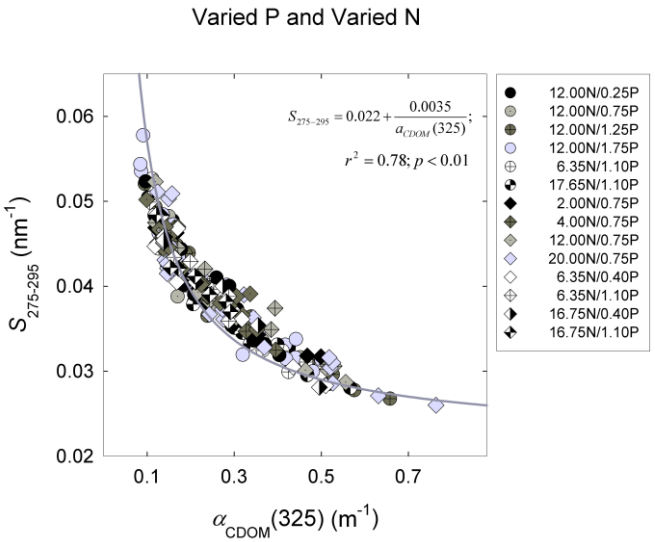

Fig.3 Spectral slope ~~S_{SEMO}~~$S_{275\text{-}295}$ against CDOM ~~at 375nm (a_{375}),~~($a_{CDOM}(325)$) obtained during both, ~~*varied*~~Varied P and ~~*varied*~~Varied N experiments (symbols). The dark-grey ~~dashed~~ line is ~~a model of Stedmon and Markager (2001) for marine CDOM with corresponding model limits (dark grey dotted lines).The reparametrized model, obtained in this study (light grey line) with model limits (light grey dotted lines), calculated according~~the best fit to ~~Stedmon and Markager (2001).~~the data

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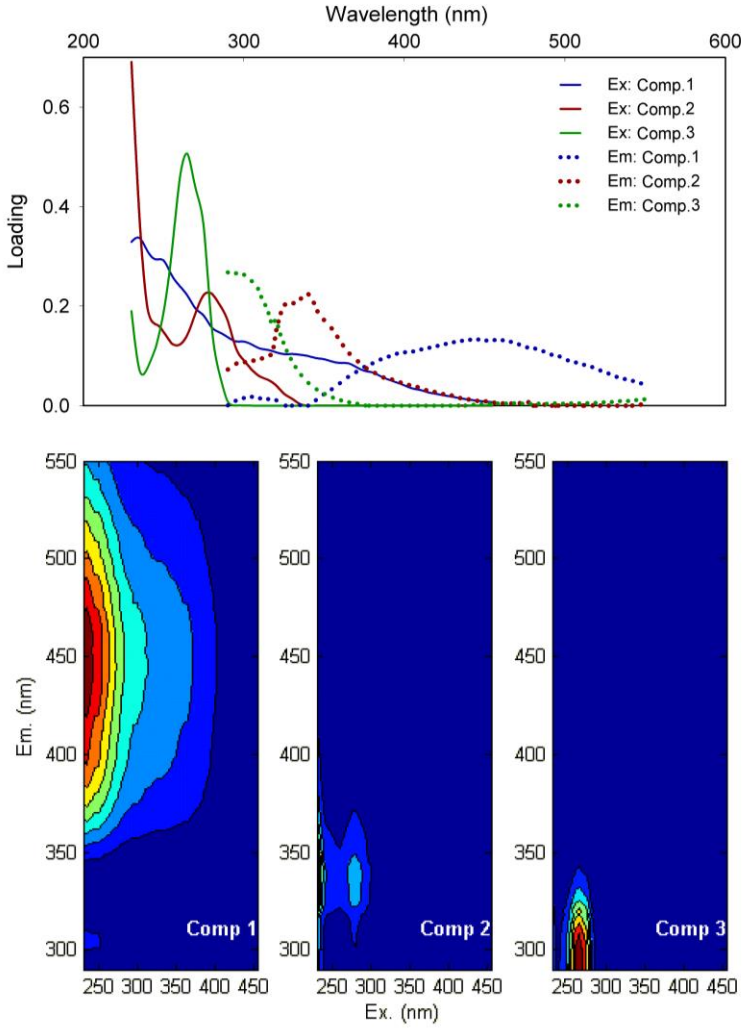

1248 ~~Fig.4.~~

1249 Fig.4. Spectral loadings (upper panel) and fingerprints (lower panel) of the FDOM components

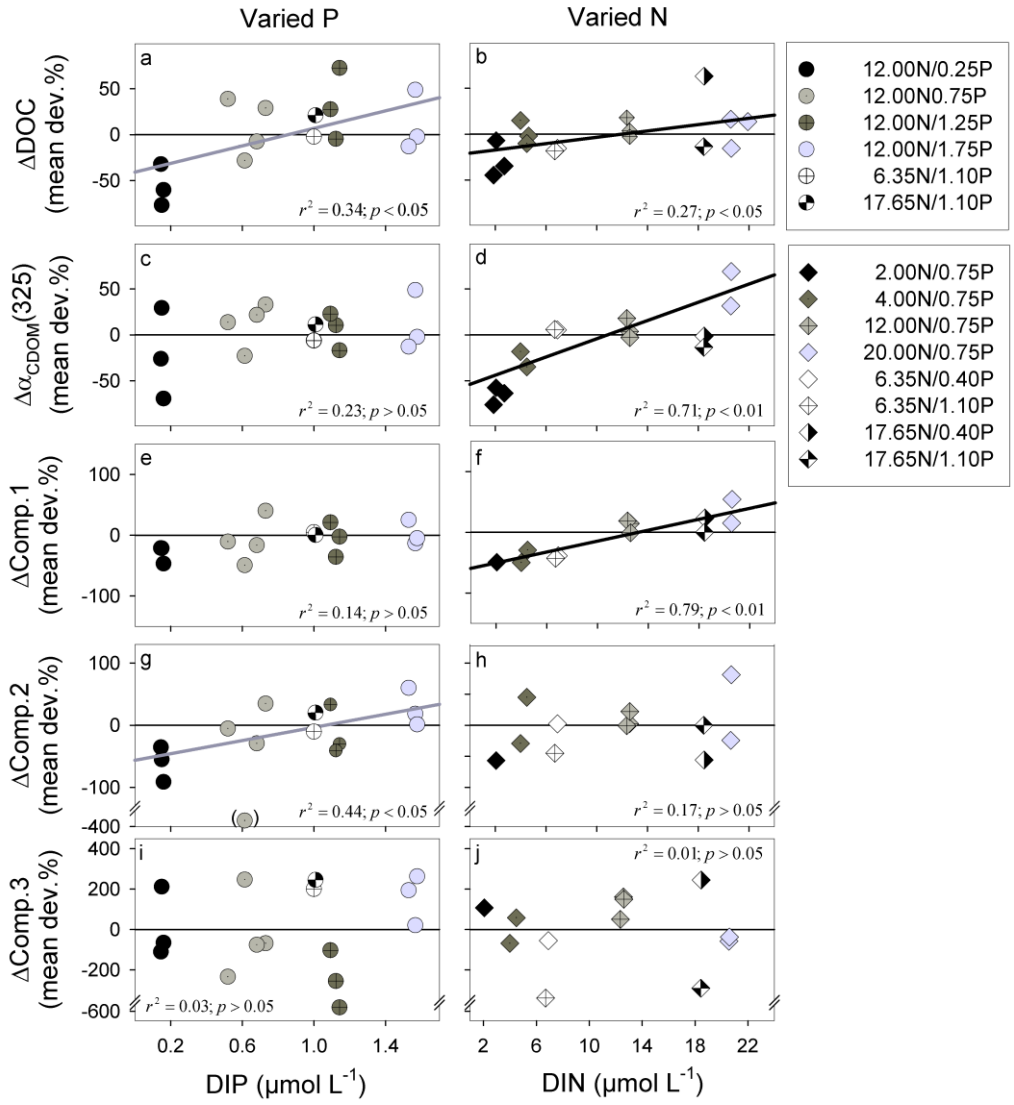

Fig.5. Mean normalized deviations of DOM accumulation against initial nutrients supply. The ΔDOC against DIP initial supply in ~~varied~~Varied P (a) and against DIN initial supply in ~~varied~~Varied N (b), the CDOM absorption at (Δa_{CDOM}(325~~ nm (Δa_{325})~~)) against DIP initial supply in ~~varied~~Varied P (c) and against DIN initial supply in ~~varied~~Varied N (d), the first FDOM component intensity (ΔComp.1) against DIP initial supply in ~~varied~~Varied P (e) and against DIN initial supply in ~~varied~~Varied N (f), the second FDOM component intensity (ΔComp.2) against DIP initial supply in ~~varied~~Varied P (g) and against DIN initial supply in ~~varied~~Varied N (h) and the third FDOM component intensity (ΔComp.3) against DIP initial supply in ~~varied~~Varied P (i) and against DIN initial supply in ~~varied~~Varied N (j) are shown as dashed symbols. The linear regressions are shown by thick light-grey lines in ~~varied~~Varied P and by thick black lines in ~~varied~~Varied N for those DOM parameters, where

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covariance with initial nutrients supply was significant. The symbol in brackets in (g) was ~~was~~ considered as an outlier and excluded from linear regression analysis.

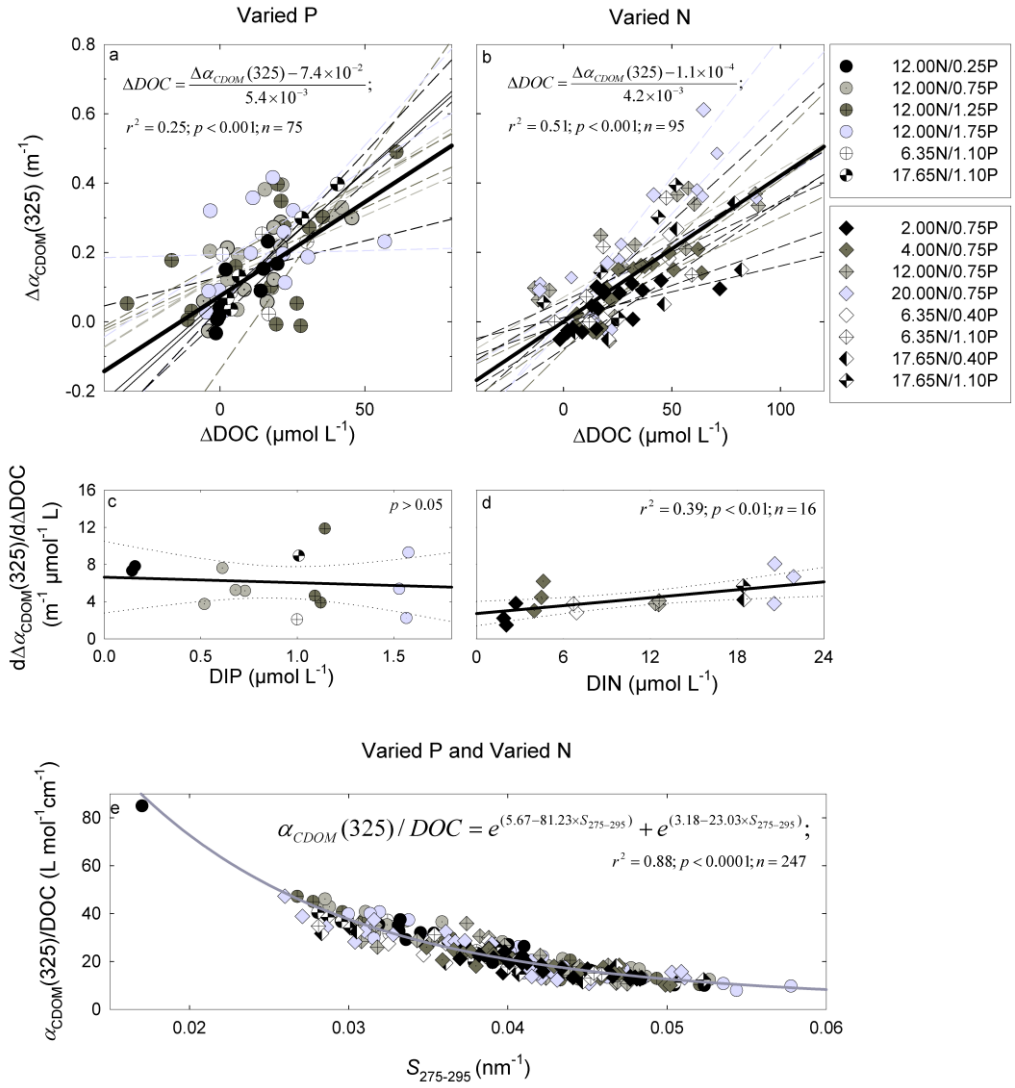

Fig.~~5~~6 Regression plots of ΔDOC against ~~ΔCDOM at 325nm~~Δ $a_{CDOM}(325)$ (a) during ~~*varied*~~Varied P (shaded circles) and (b) during ~~*varied*~~Varied N (shaded diamonds). The regression lines for each mesocosm are shown in dashed lines; thick black lines are regressions for all data from ~~*varied*~~Varied P and ~~*varied*~~Varied N respectively. The estimated slopes, of regressions for each mesocosm from (a, b) are plotted as shaded circles for ~~*varied*~~Varied P (c) and shaded diamonds for ~~*varied*~~Varied N. The thick black line is the linear regression line with 95% confidence interval (thin dotted lines). The slope estimated covariance in ~~'~~Varied ~~N² (b)~~N to DIN initial supply can be expressed as:

$$slope\ estimated = 2.7 \times 10^{-3} + 0.14 \times 10^{-3} DIN$$

~~.~~ (d). A spectral slope $S_{275\text{-}295}$ against ~~CDOM at~~

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355nm (a_{355})a_{CDOM}(325) /DOC for all mesocosms from both experiments are shown as dashedshaded symbols (e), the light). The dark-grey dashed line is the model of Fichot and Benner (2012) for DOC calculation with 8% of uncertaintybest fit to the data, obtained in a_{355}/DOC indicated by Fichot and Benner (2012) (light grey dotted lines).this study.