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June 15, 2017

Dr Oliver Zielinski,
Mrs Natascha Töpfer,
Editors
Ocean Science,

Re: Response to reviewers comments on manuscript by Drozdowska et al., entitled “Title: Study on organic matter fractions in the surface microlayer in the Baltic Sea by spectrophotometric and spectrofluorometric methods.” submitted to Ocean Science and coded OS-2017-4

We thank the reviewers for their constructive comments. We have followed their guidance, and rewritten parts of the manuscript to place the work in better context. Especially the Discussion is now much improved thanks to the suggestions of the Reviewers. We have also gone through the text thoroughly to make any edits to the text to improve the flow and any grammatical errors we found that could be corrected. With this exercise we have also rewritten the key points and abstract to better highlight the main findings of this work.

The detailed comments to the Reviews are given below. After each Reviewers comments, our responses are written using different font face and and start with **Response:**

Detailed Response to review by Reviewer #1:

General comments

The authors present an interesting data set on fluorescence and absorption measurements in the sea-surface microlayer. Such measurements are valuable as they are scarce and important to understand light penetration and photochemical processes at the sea surface.

Response: We would like to thank Reviewer #1 for appreciation of our work.

Unfortunately the authors do not discuss their results to those important processes at the sea surface. General comments: More detailed description of sampling methodology, most critical in research on the SML, are needed, and potential impacts on the results (i.e. by collected directly down the vessel's side and rather thick layers). Major data analysis to support the conclusions are lacking from the manuscript, and statistics are partly incorrect. Discussion have to be re-written, i.e. in terms of light penetration and photochemical processes, and most importantly with references to the literature. Overall, the manuscripts requires major revision, and also grammar and language editing.

Response: In the revised manuscript we have completely rewritten the Discussion section trying to link our results with physical and photochemical processes occurring at air-sea water interface. We have rewritten the Material and Methods section giving detailed information on sampling methodology in SML. We have also improved data analysis based on Reviewer #1 suggestions given in detailed remarks section. The whole revised manuscript was thoroughly rewritten with focus given to Material and Methods Results and Discussions sections. Prior to revised manuscript submission we have sent it to professional English editor to correct grammar and usage of English. **Response to detailed comments by Reviewer 1.**

Page 1 (pls see continuous line numbers, thanks)

Response: The continuous line numeration has been applied in the revised manuscript.

Line 32: Inappropriate references; both are compendiums of different topics to the SML and upper surface processes

Response:

These references are an absolutely basic about a role of SML in various processes connected to the air-sea interactions. The books are mainly focused on the physics of aqueous molecular sublayers, however, they present the valid point of view on physics, chemistry and biology of the sea surface that are closely related. They contain the chapters on the exact topic of a sea surface microlayer with analysis of the physical phenomena like: viscosity, thermal effects of a cool and freshwater skin as well as diffusion and turbulence properties, connected with the top-layer of the sea. They describe in details the huge amount of dynamic processes going in the upper millimeters of the sea in various time and spatial scales – from micro-turbulence an fluxes to the planetary boundary layer. Such an introduction allows to explain, why the study on chemical composition of the organic molecules contained in a sea surface microlayer and the processes that influence the changes in their composition are the important issues to work with.

Line 34: How about anthropogenic sources?

Response: We agree with Reviewer #1 remarks. anthropogenic sources of dissolved organic matter have important contribution to pool of organic surface active compounds. Various human activities could lead to increased presence of both natural and synthetic surface active compounds found in SML. The sentence has been rewritten to a following form:

“Sea surface films are created by organic matter from sea marine and terrestrial sources: (i) dissolved and suspended products of marine plankton contained in seawater (Engel et al., 2017), (ii) terrestrial organic matter that enter seawater transported from a land with riverine outflow (natural and synthetic), (iii) natural oil leakages from the sea-bottom and iv) various anthropogenic sources that includes discharge of hydrocarbons products from undersea oil and gas production, marine traffic pollution and terrestrial discharge hydrocarbons and persistent organic pollutants (Cunliffe et l., 2013; Engel et al., 2017)“.

Page 2

Line 1: " penetration of solar radiation and gas exchange, e.g. the generation of aerosols from the sea surface"...light penetration and gas exchange not directly related to aerosol formation. Confusing senstence.

Response: We agree with Reviewer #1 remarks. The questioned sentence has been rewritten to a following form: “Surface active molecules (surfactants) present in SML may modify the number of physical processes taking place occurring in the surface microlayer: among others the surfactants affect the solar radiation penetration depth (Santos et al., 2012; Tislstone et al., 2010), exchange of momentum between atmosphere and ocean by reducing the sea surface roughness (Nightingale et al., 2000; Frew et al., 1990) of penetration of solar radiation and gas exchange between ocean and atmosphere, , e.g. the impacting generation of aerosols from the sea surface (Vaishaya et al., 2012; Ostrowska et al., 2015; Petelski et al., 2014)..”

line 9. Most of the surfactants are not fatty acids but carbohydrates and proteins with hydrophobic groups (see also William et al., 1986)

Response: We partially agree with Reviewer #1 remarks. In the paper by Ćosović and Vojvodić (Electroanalysis, 1998, 10 No.6) authors applied the aliphatic fatty acid as a model

surface active substance to test the electrochemical technique for analysis of surface active substances in natural seawater. Secondly, a new sea surface microlayer model, developed by Sieburth (1983), showed that the lipids were no longer considered to be present in sufficient concentrations in SML (Cuncliffe et al, 2011, FEMS Microbiol Rev 35). However lipids, because of their strong hydrophobicity, can significantly influence surfactant activity of seawater surface. This is why I put the information about the important role of lipids in SML. The questioned sentence has been rewritten and the citation to Williams et al., 1986 added. The references list has been also updated.

” Surfactants comprise a complex mixture of different organic molecules of amphiphilic and aromatic structures (with hydrophobic and/or hydrophilic heads) rich in carbohydrates, polysaccharides, protein-like and humus (fulvic and humic) substances (Williams et al., 1986; Čosović and Vojvodić, 1996; Cuncliffe et al, 2011) .”

Line24-28: delete or shortened this sentence.

Response: This sentence has been shortened and rewritten according to Reviewer #1 request.

“Recent advances in applications of the absorption and fluorescence spectroscopy in environmental studies on aquatic dissolved organic matter both in fresh and marine environments and engineered water systems have been summarized in numerous text books and review papers (e.g. Coble, 2007; Hudson et al., 2007; Ishii and Boyer, 2012; Andrade-Eiroa et al., 2013ab; Nelson and Siegel, 2013; Coble, 2014; Stedmon and Nelson, 2015).”

Line 30: SML already defined above. Be consistent with terms, e.g. sea surface microlayer and surface microlayer

Response: The term surface microlayer and its abbreviation SML has been used consistently in the revised version of the manuscript..

Line 36: The authors mentioned here analysis of marine surfactant, but in fact they analyze FDOM/CDOM. Even though some surfactants share properties of CDOM/FDOM, these are two different groups of chemical compounds defined by their hydrophobic properties and light absorption. Please correct

Response: We have assumed that CDOM and FDOM constitutes a significant fraction of organic marine surfactants in the Baltic Sea and could be regarded as a proxy of its concentrations. Therefore we have changes the first sentence in the Material and Methods section.

“Sample collection for spectroscopic characterization of the dissolved organic matter contained in the SML and SS, that could be regarded as proxy for organic marine surfactants was conducted during three research cruises of r/v ‘Oceania’ in April and October (two cruises) in 2015 and one in September 2016.”

Page 3

Line 5: Sampling the SML is critical due to its thickness of several ten’s of micrometer (see Cunlicffe et al. 2013). The authors use a particular thick mesh collecting a rather thick layer of 1 mm. The platform used for collecting is also not defined, and I need to assume it has been collected directly from the research vessel. Literature describes collectig SML directly from the SML but I doubt SML with full integrity can C2 OSD Interactive comment Printer-friendly version Discussion paper be collected with this approach. My major concerns is that the authors ignore obvious sources of contamination (others than visible oil spills) and disturbance of the SML in the manuscript.

Response: The samples were collected from the board of the vessel (r/y Oceania), that is about 2 m above the sea surface. The sampling was maintained about 15 minutes after anchoring, to avoid the turbulences in the surface layer caused by the screw and ship movements. We used the Garrett Net, mesh 18 (18 wires per inch), to collect the samples from the sea surface microlayer, according to the procedure described by Garrett [1965]. The screen is 60 cm x 60 cm, made of metal and the size of holes is 1 mm while the thickness of the wire is 0.4 mm. Thus, the thickness of a collected microlayer is about 0.5 mm and the efficiency is 60%. On average, 22 such samplings were required to obtain 1 dm³ of microlayer water. The following sampling procedure was established. First, the screen was immersed at an angle of 45°. Then, once totally immersed, the screen was left under the water until the microlayer had stabilized. Finally, it was carefully raised to the surface in a horizontal position at a speed of ca 5–6 cm s⁻¹ (Carlson 1982). Water was poured from the screen into a polyethylene bottle using a special slit in the screen frame.

Line 14-17: Move to the section "Results"

Response: These sentence has been moved to beginning of Results section.

Line 27: How about optical interferences of particulates in the samples during analysis?

Response: The main task in our work was to study the luminescent properties of the molecules that form a surface microfilm. As it is well known, the seasurface microlayer is a gelatinous film created by polysaccharides, lipids, proteins, and chromophoric dissolved organic matter (Sabbaghzadeh et al., 2017; Cunliffe et al., 2013). It means, they are consisted of dissolved, colloidal and particulate matter. Thus, not to dispose the absorbing and fluorescent matter involved into a gel structure we don't filtrate the samples. In the manuscript we present the results of absorption and fluorescence indices based on CDOM absorption spectra and FDOM 3D fluorescence spectra, collected during three cruises and carried out on the unfiltered samples.

Thus, the measured spectra of unfiltered water are distorted by the effects of scattering and refraction on the large molecules of particle matted. The absorption spectra are the mostly disrupted by scattering in short wavelength-UV, due to small protein-like particles, and in long wavelength - visible range, due to scattering on particle molecules of phytoplankton and the phytoplankton's absorption from at 430 nm to 670 nm). But the applied absorption indices (spectral slope and spectral slope ratio) are calculated in the spectral region that hardly overcome the discussed (mentioned above) spectral ranges. Moreover, the fluorescent spectra may be disordered by Rayleigh and Mie scattering on particle matter. However, in the first step of the 3D fluorescence spectra analysis the scattering effects are subtracted.

The test on differences between the filtered and unfiltered water were performed in September'16. The Figure 1. presents the results of CDOM absorption coefficient at seven wavelengths (290, 300, 310, 330, 355, 375 and 412 nm) for the samples collected in a) the SML and b) SS. The Figure 2. presents the dependence between salinity and FDOM intensity at main FDOM peaks, [R.U.] for a) the SML and b) SS. The Fig. 3 shows a dependence between $a_{CDOM}(355nm)$, [m^{-1}] and FDOM intensity at peaks [R.U.] for a) unfiltered and b) filtered samples from the SML and SS. The absorption spectra show the differences in the values of the absorption coefficient, between filtered and unfiltered probes, from about $2 m^{-1}$ to $0.1 m^{-1}$ for estuary waters to the open sea, respectively, both, for the SML than SS. However, the absorption indices are calculated on the base of the shapes of the spectra (in other words: are based on the relative differences between the values of $a_{CDOM}(\lambda)$), therefore the filtration should not affect their results. Moreover, the filtration changes the fluorescence spectra (Fig. 2) for a component T (protein-like) only. However, the differences are the same for the SML and SS.

Thus, in the future we plan preparing both, filtered and unfiltered samples for laboratory analysis, to compare the results of the absorption and fluorescent indices, calculated for both, filtered and unfiltered water probes. However, based on the tests, we assume that the results of

absorption and fluorescent indices for unfiltered samples can be apply as the information about the properties of chromophoric organic matter contained in the gelatinous structures of surface biofilm.

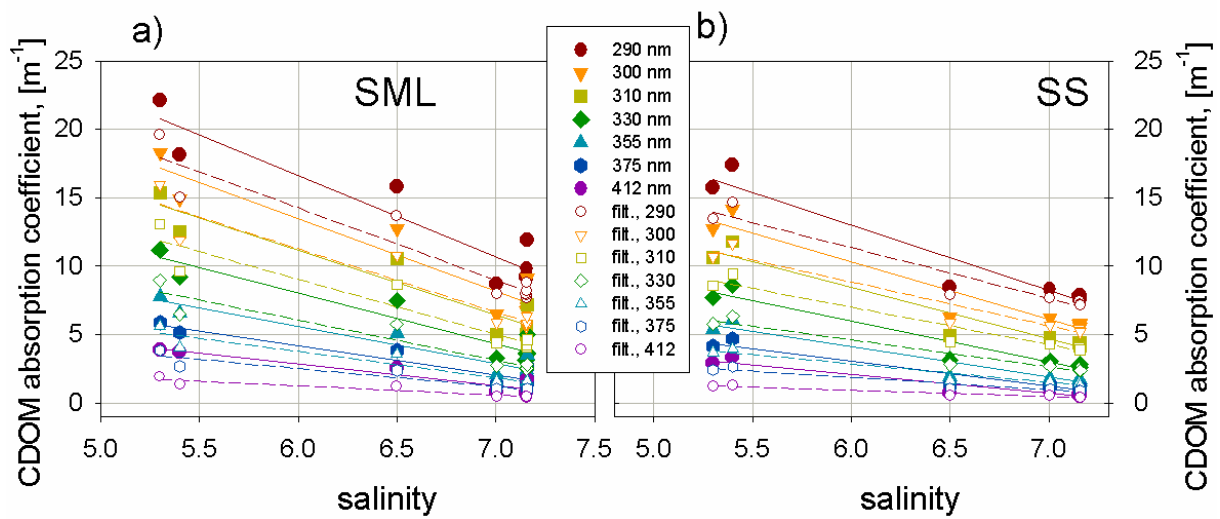


Fig.1. Dependence between salinity and $a_{CDOM}(\lambda)$, [m^{-1}] for filtered and unfiltered samples from a) the SML and b) SS.

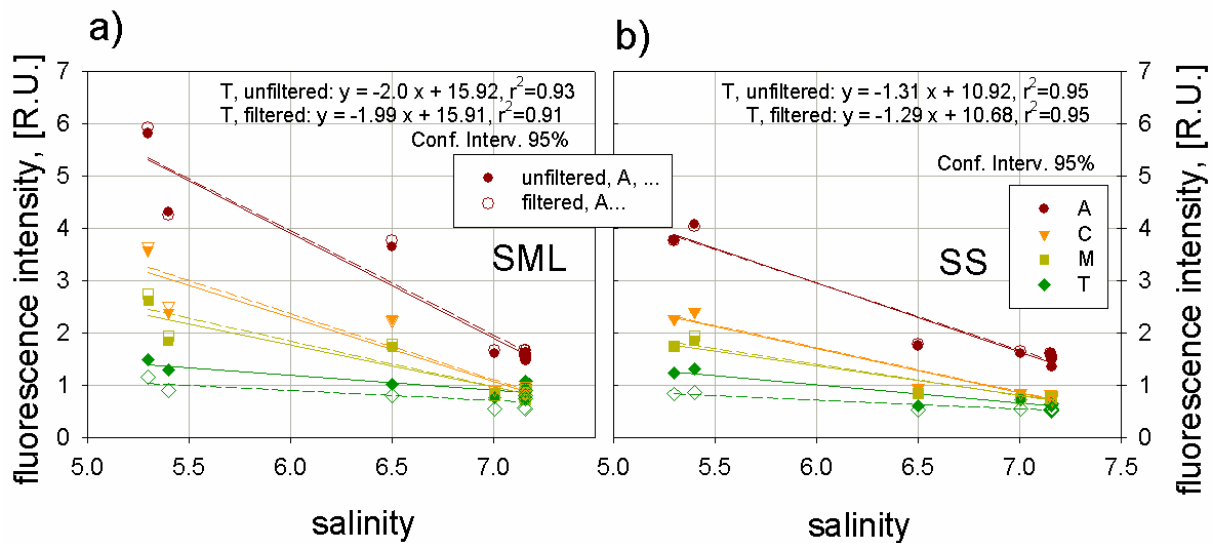


Fig. 2. Dependence between salinity and FDOM intensity at peaks, [R.U.] for filtered and unfiltered samples from a) the SML and b) SS.

Response:

To illustrate the decreasing differences between the values of absorption coefficients for SML and SS with increasing salinity, see Figure 3. Fig. 3 presents the dependence between salinity and the CDOM absorption coefficients, at several wavelengths: 254, 355 and 412 nm for the SS and SML, upper and lower graphs, respectively. The values of $a_{CDOM}(\lambda)$ decrease with salinity, in both: the SML and SS. However, the values of linear regression coefficients, for this dependence, are higher in the SML than in SS. Thus, for low salinity the values of $a_{CDOM}(\lambda)$ in the SML are higher than in SS, while with increasing salinity the values of $a_{CDOM}(\lambda)$ decrease with increasing salinity and the difference between the results of $a_{CDOM}(\lambda)$ for the SML and SS decrease as well.

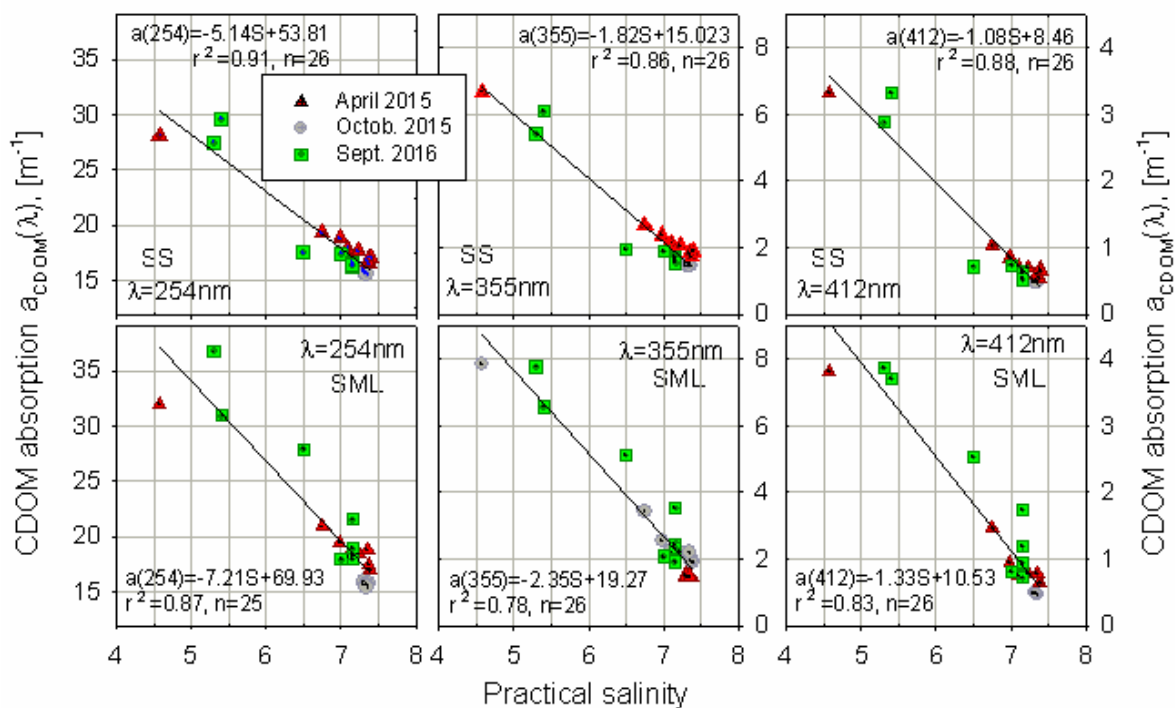


Figure 3. Dependences between salinity and CDOM absorption coefficient at several wavelengths.

Line 18: W1 is near-shore, not open sea, correct?

Response: Yes, station W1 is near the river outlet, while W9 is in open sea.

Line 24-25: The authors assumes correlation and linear regression is the same. That is incorrect (please refer to textbook for statistics). In statistics, correlation is described as correlation coefficient r , and

not as coefficient of determination (r^2 commonly used in regression analysis). Also provide p values to describe the significance of the correlation. Linear regression requires an independent and dependent variable, which is not the case here.

Response: I describe the relation between salinity and several absorption indices and use the regression coefficient to show the force of the dependency between the changes of one and the other variable. Therefore I should use ‘determination coefficient’ when I describe the linear relation (and values of the regression coefficient) between the variables. Anyway, the correlation coefficient, and R^2 , the coefficient of determination, are both measures of how well the regression model describes the data. R values near 1 indicate that the equation is a good description of the relation between the independent and dependent variables. In somehow I’d like to make prediction of the changes of absorption indices but my study are based on in-situ data and my database allow just working out the results and show the relations between the data.

For the calculations of the linear regression of the variables I applied the confidence interval 95%, so p values were smaller than 0.05 – it means that probability of being wrong in concluding that there is an association between the variables. The smaller the P value, the greater the probability that there is an association.

Line 27-38: " the processes go faster in SML than in SS." i don’t understand. What processes? Why faster? please explain.

Response: If a linear regression coefficient for a dependence described by the variables has a greater value in SML than in SS, it means that a proportion between the variables is higher in SML than in SS. And this situation means that the changes of a parameter along Axis Y vary faster with the values along Axis X, while these changes have nothing to do with time. Or, in the other words the relationship is stronger for SML and weaker in SS.

Page 9

Line 14: see above regarding regression vs correlation

Response: I write about the relation between the changes of both salinity and fluorescence intensity, emitted by the main component of marine FDOM (A, C, M and T).

Line 16-19: Are the differences significantly differences? From figure 6, it seems some of the comparison of R.U. are not significantly different, but it requires statistical test and p values, which the authors should describe.

Response:

Firstly, the ANOVA test was applied for the results presented on Figure 6. The differentiation factor for the results presented on the figure is the level of sampling: SML or SS. The null hypothesis, H_0 , is that the levels of sampling are meaningless (irrelevant), while the alternative hypothesis, H_1 , is that the levels of sampling are significant. When we apply the Standard Deviation Statistics, proposed by Fisher, for significance level 95% (2 standard deviations) we obtain that the difference presented as the bars on figs 6 are statistical insignificant. Thus, from the ANOVA test we received the results that we cannot reject the null hypothesis, H_0 . Thus, the results presented on the figure 6 might be a completely random distribution. However, in spite of the p-values indicate no statistical significance, one can see on the graphs that the values for the SML are always higher than for the SS. Hence, the distinguish between the results for the SML and SS exist. What is more, the differentiation factor is the level of sampling.

Then, we applied the ANOVA test for figure 7, where the differentiation factor for the results is salinity. The null hypothesis, H_0 , is that the different salinities are irrelevant (insignificant). The alternative hypothesis is that the salinity regimes are significant. The ANOVA test gives information that we can reject the null hypothesis. Thus, the salinity regimes for the results SML and SS are statistically significant.

Figure 6 and 7: Slightly confusing as in Figure 6 authors grouped SML and SS in a single plot, but in Figure 7 grouped between < 7 PSU and > 7 PSU.

Response: Figure 6 present the difference between fluorescence intensities for the SML and SS. While, in Figure 7 the results of percentile contribution are presented in different salinity regimes, for the SML and SS, separately. The left and right graphs, for SS and SML, respectively, show the wider range of changes of percentile contribution of the all FDOM components in the SML than SS. The statistical significance was obtain for such a presentation of the results, where the differentiation factor was salinity. Moreover, the results of percentile composition of the main components of marine FDOM (included in Figure 7) can be presented in the same way as in the results in Figure 6 (in the Manuscript), Figure 4.

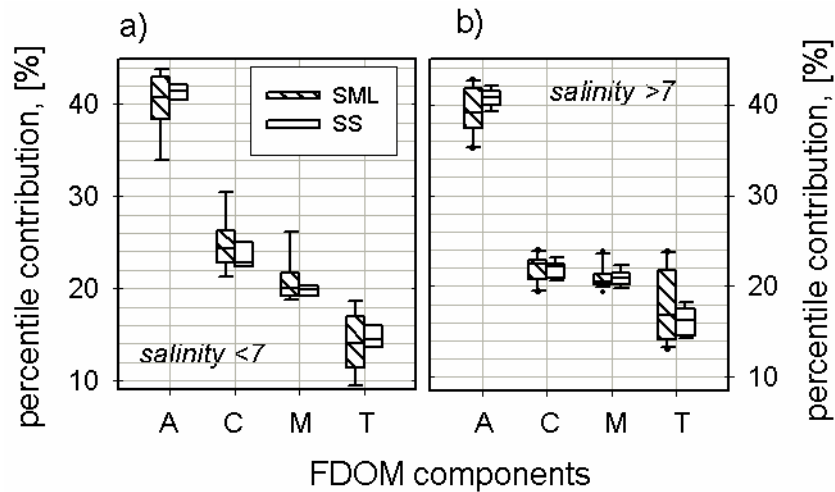


Figure 4. Dependence of percentage contribution of the main FDOM components in SML and SS as the box plots for (a) coastal waters (salinity <7) and (b) open sea (salinity >7).

Page 12:

Line 16/17: is this statistically different based on a significance level of 95%?

Response: The calculations of the linear regression were made by Sigma Plot Toolbox with the confidence interval 95%. The calculations give the values 'a', 'b' and 'r²'.

Page 13 - Discussion is short (compared to the Results) and without a single reference to the literature. The authors need to clearly define section Results and Discussion, or combined both if guidelines of the journal allows it. More importantly, the authors need to discuss their results with findings from the literature, e.g. in terms of relevant processes at the sea surface such as light penetration and photochemistry.

Response: I put the changes into the manuscript.

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June 20, 2017

Dr Oliver Zielinski,
Mrs Natascha Töpfer,
Editors
Ocean Science,

Re: Response to reviewers comments on manuscript by Drozdowska et al., entitled "Title: Study on organic matter fractions in the surface microlayer in the Baltic Sea by spectrophotometric and spectrofluorometric methods." submitted to Ocean Science and coded OS-2017-4

We thank the reviewers for their constructive comments. We have followed their guidance, and rewritten parts of the manuscript to place the work in better context. Especially the Discussion is now much improved thanks to the suggestions of the Reviewers. We have also gone through the text thoroughly to make any edits to the text to improve the flow and any grammatical errors we found that could be corrected. With this exercise we have also rewritten the key points and abstract to better highlight the main findings of this work.

The detailed comments to the Reviews are given below. After each Reviewers comments, our responses are written using different font face and start with **Response:**

Detailed Response to review by Reviewer #2:

General comments

In the manuscript entitled "Study on organic matter fractions in the surface microlayer in the Baltic Sea by spectrophotometric and spectrofluorometric methods" authors pay attention to an important

issue regarding to the influence of surfactants on the physical processes occurring in the sea surface layers. In the manuscript authors present an important results of absorption and fluorescence for samples collected from a surface microlayer (SML) and subsurface layer (SS) in the Batic Sea both in the open sea and near-shore. Based on absorption and fluorescence measurements authors determined several parameters to describe the changes of organic matter and discuss the processes occur in the sea surface layers.

The manuscript consists of 5 sections. In section 1 authors introduce the reader to the issue. In Section 2, authors present collection and characterization of samples, studied area and specification of measurements. Moreover, in this section authors present the detailed description of several specific absorption and fluorescence indices. Next, in section 3 authors present detailed description of obtained results taking into account the specific absorption and fluorescence indices and the relationships between them. Next, authors discuss obtained results in the Section 4 and finally the authors conclude the manuscript in Section 5.

The manuscript reports findings that are interesting for future work in ocean optics. Manuscript has scientific weight.

In my opinion the manuscript require several corrections to be suited for publication. The suggested corrections before the publication of the manuscript were mentioned below.

Response: We thank the Reviewer #2 for appreciating our work.

Detailed comments:

1. The name of the Section 2 "Method" should be specified. Now the name of this section suggests about description of used method, however authors describe in this section several issues: the used material, studied area and specification of measurements or specific absorption and fluorescence indices.

Response: We agree with the Reviewer #2 remarks. The Section 2. (titled: "Methods") contains the information on many aspects of the marine and laboratory measurements: a study area and sampling methodology, the equipment and laboratory measurements as well as the calculations of the collected dat. Therefore the name of the Section 2. will be changed into "**Measurements**" and, the Section 2. will be divided into 3 subsections titled : **2.1** SML sampling; **2.2** Laboratory spectroscopic measurements of CDOM and FDOM optical properties; **2.3** Optical indices of CDOM and FDOM used for calculations.

2. I suggest, that better would be if authors move the subsection 2.3 "CDOM and FDOM optical properties" and described this in separate section "Optical indices used for calculations" or "Optical indices of CDOM and FDOM used for calculations" with two subsections: absorption indices and fluorescence indices.

Response: We agree with the Reviewer #2 remarks. The Section 2.3 "CDOM and FDOM optical properties" is consisted of two parts: the first one deals with the absorption spectra analysis and calculations of the absorption indices and the second one is dedicated to fluorescence data. Hence, the Section 2.3 will be divided into two subsections: 2.3.1 Absorption indices and 2.3.2 Fluorescence indices.

3. I think that better would be, if all data of calculated optical indices have been collected in one table.

Response: In our opinion it would be better to leave two separate tables to follow the text with the data included in the tables. The data included in the Table I refer to the results of absorption analysis, discussed in section 2.3.1, while in the Table II to the results of the fluorescence analysis described in the section 2.3.2. Moreover, the results included in the Table I are calculated for the first and last station only, along the sampling transect during three research cruises. While, the median of the fluorescence indices presented in Table II are calculated for the group of samples collected in water of less salinity (< 7) and of higher salinity (> 7).

4. The English language of the manuscript is good. However, several sentences are unclear or contain colloquial phrases, for example: page 7 line 8 "...become smaller an smaller.." better would be "...decreasing..." page 12 line 2 "...the biggest relative changes..." better would be "...the highest relative changes..." page 13 line 3 "...shorter wavelength..." better would be "...lower wavelength..." page 15 line 7 "What is more..." better would be "Moreover.." I think that a little English correction can improve quality of the manuscript.

Responses: The sentences has been corrected and rewritten according to Reviewer #1 request: page 7 line 8, there was: Moreover, with an increase of a distance from the river outlet, the intensity of light absorption is decreasing significantly and the differences between the SML and SS become **smaller and smaller**.

There is: Moreover, with an increase of a distance from the river outlet, the intensity of light absorption is decreasing significantly and the differences between the SML and SS **decreasing as well**.

[page 12 line 2](#), there was: Hereby, the **biggest** relative changes of the FDOM component composition, along the transect from the Vistula River outlet to Gdansk Deep, were recorded for component T, both in SML and SS (about 18.5 % and ~12.3 %, respectively), while the relative changes of A, C and M components were: 4.1, 8.1 and 2.6 % in SML and 1.9, 3.1 and 4.7 % in SS, respectively.

It is: Hereby, the **highest** relative changes of the FDOM component composition, along the transect from the Vistula River outlet to Gdansk Deep, were recorded for component T, both in SML and SS (about 18.5 % and ~12.3 %, respectively), while the relative changes of A, C and M components were: 4.1, 8.1 and 2.6 % in SML and 1.9, 3.1 and 4.7 % in SS, respectively.

[page 13 line 3](#).

Response: In my opinion, ‘lower’ and ‘shorter’ have the same meaning with respect to the limit of wavelength range of light and may be used interchangeable. However, we agree with the Reviewer, that in this context: ‘low’ fits better.

There was: However the photochemical degradation processes, resulting in a decrease in the mass of molecules and an increase of concentration of low molecular-weighted molecules, are much more spectacular in a **shorter** wavelength range and are held primarily in the surface microlayer, SML.

There is: However the photochemical degradation processes, resulting in a decrease in the mass of molecules and an increase of concentration of low molecular-weighted molecules, are much more spectacular in a **lower** wavelength range and are held primarily in the surface microlayer, SML.

[page 15 line 7](#), there was: **What is more**, a decreasing of DOM concentration with salinity occurs faster in SML than in SS.

There is: **Moreover**, a decreasing of DOM concentration with salinity occurs faster in SML than in SS.

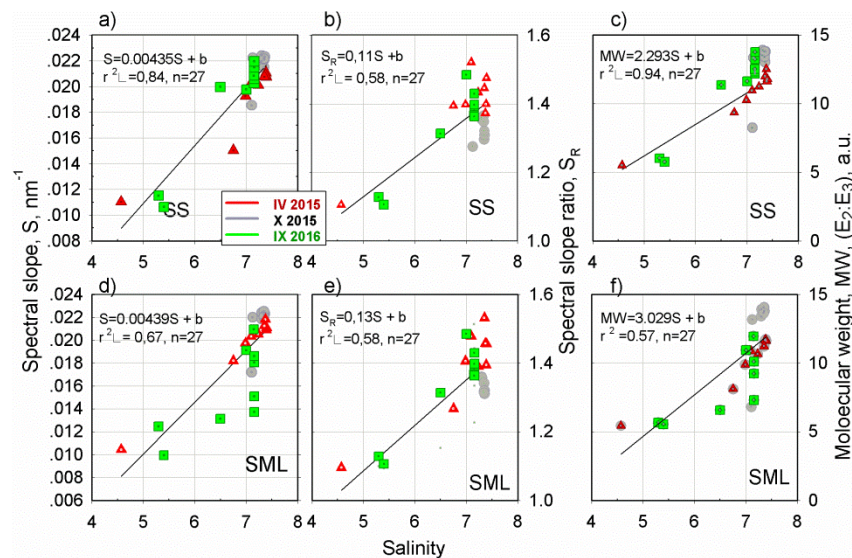
5. The data presented in tables are unnecessarily duplicated in the text, for example: - page 7 line 15-17 - duplicated data from Table 1 or - page 10 line 17-19 duplicated data from Table 2, instead the duplication, the authors should discuss this data.

Response: We agree with the Reviewer #2 that we should add some comments in this paragraph. Thus, some comments was added. However we decided to leave the text, with the numbers, unchanged.

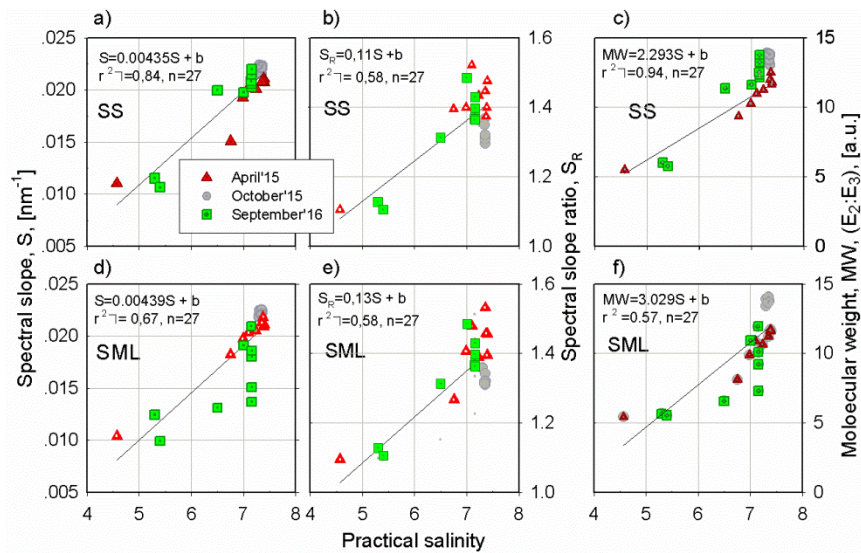
The additional sentences: The higher values of S_R in the SML in the open sea waters, mean the smaller size of CDOM that may exist due to a photodegradation process (Helmes et al., 2008). While the lower values of S_R in the SML in the vicinity of the river outlet may mean the forming of the surface structures from the hydrophobic molecules coming with freshwater (Cuncliffe et al., 2009).

6. Fig. 3 - incorrect legend.

The legend in the Figure 3 was corrected. There was:



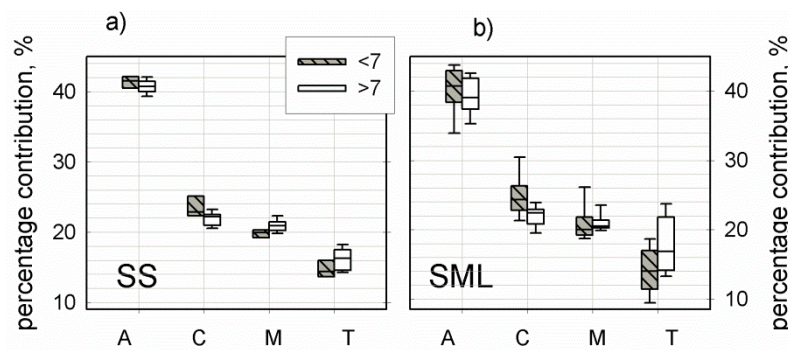
There is:



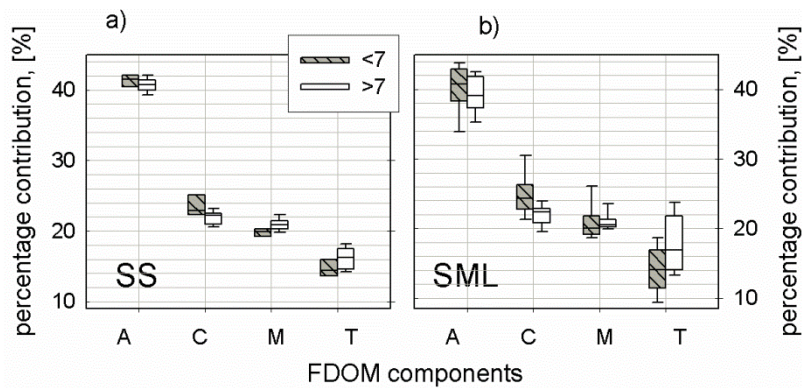
7. Fig. 7 - no description of X-axis

We corrected the Fig 7 by adding the description : “FDOM components”, to the Axis X.

There was:



It is:



8. Page 7 line 19 - W1 station describes the area near Vistula River outlet not open sea

Response: The sentence has been corrected. There was: However in **W1** (the open sea) the differences were 3.1, 1.5 and 3.5 %, while in **W9**: 10.5, 5.4 and 11.9 %.

There is: However in **W9** (the open sea) the differences were 3.1, 1.5 and 3.5 %, while in **W1**: 10.5, 5.4 and 11.9 %.

9. Page 5 line 18 - it should be S(275-295) not S(274-295)?

Response: The sentence has been corrected. There was: A spectral slope coefficient ratio, S_R , (~~S₂₇₄₋₂₉₅~~ to $S_{350-400}$) is negatively correlated with molecular weight of CDOM in humic substances.

There is: A spectral slope coefficient ratio, S_R , (~~S₂₇₅₋₂₉₅~~ to $S_{350-400}$) is negatively correlated with molecular weight of CDOM in humic substances.

The references list has been also updated.

Violetta Drozdowska
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June 20, 2017

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Detailed Response to review by Reviewer #3:

General comments:

The manuscript titled "Study on organic matter fractions in the surface microlayer in the Baltic Sea by spectrophotometric and spectrofluorometric methods" by Drozdowska et al add to our knowledge about optical parameters of the microlayer and surface layer. In my opinion, it is a step towards remote sensing of microlayer properties, something that would be extremely helpful for studying its effect on air-sea interaction fluxes. I believe the manuscript documents well what and how has been measured. I recommend publishing it after minor revision.

Response: We thank the Reviewer #3 for appreciating our work.

The open review process of the EGU journals has both advantages and disadvantages.

However, the fact that I see the previous two reviews makes it easier for me because I do not need to repeat what has already been told. So agreeing with most of the comments of my respectable anonymous peer-review colleagues, I will just comment on things which I did not see in their comments.

Response: The authors agree with most of the comments included in the reviews #1 and #2 and #3 and the prepared final manuscript has been corrected according to the advice given by Reviewers #1 and #2 and #3.

Detailed remarks:

The fluorescence intensities A, C, M and T should be explained in the abstract. Something simple like "fluorescence intensities at Coble classification peaks" should be enough to give some hint to the reader what they are.

Responses: The main fluorophores included in marine CDOM molecules were, the first time, classified by Coble (1996). The maxima of the main fluorescence peaks of marine CDOM are different for freshwater, open sea, coastal and estuary waters and are the subject of many studies. The information about naming of A, C, M and T as "fluorescence intensities at Coble classification peaks" is put to the abstract.

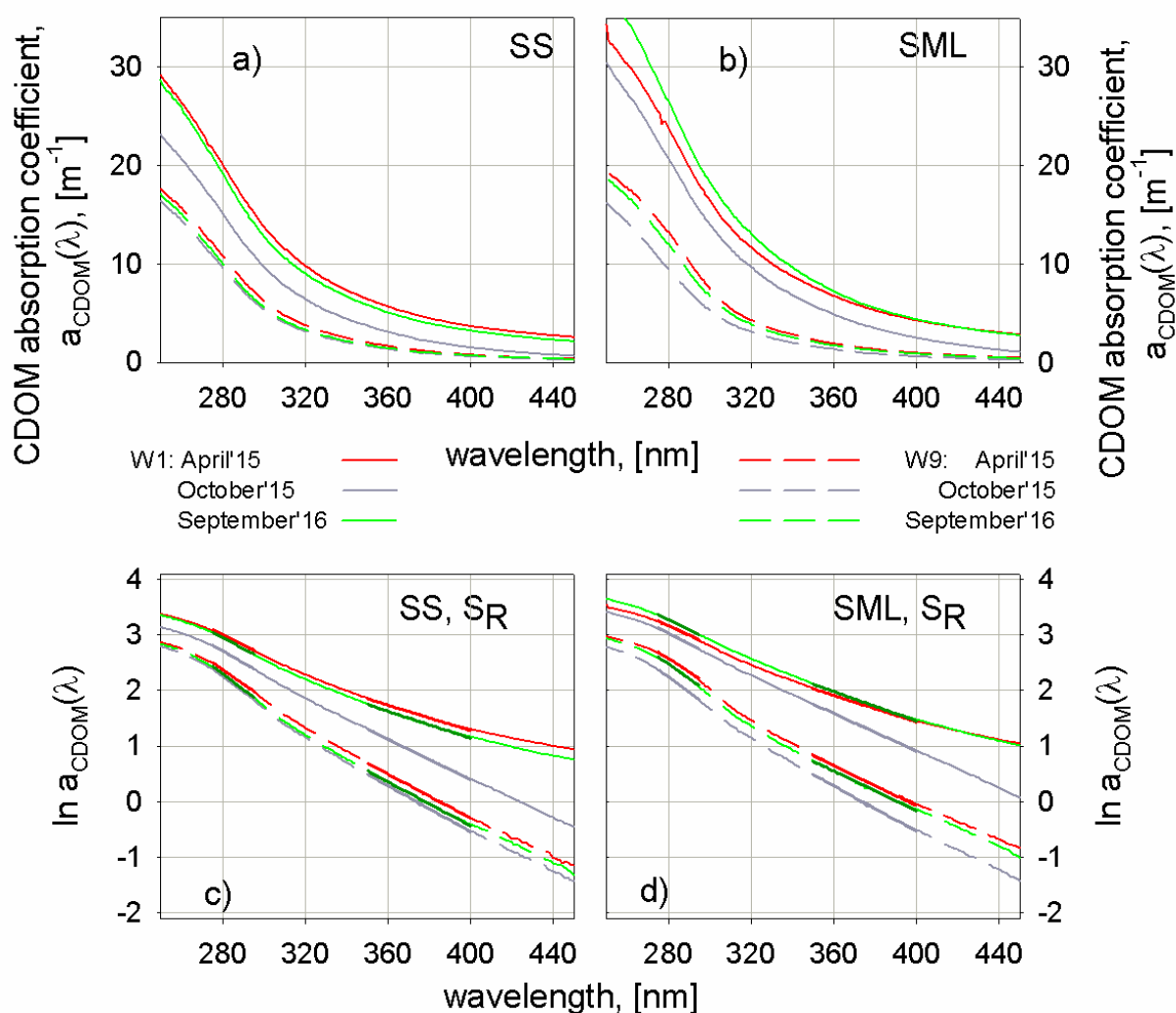
It was: . Several absorption ($E_2:E_3$, S , S_R) and fluorescence (fluorescence intensities at peaks: A, C, M, T, the ratio $(M+T)/(A+C)$, HIX) indices of colored and fluorescent organic matter (CDOM and FDOM) helped to describe the changes in molecular size and weight as well as in composition of organic matter.

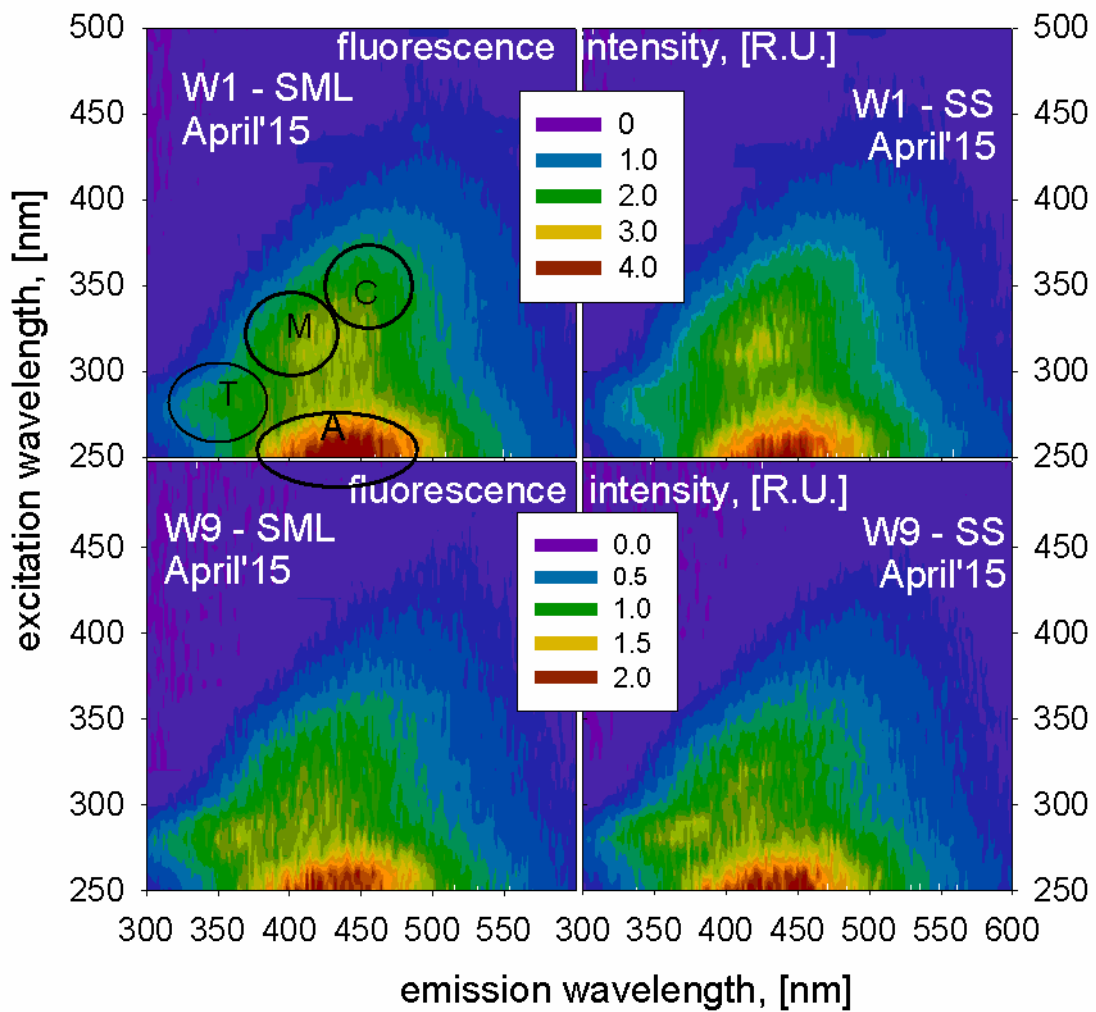
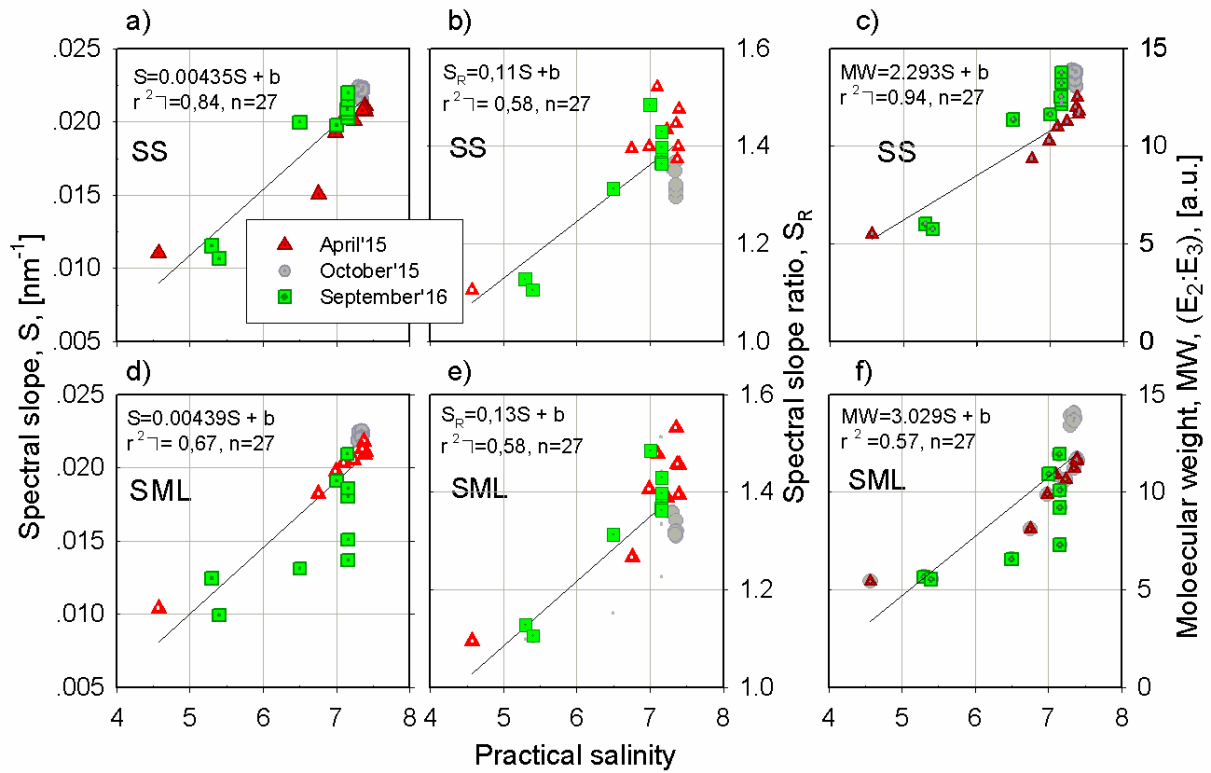
It is: . Several absorption ($E_2:E_3$, S, S_R) and fluorescence (fluorescence intensities at **Coble classification** peaks: A, C, M, T, the ratio $(M+T)/(A+C)$, HIX) indices of colored and fluorescent organic matter (CDOM and FDOM) helped to describe the changes in molecular size and weight as well as in composition of organic matter.

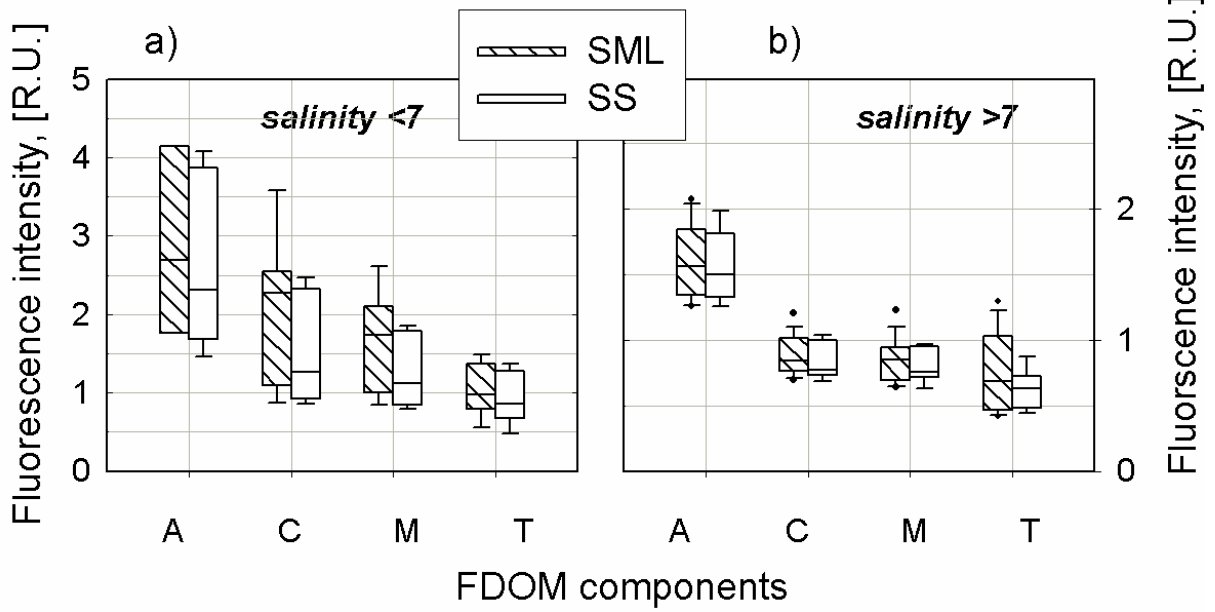
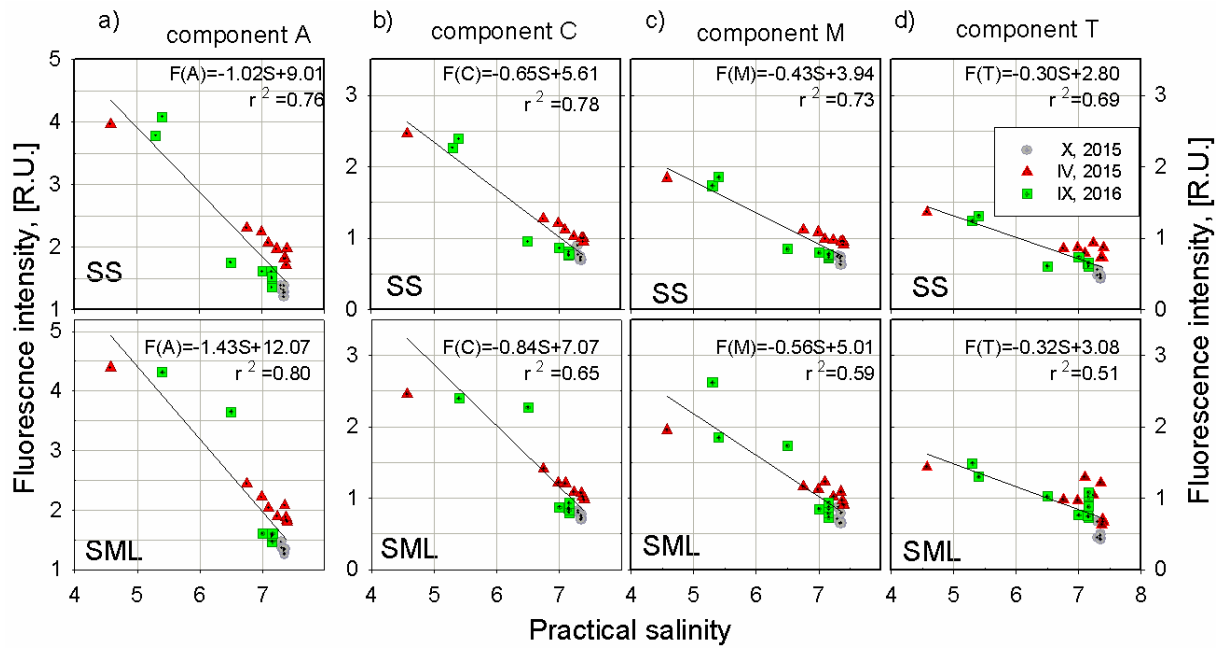
Units in the figures should be presented in [] braces.

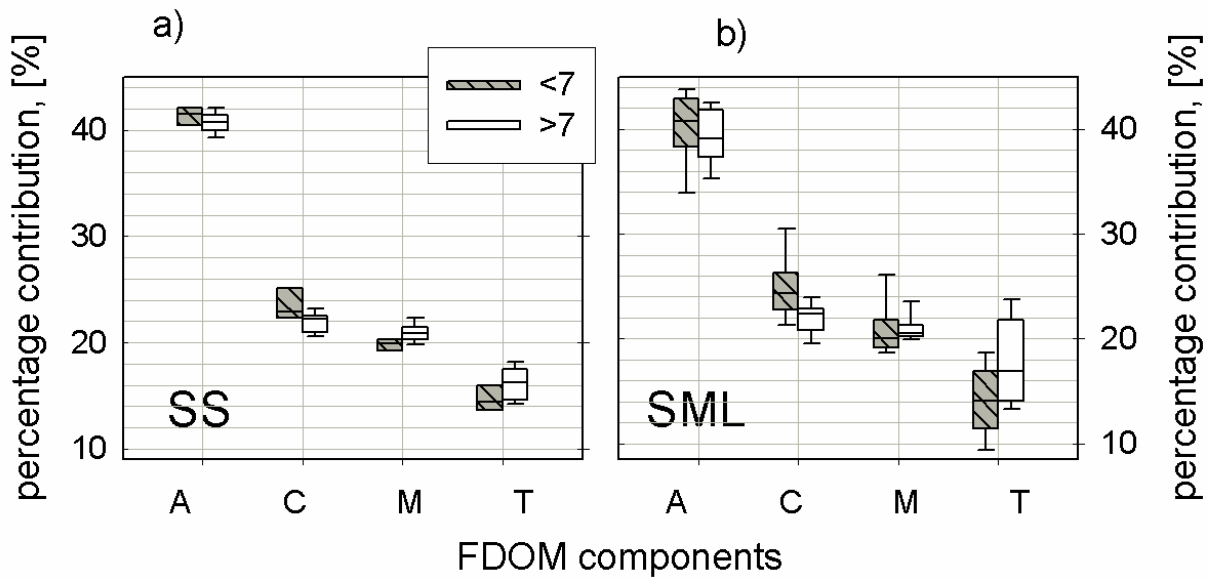
Response: The all units in the all figures were put into the brackets [...] were, except Fig. 1.

The figures: 2,3,4,5,6 and 7 are:









Date format in Table 1 is certainly not something most English native speakers will recognize. Because of the US/UK dichotomy (09/11/2001 versus 11/09/2001), I suggest using month names explicitly (11 September 2001). The hyphen in “October’2015” is not necessary (at least in two places). One uses it only to shorten the year (October ‘15).

Response: The name of date in Table 1 and in the text were written explicitly.

There was:

A slope ratio – $S_R (= S_{275-295}/S_{350-400})$						
S_R - for SS			S_R - for SML			
	28 th IV 2015	15-16 th X 2015	11 th IX 2016	28 th IV 2015	15-16 th X 2015	11 th IX 2016
W1	1.58	1.16	1.61	1.43	1.10	1.35
W9	1.30	1.33	1.40	1.34	1.35	1.45

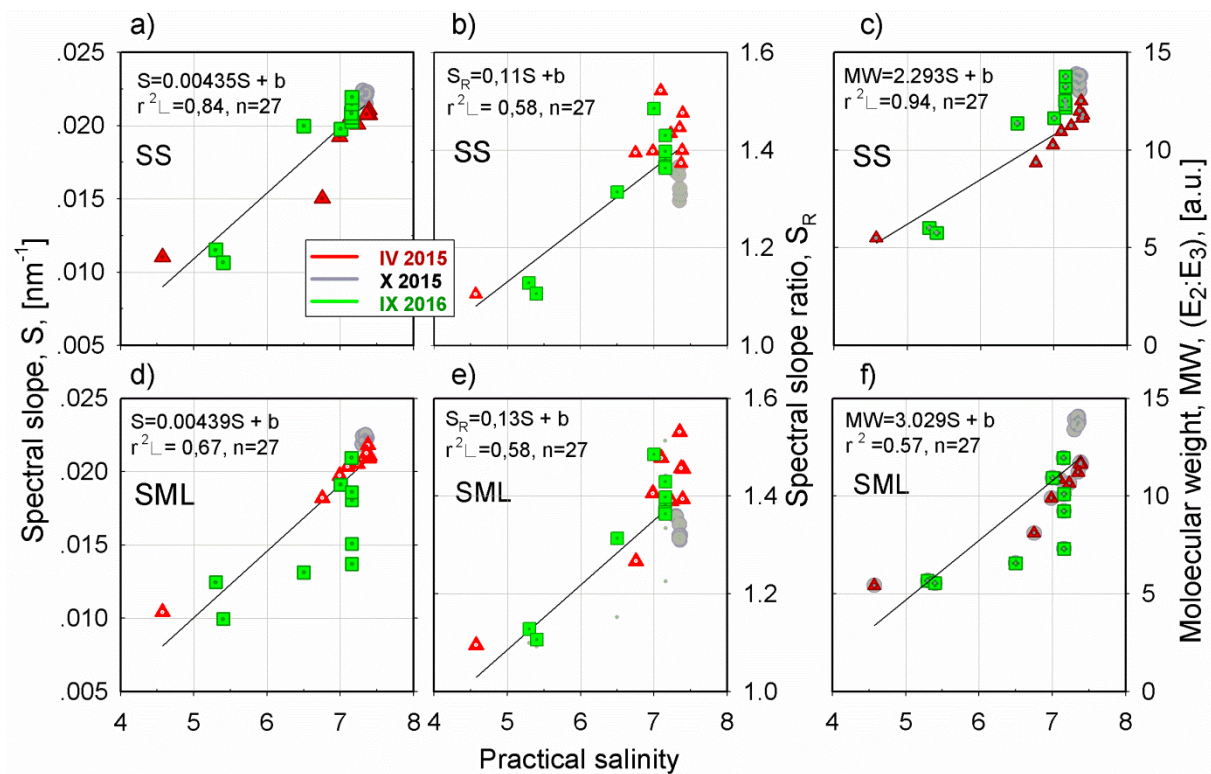
There is:

A slope ratio – $S_R (= S_{275-295}/S_{350-400})$						
S_R - for SS			S_R - for SML			
	28 April 2015	15-16 October 2015	11 September 2016	28 April 2015	15-16 October 2015	11 September 2016
W1	1.58	1.16	1.61	1.43	1.10	1.35
W9	1.30	1.33	1.40	1.34	1.35	1.45

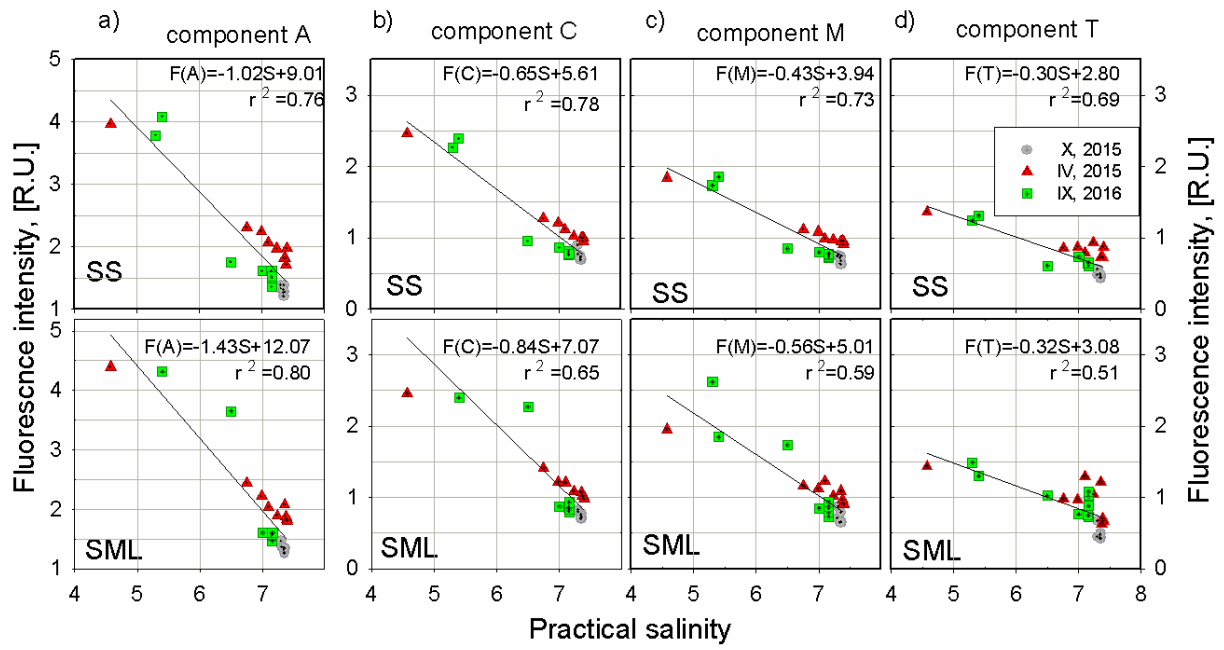
I commend the authors for using unitless practical salinity (as all the relevant standards have it). However, the word "practical" should be added somewhere before salinity to make it obvious that the salinity was not absolute.

Response: The authors agree with the Reviewer #3 remark and just put the name “Practical salinity” – as a description of the X axes – into the figures: Fig.3 and Fig.5.

There is: Figure 3



There is Figure 5:



Sformatowano: Numerowanie: ciągłe

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Sformatowano: Angielski (Stany Zjednoczone)

1 Study on organic matter fractions in the surface microlayer in
2 the Baltic Sea by spectrophotometric and spectrofluorometric
3 methods

4
5
6
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18 A revised manuscript submitted to submitted to Ocean Science and coded OS-2017-4R1,
19 June 10, 2017

20
21
22 ~~Correspondence to: Violetta Drozdowska ()~~
23

24

25 **Abstract.** The fluorescence and absorption measurements of the samples collected from a
26 surface microlayer (SML) and a subsurface layer (SS), a depth of 1 m were studied during
27 three research cruises in the Baltic Sea along with hydrophysical studies and meteorological
28 observations. Several absorption ($E_2:E_3$, S , S_R) and fluorescence (fluorescence intensities at
29 [Coble classified](#) peaks: A, C, M, T, the ratio $(M+T)/(A+C)$, HIX) indices of colored and
30 fluorescent organic matter (CDOM and FDOM) helped to describe the changes in molecular
31 size and weight as well as in composition of organic matter. The investigation allow to assess
32 a decrease in the contribution of two terrestrial components (A and C) with increasing
33 salinity (~1.64% and ~1.89 % in SML and ~0.78% and ~0.71 % in SS, respectively) and an
34 increase of in-situ produced components (M and T) with salinity (~0.52% and ~2.83% in
35 SML and ~0.98% and ~1.87% in SS, respectively). Hence, a component T reveals the
36 biggest relative changes along the transect from the Vistula River outlet to Gdansk Deep,
37 both in SML and SS, however an increase was higher in SML than in SS (~18.5% and
38 ~12.3%, respectively). The ratio $E_2:E_3$ points to greater changes in a molecular weight of
39 CDOM affected by a higher rate of photobleaching in SML. HIX index reflects a more
40 advanced stage of humification and condensation processes in SS. Finally, the results reveal
41 a higher rate of degradation processes occurring in SML than in SS. Thus, the specific
42 physical properties of surface active organic molecules (surfactants) may modify, in a
43 specific way, the solar light spectrum entering the sea and a penetration depth of the solar
44 radiation. Research on the influence of surfactants on the physical processes linked to the
45 sea surface become an important task, especially in coastal waters and in vicinity of the river
46 mouths.

47 **+1 Introduction**

48 The sea surface is a highly ~~productive and dynamic~~ active interface between the sea
49 and the atmosphere ([Soloviev and Lukas, 2006; Liss and Duce, 2005](#)). The physicochemical
50 and biological properties of a surface microlayer (SML, a surface film), are clearly and
51 measurably different from the underlying water due to the molecules forming SML, called
52 surfactants ([Soloviev and Lukas, 2006; Liss and Duce, 2005](#)). Sea surface films are created
53 by organic matter from ~~sea-marine~~ and ~~land~~ terrestrial sources: (i) dissolved and suspended
54 products of marine plankton contained in seawater ([citationEngel et al., 2017](#)), (ii) terrestrial
55 organic matter ~~that enter seawater~~ transported from a ~~land~~ with riverine outflow (natural and

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Z komentarzem [A1]: Cos trzeba zrobic z tymi cytowaniami. – Przesunęłam je o 1 zdanie wyżej. A w odpowiedzi wyjaśniłam, że: “The books are mainly focused on the physics of aqueous molecular sublayers, however, they present the valid point of view on physics, chemistry and biology of the sea surface that are closely related.”

Z komentarzem [A2]: „Cos trzeba zrobic z tymi cytowaniami.

56 synthetic) and (iii) natural oil leakages from the sea-bottom, iv) and various anthropogenic
57 sources that includes discharge of hydrocarbons products from undersea oil and gas
58 production, marine traffic pollution and terrestrial discharge hydrocarbons and persistent
59 organic pollutants (Cuncliffe et al., 2013; Engel et al., 2017 citation). — products from
60 leakages of the sea-bottom. Surface films dissipate due to loss of material at the sea surface,
61 including microbial degradation, chemical and photo chemical processes, as well as due to
62 absorption and adsorption onto particulates (Liss et al., 1997). ~~However~~ ~~†~~The surface
63 microlayer is almost ubiquitous and cover most of the surface of the ocean, even under high
64 turbulence conditions ~~of high turbulence~~ (Cuncliffe et al., 2013). Surface active molecules
65 (surfactants) present in SML may modify ~~the~~ number of physical processes taking place
66 occurring in the surface microlayer: ~~among others the~~ surfactants affect the solar radiation
67 penetration depth (Santos et al., 2012; Carlucci et al., 1985 citation), exchange of momentum
68 between atmosphere and ocean by reducing the sea surface roughness (Nightingale et al.,
69 2000; Frew et al., 1990 citation) ~~of penetration of solar radiation~~ and gas exchange between
70 ocean and atmosphere. ~~e.g. the~~ impacting generation of aerosols from the sea surface
71 (Vaishaya et al., 2012; Ostrowska et al., 2015; Petelski et al., 2014). Therefore, research on
72 the influence of surfactants on the sea surface properties become an important task,
73 especially in coastal waters and in a vicinity of the river mouths (Maciejewska and
74 Pempkowiak, 2015).

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75 Surfactants comprise a complex mixture of different organic molecules of
76 amphiphilic and aromatic structures (with hydrophobic and/or hydrophilic heads) rich in
77 carbohydrates, polysaccharides, protein-like and humus (fulvic and humic) substances
78 (Williams et al., 1986; Čosović and Vojvodić, 19968; Cuncliffe et al, 2011) Surfactants
79 comprises a mixture of organic molecules rich in lipids (fatty acids, sterols), polymeric and
80 humus which proportions determine the various properties of the SML. Some dissolved
81 organic compounds possess, especially fulvic and humic substances, the optically active
82 parts of ~~the~~ molecules that absorb the light, called i.e. chromophores, that absorb the light
83 energy (CDOM, *chromophoric* dissolved organic matter), and fluorophores, that absorb and
84 emit ~~the~~ light (FDOM – fluorescent dissolved organic matter). Due to the complexity and
85 ~~variability of the~~ compositional variability of the dissolved marine organic matter mixture,
86 ~~the~~ the absorption and fluorescence (excitation-emission matrix) spectroscopy (Stedmon et
87 at, 2003; Hudson et al., 2007; Coble, 2007). ~~best~~ were found as fast and reliable available
88 tool-methods (fast and reliable) to for detection and identification the of the dissolved

Z komentarzem [A3]: ??? - czy nie miało być aliphatic ? - Jest ok. „Amfifilowe”, to takie hydrofobowo-hydrofilowe.

Z komentarzem [A4]: Niedobre słowo – czy chodziło o podstawnik – jeśli tak to trzeba znaleźć odpowiednie słowo w słowniku. – W literaturze przedmiotu również używa się tego określenia „head”

89 organic matter in seawater (Stedmon et al., 2003; Hudson et al., 2007; Coble, 2007; Jørgensen
90 et al., 2011). ~~is the absorption and fluorescence (excitation emission matrix) spectroscopy~~
91 ~~(Stedmon et al., 2003; Hudson et al., 2007; Coble, 2007).~~ A unique structure of the energy
92 levels of these organic molecules results in a specific spectral distribution of the light
93 intensities absorbed and emitted by the molecules. Hence, the ~~a~~ absorption and fluorescence
94 spectra of specific organic compounds groups may allow ~~the~~ identification of ~~the~~ sources
95 transformations of dissolved organic matter (Coble, 1996; Lakowicz, 2006). Several indices
96 describing the changes of a concentration (~~citation~~ Blough and Del Vecchio, 2002), a
97 molecular weight (Peuravuori and Pihlaja, 1997) (~~citation~~), a composition of CDOM/FDOM
98 (Stedmon and Bro, 2008; Boehme and Wells, 2006) (~~citation~~) and a rate of degradation
99 processes (Milori et al., 2002; Glatzel et al., 2003; Zsolnay, 2003) (~~citation~~) can be calculated
100 from ~~The analysis of the~~ CDOM absorption and 3D-FDOM fluorescence excitation and
101 emission matrix fluorescence spectra EEMs, that could be useful to study dissolved organic
102 matter dynamics and composition in surface micro layer. ~~enabled to calculate several indices~~
103 ~~describing the changes of a concentration, a molecular weight, a composition of~~
104 ~~CDOM/FDOM and a rate of degradation processes of the organic matter occurring in the~~
105 ~~study surface layers.~~

106 There are many applications ~~Recent advances in applications~~ of the absorption -and
107 fluorescence spectroscopy in environmental studies on oceanographic-aquatic dissolved
108 organic matter both in fresh and marine environments and engineered water systems have
109 been summarized in numerous text books and review papers (e.g. Coble, 2007; Hudson et
110 al., 2007; Ishii and Boyer, 2012; Andrade-Eiroa et al., 2013~~ab~~; Nelson and Siegel, 2013;
111 Coble et al., 2014; Stedmon and Nelson, 2015). The humic substances contribute
112 significantly both to CDOM pool in the water column as well as to surfactants concentrations
113 especially in coastal ocean, estuaries and semi-enclosed marine basin that are impacted by
114 terrestrial runoff and marine traffic. Therefore optical methods could be used ~~efficiently~~ for
115 determination of natural and anthropogenic organic surface active substances in SML
116 (Drozdowska et al. 2013; Drozdowska et al., 2015; ~~;~~ Pereira et al., 2016; Frew et al., 2004;
117 Zhang et al., 2009; McKnight et al., 1997; Guéguen et al., 2007; ~~Baszanowska (22)~~ studies
118 on mixing water masses locally, e.g. in estuaries (Williams et al., 2010) and in global scale
119 (Jørgensen et al., 2011). The studies were conducted in various natural waters as e.g. Chinese
120 lakes (Zhang et al 2013; Chen et al., 2011), Indian Ocean (Chari et al., 2012), American

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Z komentarzem [A5]: Jakiś inne międzynarodowe publikacje???

121 estuaries (Glatzel et al., 2003; McKnight et al., 1997; Moran et al., 2000) and in studies on
122 dilution sea basins,

123 Baltic Sea is a semi-enclosed marine basin with annual riverine discharge reaching
124 ca. ~~0.5~~ 10^3 km^3 of fresh water (Leppäranta and Myrberg, 2009). Maximum freshwater
125 runoff occurs in April/May. The fresh water carries both high concentrations of CDOM
126 (Drozdowska and Kowalczyk, 1999; Kowalczyk, 1999; Kowalczyk et al., 2010; Ylostallo
127 et al., 2016) and substantial loads anthropogenic pollutants and inorganic nutrients
128 (Drozdowska et al., 2002; Pastuszek et al., 2012) that stimulates phytoplankton blooms. This
129 marine basin is also impacted by significant pollution caused by the high marine traffic
130 (Klonik and Bradtke, 2016). such as the Baltic (Kowalczyk et al., 2010; Drozdowska et
131 al., 2002) and Arctic (Gueguen et al., 2007) that considered the differences in FDOM
132 components from the rivers, lakes and inland water.

133 ~~This~~The main goal of this study was i) to distribution of concentration of specific
134 CDOM/FDOM components in the SML and subsurface waters (SS - 1 m depth) in the
135 salinity gradient along a transect from the Vistula River mouth to Gdansk Deep, Gulf of
136 Gdansk, Baltic Sea; ii) observe the compositional changes of CDOM/FDOM derived from
137 changes of spectral indices calculated from absorption and EEM spectra; paper is focus on
138 iii) describe and iii) distinguishing fate and concentration of specific CDOM/FDOM
139 components of organic matter to detect and describe the processes that lead to observed
140 differences in CDOM/FDOM concentration and that composition in the SML and SS along
141 sampled transect. occur in the sea surface microlayers (SML) and in subsurface layers (SS),
142 a depth of 1 m. Research are based on the absorption and fluorescence spectra and several
143 absorption and fluorescence indices. Investigations concern the region of Gulf of Gdansk,
144 along a transect from the Vistula River outlet (the biggest Polish river) to open sea.

145 ~~2 Measurements~~ ~~Methods~~ ~~Measurements~~ ~~Materials and methods~~

146 ~~2.1~~ ~~Materials and study area~~ ~~SML sampling~~

147 ~~Sample collection for spectroscopic characterization~~ ~~Research to identify~~ of the
148 dissolved organic matter contained in the SML and SS, that could be regarded as proxy for
149 marine surfactants were conducted during three research cruises of r-/-y-‘Oceania’ in April
150 and October (two cruises in 2015 and one in September 2016). The study was conducted
151 Measurement of physical parameters of sea water and samples collection -were performed
152 at nine stations along the transect 'W' - from the mouth of the Vistula River, W1, along the

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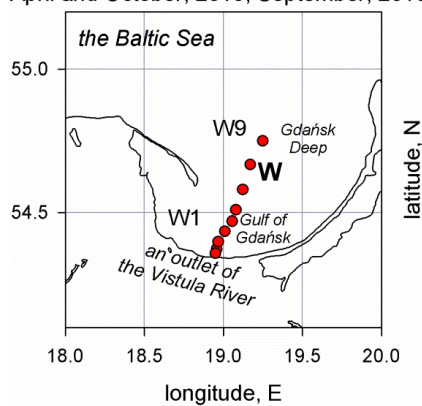
153 Gulf of Gdansk to the Gdansk Deep in the open sea, W9, (Figure 1). ~~The study area~~ Gulf of
154 Gdansk is under direct influence of the main Polish river system, Vistula, which drains the
155 majority of Poland (Uścińowicz, 2011). Meteorological observations (wind speed and wind
156 direction, and a surface waves high were recorded) and CTD cast with use of the SeaBird
157 SBE 19 probe was performed ~~The following tasks were performed at every station. Water~~
158 samples were collected at SML and SS: (i) measurement of the hydrophysical parameters
159 (CTD), (ii) sampling the seawater from SML and SS, (iii) preparation the samples to the
160 appropriate laboratory tests (filtration and proper maintenance) and (iv) meteorological
161 observations. The SML sampling was carried out when the sea state was 1-4 B only, and
162 there were no detectable oil spills. The samples were collected from the board of the vessel
163 (r/y Oceania), that is about 2 m above the sea surface. The sampling was maintained about
164 15 minutes after anchoring, to avoid the turbulences in the surface layer caused by the screw
165 and ship movements. We used the Garrett Net, mesh 18, (18 wires per inch), to collect the
166 samples from the sea surface microlayer, according to the procedure described by Garrett
167 (1965). The mesh screen is 650 cm x 650 cm, made of metal, and the size of holes is 1 mm,
168 while the thickness/diameter of the wire is 0.4 mm. Thus, the thickness of a collected
169 microlayer is about 0.5 mm, and the efficiency is 60%. On average, 22 such samplings were
170 required to obtain 1 dm³ of microlayer water. The following sampling procedure was
171 established. First, the screen was immersed, at an angle of 45°. Then, once totally immersed,
172 the screen was left under the water until the microlayer had stabilized. Finally, it was
173 carefully raised to the surface in a horizontal position at a speed of ca 5–6 cm s⁻¹ (Carlson
174 1982). Water was poured from the screen into a polyethylene bottle using a special slit in
175 the screen frame. The SML samples were collected by the metal Garret's net of 500 µm mesh.
176 This technique allows collecting water from the top layer of an approximately 1 millimeter
177 (Garrett, 1965). In the same places the SS samples from a depth of 1 m were taken by a
178 Niskin bottle. The unfiltered samples were placed into dark bottles and stored at 4°C.
179 Collected, unfiltered water samples were stored in amber glass bottles in the dark at 4°C
180 until analysis in the land based laboratory. During sampling the measurements of temperature
181 and salinity of a surface layer were conducted. Sampling was carried out when the sea state
182 was 1-4 B only, and there were no detectable oil spills. Additionally, the meteorological
183 observations (e.g. recorded wind speed and wind direction and a high of a wave) during
184 sampling, proved to be valuable in the interpretation of extraordinary results. During
185 sampling, in two research cruises, at April in 2015 and September in 2016, the wind speed
186 was almost equally to zero. However, in October in 2015, a northern west wind was recorded

Z komentarzem [A6]: Recenzent chce dokładnego opisu poboru próbek w SML – to jest za mało.

187 ~~(3.4 B). In October the cruise started after a week long storm of northerly winds resulting in~~
 188 ~~the influx of water from the open sea and strong mixing of fresh with coastal and sea water.~~
 189 ~~That allows the explanation of the surprisingly low concentrations (typical for a salinity~~
 190 ~~above 7) of organic matter recorded along entirely transect W, even at the vicinity of the~~
 191 ~~mouth of the Vistula River.~~

192

April and October, 2015; September, 2016



193

194 Figure 1 . Measurements stations realized-sampled during research cruises of
 195 r/y Oceania: 28th April and 15-16th October in 2015 and 11th September
 196 in 2016.

197 **2.2. Laboratory spectroscopic measurements of CDOM and FDOM optical properties**
 198 **laboratory measurements.**

199 The studies conducted in laboratory are: (i) measurements of absorption and (ii) 3D
 200 fluorescence (EEM) spectra of the surface (SML) and subsurface (SS) samples, from 27
 201 stations. Spectrophotometric and spectrofluorometric measurements of the collected
 202 samples were carried-conducted in laboratory the Institute of Oceanology Polish Academy
 203 of Sciences, Sopot, Poland, within a week 24 h after the cruise end. Before any spectroscopic
 204 measurements water samples were left to warm up to room temperature. out in 24 hours after
 205 collection without any previous treatment at room temperature.

206 The main task in our work was to study the luminescent properties of the molecules
 207 that form a surface microfilm. However, As it is well known, (The seasurface microlayer is
 208 a gelatinous film created by polysaccharides, lipids, proteins, and chromophoric dissolved

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209 organic matter (Sabbaghzadeh et al., 2017; Cunliffe et al., 2013) and ~~It means,~~ consisted of
210 dissolved, colloidal and particulate matter. Thus, not to dispose the absorbing and fluorescent
211 matter involved into a gel structure we do ~~no~~ filtrate the samples. In the manuscript the
212 results of absorption and fluorescence indices based on CDOM absorption spectra and
213 FDOM 3D fluorescence spectra, collected during three cruises and carried out on the
214 unfiltered samples are presented. ~~There were performed~~ There were performed the tests on
215 filtrated and unfiltrated probes, sampled during one cruise (not published). Changes in the
216 absorption spectra resulting from the unfiltering of the samples occur mainly in the short UV
217 and far VIS range. However, these differences do not cause significant changes in the
218 absorption indices, because they are calculated on the basis of the shapes of the spectra (in
219 other words: are based on the relative differences between the values of $a_{CDOM}(\lambda)$) in the
220 range between the affected ends of the measuring range ~~We obtain that in spite of the~~
221 differences in the values of the absolute values of the absorption coefficient, between filtered
222 and unfiltered probes, the absorption indices are calculated on the base of the shapes of the
223 spectra (in other words: are based on the relative differences between the values of
224 $a_{CDOM}(\lambda)$). Moreover, in the studied fluorescence spectra, due to lack of filtration, we obtain
225 a strong elastic and non-elastic scatter band, which, however, is removed in the first step of
226 the analysis, ~~therefore the filtration do not effect their results. Moreover, The the filtration~~
227 procedure affects ~~changes~~ the fluorescence spectral band (Fig. 2) for a component T
228 (protein-like) only, that is much effectively retained on the filter. ~~How~~ however, the differences
229 are the same for the SML and SS. ~~It is well known that, filtration separates particulate~~
230 fraction from dissolved and colloidal ones. On the other hand, during filtration the strongly
231 surface active structures of organic molecules or macromolecules might be retained on the
232 filter by sorption processes (Ćosović and Vojvodić, 1998). Knowing the limitations of the
233 applied procedures, we decide to conduct research on unfiltered water. Therefore, the all
234 studied samples are analyzed without filtration (Ćosović and Vojvodić, 1998; Drozdowska
235 et al., 2015). Samples for absorption and fluorescence measurements were treated in the
236 same manner.

237 CDOM absorption measurements were done with use of Perkin Elmer Lambda 650
238 spectrophotometers in the spectral range 240 – 700. All spectroscopic measurements were
239 done with use of 10-cm quartz cell and ultrapure water MilliQ water was used as the
240 reference for all measurements. Raw recorded absorbance $A(\lambda)$ spectra were processed and
241 the CDOM absorption coefficients $a_{CDOM}(\lambda)$ in $[m^{-1}]$ were calculated by:

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Z komentarzem [A7]: Jak uwzględniałaś rozpraszanie i absorpcję cząstek w pomiarach spektrofotometrem. Jak uwzględniałaś rozpraszanie w pomiarach fluorescencji?

242
$$a_{CDOM}(\lambda) = 2.303 \cdot A(\lambda) / l \quad (1)$$

243 where, $A(\lambda)$ is the corrected spectrophotometer absorbance reading at wavelength λ and l is
244 the optical path length in meters.

245 A nonlinear least squares fitting method using a Trust-Region algorithm
246 implemented in Matlab R2011b was applied (Stedmon et al., 2000, Kowalczyk et al., 2006)
247 to calculate CDOM absorption spectrum slope coefficient, S , in the spectral range 300-600
248 nm using the following equation:

249
$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0) e^{-S(\lambda_0 - \lambda)} + K \quad (2)$$

250 where: λ_0 is 350 nm, and K is a background constant that allows for any baseline shift caused
251 by residual scattering by fine size particle fractions, micro-air bubbles or colloidal material
252 present in the sample, refractive index differences between sample and the reference, or
253 attenuation not due to CDOM. The parameters $a_{CDOM}(350)$, S , and K were estimated
254 simultaneously via non-linear regression using Equation 2 in the spectral range 300-600 nm.

255 Absorbance scans, from 240 to 800 nm (1 nm slit width), were conducted using 10
256 cm cuvette by Perkin Elmer Lambda 650 dual beam spectrophotometer connected to a PC
257 computer. Milli-Q water was used in the reference cell. Absorbance measurements, A , at
258 each wavelength (λ) were baseline corrected. CDOM absorption coefficients were
259 calculated by multiplying the corrected optical density by $2.303/l$, where l is the cuvette path
260 length in meters. The detection limit for the equipment was generally less than 0.002 (so the
261 precision was 0.046 m^{-1} using 10 cm cells).

262 The 3D steady state fluorescence spectra (3D EEMs) organic matter fluorescence
263 Excitation Emission matrix spectra of all collected samples the samples, and of Milli-Q
264 water, were carried out made using Varian Cary Eclipse scanning spectrofluorometer in a 1
265 cm path length quartz cuvette using a 4 ml sample volume. A series of emission scans (280–
266 600 nm at 2 nm resolution) were taken over an excitation wavelength range from 250 to 500
267 nm at 5 nm increments. The instrument was configured to collect the signal using maximum
268 lamp energy and 5 nm band pass on both the excitation and emission monochromators. Prior
269 the measurements of each batch of samples the fluorescence EEM spectrum of Mili-Q water
270 blank sample was measured using the same instrumental set up. Tthe intensity of the MiliQ
271 water Raman emission band as the area was calculated by integrating the area under emission
272 spectrum ~~in a the spectral range: 374 - 424nm, below the Raman emission curve induc~~ exited

Kod pola został zmieniony

273 ~~ed at 350 nm (in literature: 355nm) was calculated (Murphy et al., 2010). The blank MiliQ~~
274 ~~fluorescence signal was subtracted from all EEMs samples. All blank corrected spectra were~~
275 ~~normalized to MiliQ water Raman emission (scaled to Raman units R.U.) by dividing the~~
276 ~~resulting spectra by calculated Raman emission intensity value.~~

277 VARIAN Cary Eclipse spectrofluorometer using a 1 cm high sensitivity quartz cell
278 and with 5 nm bandwidth in both excitation and emission, respectively. The excitation of the
279 3D EEM was fixed in a spectral range 250–500 nm, with a step 10 nm. The emission of the
280 3D EEM was recorded in a spectral range 300–600 nm, with a step 2 nm. ~~To make the~~
281 ~~normalization of 3D EEM spectra, the 3D EEM of Mili Q water was measured at the~~
282 ~~beginning of lab measurements every time after the cruise (sampling). Next, the intensity of~~
283 ~~the Raman emission band as the area, in a range: 374–424nm, below the Raman emission~~
284 ~~curve induced at 350 nm (in literature: 355nm) was calculated (Murphy et al., 2010).~~
285 ~~Normalization of 3D EEM spectra of the samples, i.e. conversion into Raman units (R.U.),~~
286 ~~was performed by subtracting the 3D EEM of Milli-Q water from the 3D EEM of the samples~~
287 ~~and then by dividing the resulting spectra by the respective value of Milli-Q water Raman~~
288 ~~intensity.~~

289 
290 ~~2.3 CDOM and FDOM optical properties.~~ Optical indices of CDOM and FDOM used for
291 calculations

292 ~~2.3.1 Absorption indices~~

293 ~~2.3.1 Absorption indices~~

294 ~~Based on measured absorption spectra calculate the absorption coefficient,~~
295 ~~$a_{CDOM}(\lambda)$, (applied as a proxy of CDOM concentration) and several spectral absorption~~
296 ~~indices have been calculated. The proposed spectral indices, defined as the ratios of~~
297 ~~absorption coefficients, are independent on the CDOM concentration, that is very important,~~
298 ~~because CDOM concentration may vary in a small basin even several times (up to 5 times).~~
299 ~~The ratios of CDOM absorption coefficients at 250 to 365nm, $a_{CDOM}(250)/a_{CDOM}(365)$~~
300 ~~(called E₂:E₃) and at 450 to 650 nm, $a_{CDOM}(450)/a_{CDOM}(650)$, (called E₄:E₅) are used to~~
301 ~~track changes in the relative size and the aromaticity of CDOM molecules. (De Haan and De~~
302 ~~Boer, 1987; Peuravuori and Pihlaja, 1997; Chin et al. 1994 citation that give definition):~~
303 ~~briefly, w~~When a molecular size and aromaticity increase, the values of the ratios E₂:E₃ and

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304 E₄:E₅ decrease. This is caused by the stronger absorption at the longer wavelengths occurring
305 due to the presence of larger and higher molecular weighted (HMW) CDOM molecules (De
306 Haan and De Boer, 1987; Peuravouri and Pihlaja, 1997; Chin et al., 1994; Helms et al., 2008,
307 Summers et al., 1987). However, in optically clear in many natural waters the absorption at
308 664 nm is often little or immeasurable and then the absorption at 254 nm (or 280 nm) is used
309 in lieu of the E₄:E₆ ratio as an indicator of humification or aromaticity (Summers et al., 1987).

310 The next parameter is the absorption spectral slope coefficient, *S*, calculated as follow:

$$311 \quad a_{\lambda} = a_{ref} e^{-S(\lambda - \lambda_{ref})} + K \quad (1)$$

312 where *a*—absorption coefficient, m⁻¹, *λ*—wavelength (nm), *S*—absorption spectral slope (nm⁻¹) and
313 *K*—a background constant, arising from residual scattering or attenuation by non-chromophoric organic matter.

314 The spectral slope coefficient, *S*, of the absorption spectra, calculated in various spectral
315 windows range (Carder et al., 1989; Blough and Green, 1995) is may be considered as used
316 as a proxy for CDOM composition, including the ratio of fulvic to humic acids and molecular
317 weight (Stedmon and Markager, 2003; Bracchini et al., 2006). The use of *S* in the narrow
318 spectral range allows to reveal subtle differences in the shape of the spectrum and this in
319 turn gives insight into the origin of organic matter (Sarpal et al., 1995). Therefore to calculate
320 the slopes of the absorption spectra the smaller and more discrete spectral ranges are used as
321 they show a great variability depending on the origin of marine CDOM (marsh, riverine,
322 estuarine, coastal and open sea). The use of narrow wavelength intervals is advantageous as
323 they minimize variations in *S* caused by dilution (Brown, 1977). The ratio of the spectral
324 slope coefficients (*S*₂₇₅₋₂₉₅ and *S*₃₅₀₋₄₀₀), *S_R*, is related correlated with to DOM molecular
325 weight (MW) and to photochemically induced shifts in MW that consistently increased upon
326 irradiation and suggested they are potential indicators of photobleaching in the marine
327 environment (Helms et al., 2008; Zhang et al., 2009; Loiselle et al., 2009). The slope of the
328 absorption curve in the 300-600 nm range, (*S*), is calculated by fitting the exponential
329 function to the expression (1) over a respective spectral window. The spectral slope ratio,
330 *S_R*, was calculated as spectral slopes coefficient ratio estimated by linear fitting of log
331 transformed absorption spectra in the spectral ranges While the slope coefficients in the
332 ranges 275-295 nm, (*S*₂₇₅₋₂₉₅), and 350-400, (*S*₃₅₀₋₄₀₀), are fitted linearly in two narrower
333 wavelength windows. The steeper slope coefficient (higher values of *S*) means a faster
334 decrease in absorption with increasing wavelength. A spectral slope coefficient ratio, *S_R*,
335 (*S*₂₇₄₋₂₇₅₋₂₉₅ to *S*₃₅₀₋₄₀₀) is negatively correlated with molecular weight of CDOM in humic
336 substances. The relationship between *S_R* and molecular weight is very useful to explain the

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337 observed variations in S_R caused by aerobic activity or by photobleaching of CDOM (Helms
338 et al., (2008). It was reported that the photochemical degradation of terrestrial DOM
339 generally causes an lead to increase in the absolute value of the spectral slope coefficient ratio.
340 , while biological degradation did not affect the spectral slope coefficient, or unless DOM
341 molecules had undergone photo-degradation process, it causes a decrease of a spectral slope
342 coefficient. Hence, the simultaneous photo- and biodegradation processes may compensate
343 their effects on the spectral slope coefficient values (Moran et al., 2000).

344

345 2.3.2 Fluorescence indices

346 **2.3.2 Fluorescence indices**

347 Analysis of 3D-EEM fluorescence spectra of marine waters are based on
348 interpretation of distinct fluorescence intensity peaks proposed first time by Coble (1996;
349 Loisel et al., 2009) for different types fluorophores found in natural waters, where peak
350 A (ex./em. 250/437 nm) was attributed to the terrestrial humic substances; peak
351 C (ex./em. 310/429 nm) represented the terrestrial fulvic substances; peak M
352 (ex./em. 300/387 nm) characterized the marine fulvic substances; and peak T
353 (ex./em. 270/349 nm) the proteinaceous substances. The
354 recognized positions (energies) of excitation and emission wavelengths (in: nm/nm) of the
355 main components (A, C, M, T) of marine FDOM at the 3D spectrum, for the Baltic Sea, are:
356 250/437, 310/429, 300/387 and 270/349, respectively; $\Delta\lambda_{em} = \pm 5$ nm, (Kowalczyk et al.,
357 2005; Drozdowska et al., 2015). Based on the 3D (EEM) fluorescence spectra several indices
358 are calculated. The fluorescence intensities of the main FDOM components: A, C, M and
359 T (in Raman units, [R.U.]) were used as a proxy of FDOM concentration. A percentile
360 contribution of the main FDOM fluorophores, calculated as the ratio of the respective peak
361 intensity (A, C, M or T) to the sum (A+C+M+T) of all peak intensities, gives information
362 about the relative changes of a fluorophore composition in a sample (Kowalczyk et al., 2005;
363 Drozdowska and Józefowicz, 2015). Another fluorescence indices are the ratio
364 (M+T)/(A+C) (Parlanti et al., 2000) and HIX index. The ratio (M+T)/(A+C) (Drozdowska
365 et al., 2013) allows to assess a relative contribution of recently in-situ produced
366 dissolved organic matter recently produced, in-situ, (M+T) in the sea to molecules to
367 humic substance characterized by highly complex HMW structures (A+C) (Parlanti et al.,
368 2000; Drozdowska et al., 2013). The values of (M+T)/(A+C) ratio > 1 indicated the
369 predominant amount of autochthonous DOM molecules, while < 0.6 indicated the

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allochthonous ones. HIX index is calculated as a ratio of fluorescence intensity at a long wavelength blue part electromagnetic radiation spectrum (435-480) of the fluorescence spectrum (induced in 255nm) to a fluorescence intensity at the UV-C short part wavelength band (330-346 nm), excited at 255 nm (Chen et al., 2011; Zsolnay et al., 1999; Milori et al., 2002). HIX index reflects the structural changes that occurred in the during humification process of humification, causing an increase in both aromaticity (the ratio C/H) and molecular weight of DOM molecules. The applied indices enable to evaluate a relative contribution of the organic matter recently produced, in situ, in the sea (M and T / an intensity of a short wavelength fluorescence band) and the molecules characterized by a highly complex structure (A and C / an intensity of a long wavelength fluorescence band). Thus, the applied Calculated spectral indices allowed you to assess whether DOM structural and compositional changes, and quantification of the allochthonous (terrestrial, aromatic and highly weighted molecules) or vs. autochthonous (marine humic-like and protein-like and low molecular weighted ones) DOM fractions in the sampled transect organic matter predominate (Chari et al., 2012).

3 Results

During The SML and SS Sampling, in during two research cruises, at April in 2015 and September in 2016, was conducted in calm sea - the wind speed was almost equally to zero. However, in October in 2015, fresh, a northern-western wind was recorded (3-4 B). In This cruise October the cruise started after a week-long storm of northerly winds resulting that caused increase of sea level at the southern part of the Gulf of Gdansk and periodically stopped the Vistula River. in the influx of water from the open sea and strong mixing of fresh with coastal and sea water. As the consequence, measured salinity along entire transect W was > 7, and That allows the explanation of the surprisingly values of CDOM absorption and FDOM intensities were low concentrations (typical for a salinity above 7) of organic matter recorded along entirely transect W, even at the vicinity of the Vistula River mouth. of the Vistula River.

3.1 Absorption analysis

Analysis of the absorption spectra enabled to calculate the absorption coefficients. The absorption at 254 nm exhibits the greater sensitivity to salinity changes than other wavelengths and will be applied as a proxy of CDOM concentration. In the Baltic Sea CDOM absorption decreases with increased salinity (Kowalczuk, 1999, Kowalczuk et al.,

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Z komentarzem [P8]: Viola w wynikach nie ma ani jednej tabelki i rysunku, który pokazuje aCDOM(254). Po co to piesz

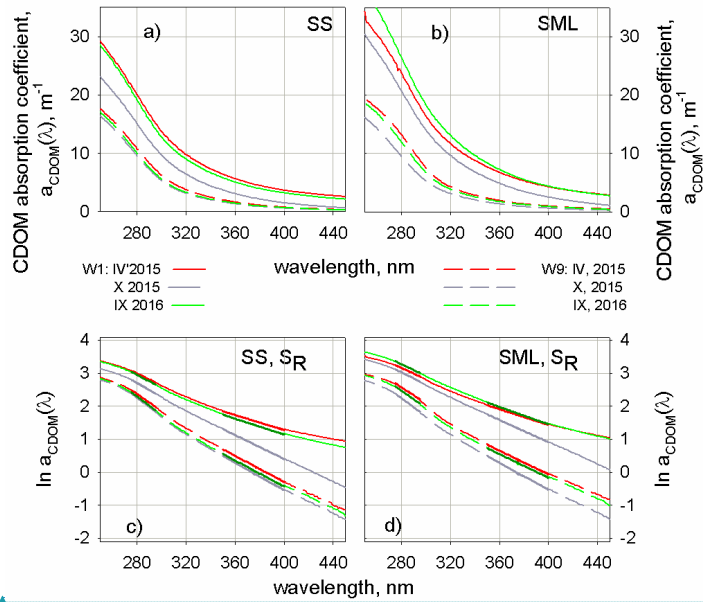
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402 2006; Drozdowska and Kowalczyk, 1999), therefore as expected CDOM absorption spectra
403 measured at the nearest-shore station W1, ~~w~~are higher than compared to those measured in
404 outermost station W9 in the Gdansk Deep, as shown on Figure 2. ~~presents the absorption~~
405 ~~spectra, for the nearest shore, W1, and the most off shore, W9, stations.~~

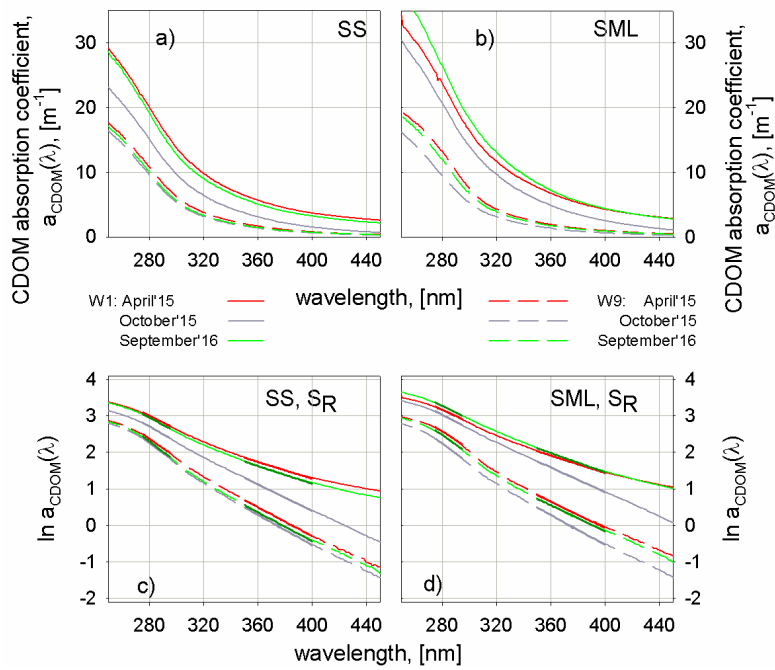
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407

408 **Figure 2.** Absorption spectra - collected during three Baltic cruises at 28th April,
 409 2015 (red lines), 15-16th October, 2015 (grey) and 11th September 2016
 410 (green) - for W1 (solid lines) and W9 (dash lines) stations – presented in
 411 linear scale (top panels: a, b). Natural log-transformed absorption spectra
 412 with best-fit regression lines for two regions (275-295 nm and 350-400
 413 nm) (bottom panels: c, d).

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415 ~~The absorption spectra present the typical distribution of the values of the absorption~~
 416 ~~coefficients that decrease exponentially with increasing the wavelengths in a spectral range~~
 417 ~~from UV to visible light.~~ The values of the absorption coefficient, $a_{CDOM}(\lambda)$ are the highest
 418 in the station W1, located in the vicinity of a river outlet, and the lowest in W9, in the open
 419 sea. Moreover, ~~the intensity of light absorption is higher in the SML than in SS because of~~
 420 ~~the enrichment effect of the surface layer (Williams et al., 1986; Cunliffe et al., 2009), while~~
 421 ~~with an increase of a distance from the river outlet, the intensity of light absorption is~~
 422 ~~decreasing significantly and the differences between the SML and SS become smaller and~~
 423 ~~smaller decrease (the calculations published in open discussion).~~ Furthermore, the slope ratio
 424 S_R , as a ratio of spectral slope coefficients in two spectral ranges of the absorption spectra,
 425 $S_{275-295}$ and $S_{350-400}$, was calculated. The sections of the absorption curves, marked in the
 426 appropriate narrow spectral ranges and, corresponded to them, the values of S_R are presented
 427 in Fig. 2 (c and d) and Table 1, respectively.

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428
 429 **Table 1.** Results of a slope ratio, S_R , for SML and SS, at W1 and W9 stations.

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	A slope ratio – $S_R (= S_{275-295}/S_{350-400})$					
	S_R - for SS			S_R - for SML		
	28 th April 2015	15-16 th October 2015	11 th September 2016	28 th April 2015	15-16 th October 2015	11 th September 2016
W1	1.58	1.16	1.61	1.43	1.10	1.35
W9	1.30	1.33	1.40	1.34	1.35	1.45

430
 431 The values of S_R obtained in three cruises at W1 station (near the Vistula River outlet) were:
 432 1.58, 1.16 and 1.61 for SS and 1.43, 1.10 and 1.35 for SML, respectively. While at W9 (open
 433 sea) were: 1.30, 1.33 and 1.40 for SS and 1.34, 1.35 and 1.45 for SML, respectively. Hereof,
 434 the slope ratio, S_R , was higher in SML than in SS in the open sea (W9), while it was opposite

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435 in a region around the Vistula river mouth (W1). However in W1-W9 (the open sea) the
436 differences were 3.1%, 1.5% and 3.5%, while in W9W1: 10.5%, 5.4% and 11.9%. The
437 higher values of S_R in the SML in the open sea waters, mean the smaller size of CDOM that
438 may exist due to a photodegradation process (Helmes et al., 2008). While the lower values
439 of S_R in the SML in the vicinity of the river outlet may mean the forming of the surface
440 structures from the hydrophobic molecules coming with freshwater.
441 Next, another absorption indices that describe the changes of molecular size/weight (the
442 $E_2:E_3$ ratio) and chemical composition of organic matter (a spectral slope coefficient, S),
443 were calculated. The results of $E_2:E_3$ and S and S_R in a relation to salinity are presented on
444 Fig. 3. The satisfying correlation between salinity and (i) the spectral slope coefficient, S
445 ($r^2=0.84$ for SS and $r^2=0.67$ for SML), (ii) the slope ratio S_R ($r^2=0.58$ for SS and SML) and
446 (iii) relative changes in the molecular weight MW ($r^2=0.94$ for SS and $r^2=0.57$ for SML)
447 were received. The calculations were performed by Regression Statistics, with the
448 Confidence interval 95 %. Moreover, the linear regression coefficients for the relations
449 between salinity and: S , S_R and MW are, respectively 0.00439, 0.13 and 3.029 for SML and
450 0.00435, 0.11 and 2.293 for SS. As one can see, the linear regression coefficients achieved
451 higher values for SML than SS, so the processes go faster in SML than in SS.

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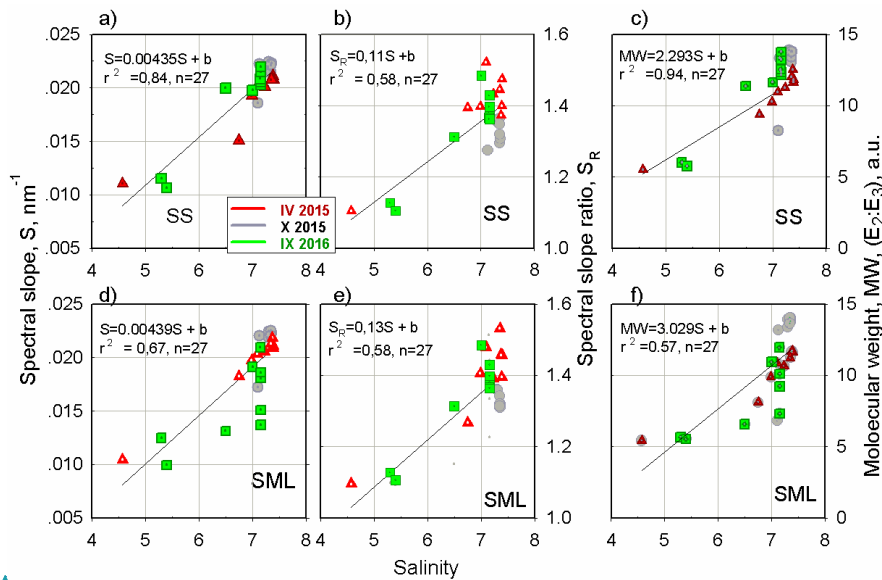
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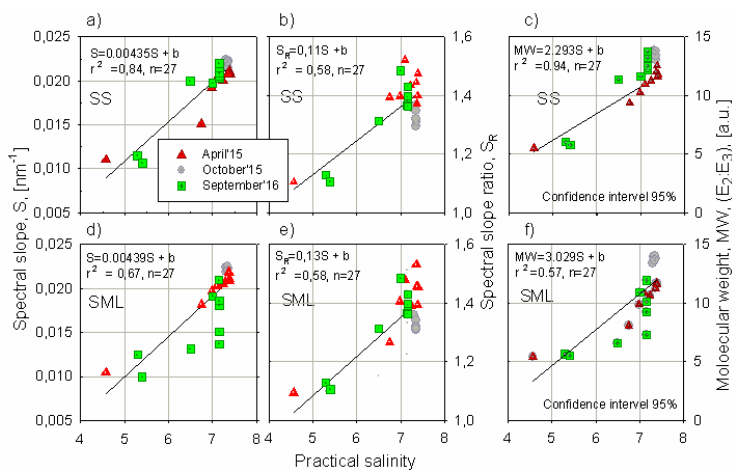
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Fig. 3. The relationship between salinity and: (a) the spectral slope coefficient, S , measured in the 300-600nm, (b) the slope ratio $S_R = S_{275-295} / S_{350-400}$, and (c) the relative changes in the molecular weight, $MW (E_2 : E_3)$ for SS; and: (d), (e) and (f) for SML, respectively.

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459

Furthermore, the values of S , S_R and MW are 2-, 0.5- and 3-times higher, respectively, in a vicinity of the river outlet than in open sea.

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3.2 Fluorescence analysis

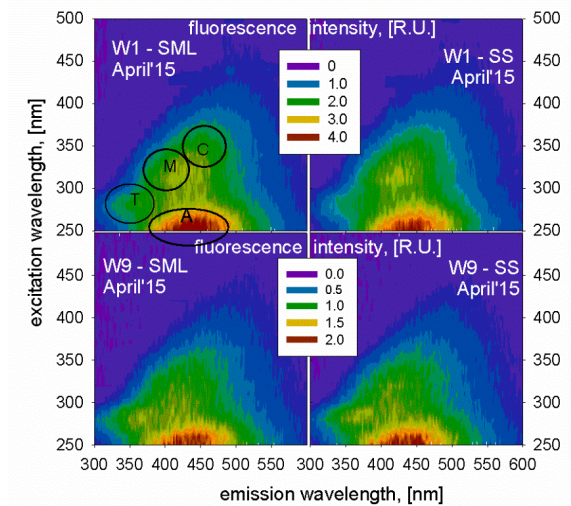
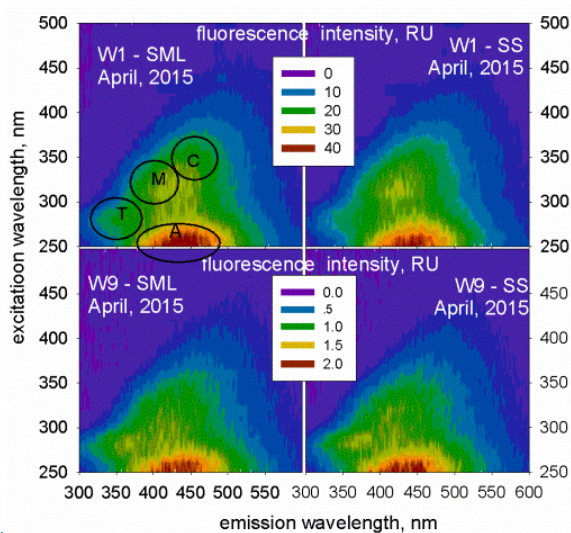
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461 [The studies on the fluorescence properties of seawater, focused on the surface layer, were](#)
462 [developed in the Baltic Sea for years \(Ferrari and Dowell, 1998; Drozdowska and](#)
463 [Kowalczyk, 2009; Drozdowska, 2007a,b\) and allowed for complex analysis of the natural](#)
464 [components of the Baltic water \(Kowalczyk et al., 2005; Stedmon et al., 2003\).](#) Based on the
465 analysis of 54 EEM spectra of seawater (27 samples for SML and 27 ones for SS) the
466 intensities of four emission bands (in [\[R.U.\]](#)), belonging to the main components (A, C, M
467 and T) of the marine CDOM were calculated. The Fig. 4 presents the 3D EEM spectra,
468 typical for the open sea water (the most salty) , W9, and estuarine waters (the most fresh),
469 W1, for the samples collected from SML and SS.

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470
471
472 **Figure 4.** Examples of 3D fluorescence spectra (EEM) of the samples collected
473 at stations W1, near the Vistula River outlet (top panels) and W9, Gdansk
474 Deep (bottom panels), 28 April 2015.

475 **The relationships between the fluorescence intensities of the main fluorescence bands (proxy**
476 **of FDOM components concentration) and salinity as well as the relative contribution of the**
477 **fluorescent components and salinity are demonstrated in Fig. 5 and 6. The changes of the**
478 **FDOM peak intensities and their relative contributions (composition of FDOM components)**

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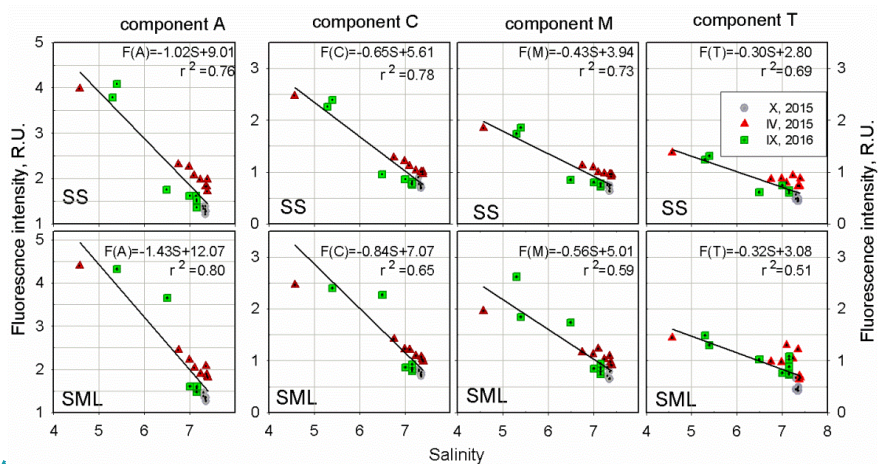
479 in EEM were quantify by calculating the median and its percentile distribution of both the
480 fluorescence intensities and the relative contributions of FDOM components, for the SML
481 and SS in two water masses. Table 2 contains the median values of (i) fluorescence
482 intensities (R.U.) and (ii) percentage contribution (%) of respective peaks in the SML and
483 SS in two distinct water masses: one characterized by salinity <7, which is influenced by
484 direct fresh water discharge from Vistula River and the other characterized by salinity >7,
485 which is typical for open Baltic Sea waters. The ANOVA test was applied to the mentioned
486 median values for two cases: when the differentiation factor was (i) salinity regime and (ii)
487 the sampling layer. The salinity was a good factor to differentiate the variances of the median
488 values, while the sampling layer not. However, in spite of the p-values indicate no statistical
489 significance, one can see on the graphs and Table 2 that the values for the SML are always
490 higher than for the SS. Hence, the distinguish between the results for the SML and SS exist.
491 What is more, the differentiation factor is the level of sampling.

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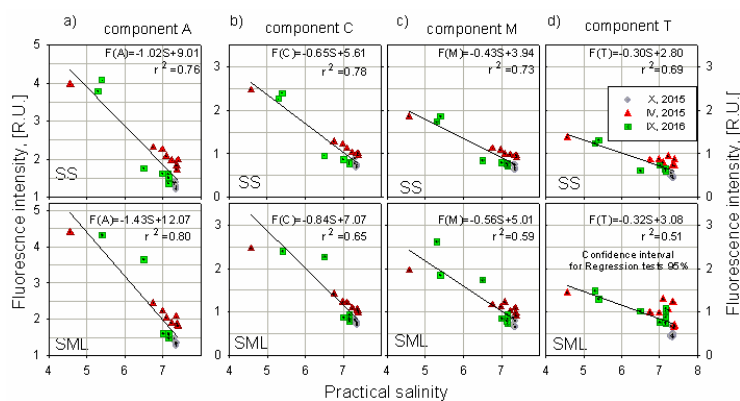
492 The fluorescence intensities of the main FDOM components referred to salinity demonstrate
493 the constant linear relationships both in SS and SML (Fig. 5, upper and lower graphs,
494 respectively). The linear regression coefficients were calculated by Regression test in Sigma
495 Plot, with the Confident interval 95%. The linear coefficients in SML and SS, for every
496 FDOM component, are: -1.43 and -1.02 for a component A; -0.84 and -0.65 for a component
497 C; -0.56 and -0.43 for a component M; -0.32 and -0.3 a component T, respectively. Hence,
498 the regression coefficients are higher in SML than in SS.

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500

501 **Figure 5.** Dependence of the fluorescence intensity of the main FDOM
 502 components: a) A, b) C, c) M and d) T as a linear relation to salinity for
 503 the samples from the sub-surface water (SS; top panels) and the sea
 504 surface microlayer (SML; bottom panels).

505

506 **Table 2.** Medians of FI* and PC** of FDOM components for coastal zone*** and open sea
 507 waters****

FDOM components		Salinity < 7				Salinity > 7			
		A	C	M	T	A	C	M	T
exc./ em. (nm/nm)		250/437	310/429	300/387	270/349				
fluorescence intensity, R.U.	SML	2.69	2.27	1.74	0.98	1.56	0.84	0.85	0.69
	SS	2.31	1.27	1.12	0.86	1.50	0.77	0.76	0.63

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percentile contribution, %	median	SML	40.72	24.32	20.01	14.06	39.08	22.43	20.53	16.89
		SS	41.52	22.87	19.92	14.40	40.75	22.17	20.90	16.27

508 *FI - a fluorescence intensity; **PC - a percentage contribution; *** typical for salinity <7;
509 **** typical for salinity >7.

510

511 The percentile statistical distribution of fluorescence peak intensities in the SML and SS
512 layer in two water masses characterized by salinity threshold less than 7 and higher than 7,
513 have been presented in Fig. 6a and Fig.6b, respectively. The box-whisker plots in Fig. 6
514 present median values (solid line), 25th and 75th percentiles (the boundaries of the box:
515 closest to and farthest from zero, respectively) and 5th and 95th percentiles (whiskers below
516 and above the box, respectively) of the respective fluorescence intensity. There has been a
517 clear spatial pattern (for the coastal zone and open sea) shown on both figures that the higher
518 median values of -A, C, M and T were observed in the SML than in SS. For salinity <7, the
519 median of fluorescence intensities of main FDOM components in SML were: 2.69, 2.27,
520 1.74 and 0.98 R.U., while in SS: 2.31, 1.27, 1.12 and 0.86 R.U. In open waters (salinity >7)
521 the median of fluorescence intensities of the FDOM components were in SML: 1.56, 0.84,
522 0.85 and 0.69 R.U., while in SS: 1.5, 0.77, 0.76 and 0.63 R.U. The median values of
523 respective peaks intensities are higher in SML than in SS both in coastal zone (salinity <7)
524 and in open sea (salinity >7). Additionally, the boundaries of the boxes show much greater
525 dispersion of the results in SML than in SS and greater variation in coastal zone (salinity <7)
526 than in open sea (salinity >7).

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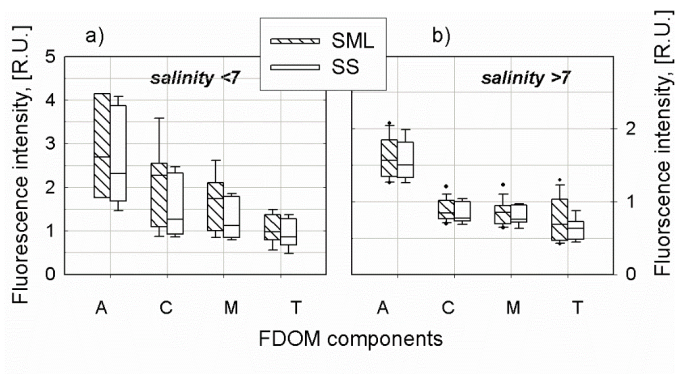
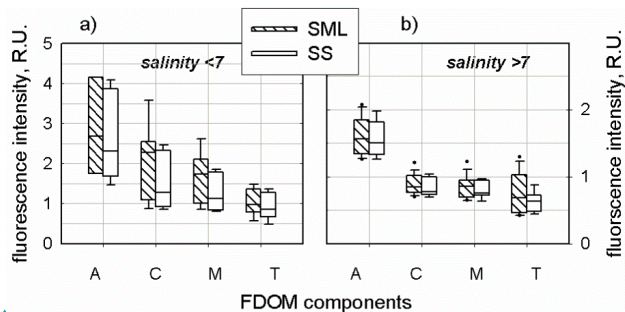


Figure 6. Dependence of the fluorescence intensity of the main FDOM components in SML and SS as the box plots for (a) coastal water (salinity <7) and (b) open sea (salinity >7).

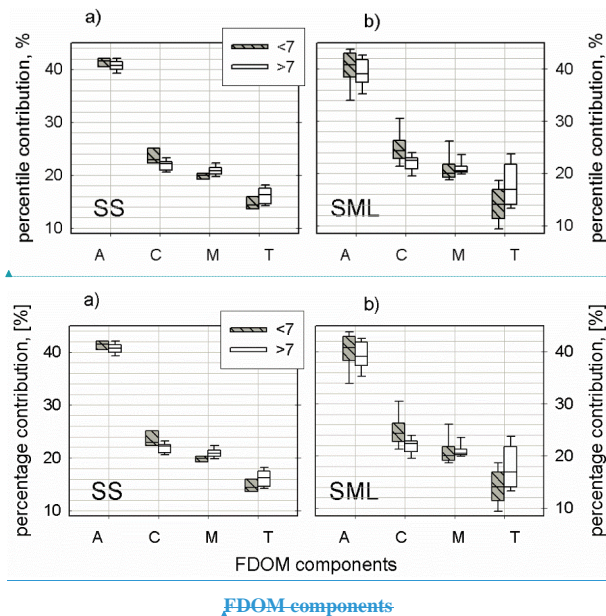
The Fig. 7 shows the percentage contribution of the individual FDOM peaks calculated as the ratio of its fluorescence intensity to the sum of the all fluorescence peak intensities (e.g. $A/(A+C+M+T)$) for SS and SML samples (a left and a right graph, respectively). The box-whisker plots in Fig. 7 present median values (solid line), 25th and 75th percentile (the boundaries of the box: closest to and farthest from zero, respectively) and 5th and 95th percentiles (whiskers below and above the box, respectively) of the respective percentage contribution (a relative composition of fluorescing components of CDOM).

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Figure. 7. Dependence of percentage contribution of the main FDOM components as the box plots for (a) the sub-surface water, SS and (b) the sea surface microlayer, SML; for the coastal waters (salinity <7) and open sea (salinity >7).

For salinity <7, the medians of percentage contribution of A, C, M and T components of marine FDOM in SML were: 40.72%, 24.32%, 20.01% and 14.06 % while in SS: 41.52%, 22.87, 19.92 and 14.40 %, respectively. In open waters (salinity >7) the median values of FDOM components composition were in SML 39.08, 22.43, 20.53 and 16.89 % while in SS: 40.75, 22.17, 20.90 and 16.27 %. So, the contribution of two terrestrial components (A and C) decreased with increasing salinity (~1.64% and ~1.89 % in SML and ~0.78% and ~0.71 % in SS, respectively), while the contribution of, in-situ, in the sea produced components (M and T) increased with salinity (~0.52% and ~2.83% in SML and ~0.98% and ~1.87 % in SS, respectively), Fig. 7. Considering the aforementioned changes for an individual component in relation to its percentage contribution, the values of their relative changes can be calculated. Hereby, the biggest highest relative changes of the FDOM component composition, along the transect from the Vistula River outlet to Gdansk Deep, were recorded for component T, both in SML and SS (about 18.5 % and ~12.3 %, respectively).

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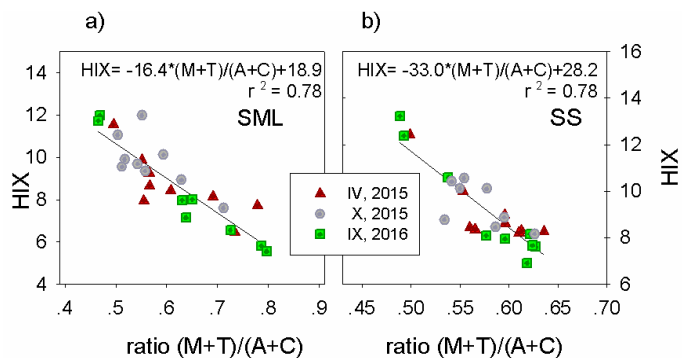
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559 respectively), while the relative changes of A, C and M components were: 4.1, 8.1 and 2.6 %
 560 in SML and 1.9, 3.1 and 4.7 % in SS, respectively.

561 The values of peak intensities (A, C, M and T) allowed to calculate (i) the ratio
 562 (M+T)/(A+C) and (ii) index HIX in SML and SS water, presented on Fig. 8.



563
 564 Figure 8. The relationship between the ratio (M+T)/(A+C) and HIX index for (a)
 565 SML and (b) SS water.

The low values of the ratio (M + T)/(A + C), (<~0.6), were recorded in almost all samples from a sub-surface layer, SS, while in SML samples only from the Gulf of Gdansk. The results of the ratio varied along the transect W in the range 0.47 to 0.79 for SML and 0.49 to 0.63 for SS, from W1 to W9 respectively. Thus, the ratio describes the process that occurs more effectively in SML. The results of the index HIX achieved the higher values in the SS than in SML. What is more, the HIX index changed in SML in a range: 5.8 – 11.9 while in SS: 6.9 – 13.2. The elevated values of HIX in the SS indicate a presence of the molecules of higher molecular weight and more condensed, with higher aromaticity, in SS than in SML, Fig. 8.

575 **3.3** The absorption and fluorescence dependences.

The absorption and fluorescence results allow comparing the spectral slope ratio, S_R , with the HIX index and the ratio $E_2:E_3$ to find the dependences of the molecular size/weight in SML and SS with condensation degree of organic molecules and with the changes in chemical composition of organic matter, Fig. 9 (Helmes et al., 2008; Chen et al., 2011; Väähä-talo and Wentzel, 2004; Zhang et al., 2013). High values of HIX index ca. 10-16, coincide with low values of S_R , ca. 1-1.2 (Zsolnay et al., 1999; Chari et al., 2012; citation). While $S_{275-295} < S_{350-400}$ means the occurrence and predominance of highly

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condensed matter, as a dominance of –and/or terrestrial DOM, with HMW molecules absorbing in a long wavelength range (Helmes et al., 2008; Chen et al., 2011). Whereas, the lower HIX and higher S_R values ($S_{275-295} > S_{350-400}$) mean the predominance of marine-derived, LMW molecules absorbing in a short wavelength range (Chen et al., 2011). The relation between HIX index and S_R show a simple linear relation in sub-surface waters, SS. However in the sea surface microlayer, SML, the changes in organic matter composition, S_R , are not linear-related with the changes taking place in DOM molecules undergoing the degradation processes reflected by HIX values. HIX index is sensitive to the humification and condensation processes, focused on large, high weighted organic molecules, that reflect the changes in a long-wavelength range mainly (above 330 nm). However the photochemical degradation processes, resulting in a decrease in the mass of molecules and an increase of concentration of low molecular-weighted molecules, are much more spectacular in a shorter lower wavelength range and are held primarily in the surface microlayer, SML (Chin et al., 1994; Fuentes et al., 2006). For the same reason as was mentioned above, the relation between the ratio $E_2:E_3$ and S_R is better correlated in SML than SS water (Helmes et al., 2008). Moreover, the relation between the $E_2:E_3$ and S_R (both inversely proportional to molecular size and weight) shows more discrete differences in molecular structure of the organic molecules studied in different seasons and allows to note the different nature of the water tested in October'2015 (Helmes et al., 2008). The values of the ratio $E_2:E_3$ (inversely proportional to molecular size and weight of molecules), calculated for the data collected in October'2015, point to the extremely small size as well as almost the same size/weight of organic molecules investigated in the entirely study region both in SML and SS (Dee Haan and De Boer, 1987; Helmes et al., 2008). That confirms a very well mixed water and the surface layer in the study area during October'15, suggested previously by the meteorological observations.

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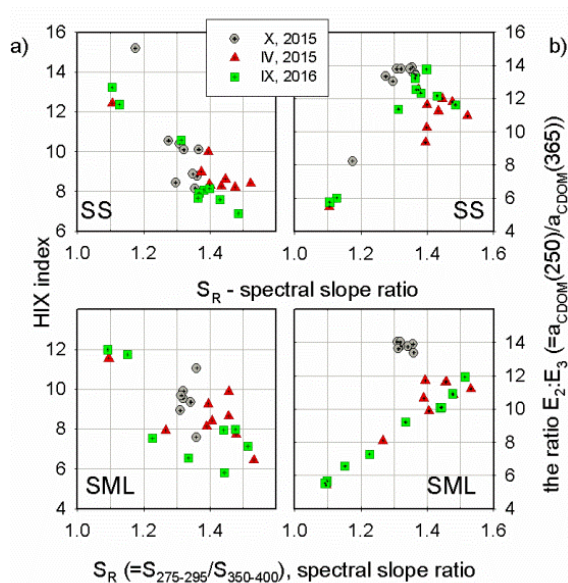


Figure 9. The relationship between the spectral slope ratio, S_R , and (a) HIX index and (b) the ratio $E_2:E_3$ - for SS (top panels) and SML (bottom panels).

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4. Discussion

The values of the absorption coefficient, $a_{CDOM}(\lambda)$, show that with an increase of a distance from the river outlet, the intensity of light absorption (a proxy of amount of organic matter) is decreasing significantly, both in SML and SS (Tilstone et al., 2010; Stedmon et al., 2000; Twardowski and Donaghay, 2001; Kowalczyk et al., 1999). It shows that the main source of CDOM in the study area is the Vistula River (Ferrari and Dowell, 1998; Kowalczyk et al., 2005). Additionally, the differences between the higher absorption values f of the absorption were detected ~~or in the SML and then in SS~~, what is called the enrichment effect, that was studied for diverse range of microlayer components in different aquatic systems (Carlson, 1983; Williams et al., 1986; Wurl et al., 2009). Moreover, the differences between the values of the absorption coefficients calculated for the SML and SS decrease with the increase of salinity, that was reported as the effect of conversion POM to DOM, enhanced in the SML, by extracellular enzyme activity and export of DOM formed in the SML to subsurface layers (Kuznetsowa and Lee; 2001; Wurl et al., 2009), ~~become smaller and smaller~~. The analysis of several absorption indices (S , S_R and $E_2:E_3$) ~~may~~ reveal the changes

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in composition and a decrease in molecular weight of organic matter with an increase of salinity and a distance from the mouth of the river (Helmes et al., 2008). Molecules brought into the sea with the river waters, with increasing salinity (and time and the distance from the mouth of the river) undergo such processes as the dilution of the fresh waters in sea waters and the degradation of the organic particles, induced by solar radiation (photo-bleaching) and by bacterial activity (biodegradation) (Moran et al., 2000; Helmes et al., 2008). The increase of S and S_R and $E_2:E_3$ (a proxy of a decrease of molecular weight, MW) with salinity suggest a transfer of colored material from HMW fraction to the LMW fraction (Helmes et al., 2008). Moreover, the linear regression coefficients for the relations between salinity and: S, S_R and $E_2:E_3$ achieved higher values for SML than SS (Zhang et al., 2013). The values of the linear regression coefficients can illustrate a rate of the breakdown of large molecules to smaller ones (HMW to LMW) (Zhang et al., 2013; Timko et al., 2015; Helmes et al., 2008). They achieve the higher values in SML than in SS, thus show that in SML the processes dependence is stronger in the SML, faster than in SS (citation). Furthermore, the values of S, S_R and MW, are smaller in a vicinity of the river outlet about 2-, 0.5- and 3-times, respectively, than in open sea depict a presence of higher molecular weighted molecules in the estuarine waters, both in SML and SS (citation). Hence, the higher values of S_R indicate an increase of absorption in a short wavelength range (via an increase in concentration of low-weighted molecules, LWM) and a decrease of absorption in a longer wavelength range (a decrease in the concentration of big and more condensed and high-weighted molecules, HWM) (Helmes et al., 2008; Peravuori and Pihlaja, 1997; Osburn et al., 2011). However, in a vicinity of the river mouth (W1), the studied absorption indices reached the lower values in SML than in SS. It suggests that the molecules with large molecular mass predominate in a surface microlayer. Such results may be caused by the presence of the surface slicks, visible by a naked eye, made of big surface molecular structures (citation). A riverine water brings into the sea a huge amount of the terrestrial amphiphilic (the molecules with hydrophobic and hydrophilic heads) organic molecules that form the surface slicks and despite the large weight of the surface molecular structures their hydrophobic properties make them float on the sea surface (Cunliffe et al., 2011).

The spectrofluorometric studies complete and confirm the absorption studies. Wherein the concentration of components A, C, M and T were higher in SML than in SS in both coastal zone and open sea; the contribution of A and C components in FDOM composition decreased, while M and T increased, with an increase of salinity (Yamashita et al.,

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660 [2008; McKnight et al., 2001](#)). Moreover, the values of the fluorescence intensity of FDOM
components change linearly with salinity and the linear regression coefficients show higher
values in SML than in SS ([citationVodacek et al., 1997; Williams et al., 2010](#)). This may
confirm a higher rate of the degradation processes occurring in SML. The relative changes
of percentage contribution of FDOM components, with an increase of salinity, depict that a
665 component which quantity varies the most, is a fluorophore T ([citation](#)). It may indicate on
production of protein-like fluorophores caused by photobleaching and biological activity
([Blough and Del Vecchio 2002; citation](#)). Additionally the results of the FDOM
measurements indicate that FDOM concentration is about 2-3 times higher in the coastal
zone (salinity <7) than in the open sea (> 7). The results of FDOM concentration indicate
670 the dominance of terrestrial molecules (allochthonous) in estuarine waters - due to high
concentration of molecules brought by a river (A and C). The ratio (M+T)/(A+C) increased
with salinity and reached the highest values in the open sea: 0.79 and 0.63 in SML and SS,
respectively ([Parlanti et al., 2000; Wilson and Xenopoulos, 2009; Huguet et al.,
2009; citation](#)). Photo-degradation effect, induced by solar radiation on the molecules in a sea
675 surface layer, results in degradation of macromolecules into particles with a lower molecular
weight (i.e., a decrease of A and C and the increase the amount of molecules of lower
molecular weight produced in the sea (M and T) and this process acts more rapidly in SML,
(Fig. 8) ([citationHuguet et al., 2009](#)). The above conclusion is confirmed by the results of
the ratio (M+T)/(A+C) and HIX index, which achieve respective higher and lower values in
680 the SML than in SS due to higher fluorescence intensity at a short wavelength band
belonging to marine FDOM components (M and T) ([citationChari et al., 2012; Stedmon and
Markanger, 2005; Murphy et al., 2008; Mopper and Schults, 1993](#)). The elevated values
of HIX in the SS are an evidence of a more advance humification process of the organic
molecules that make the organic molecules more condensed and with higher aromaticity
685 ([citationZsolnay et al., 1999](#)).

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5. Conclusions

The results of the studies on the absorption and fluorescence properties of the organic matter
included in the SML and SS waters are complementary. The values of the absorption
coefficients as well as the fluorescence intensity give information about the decline in the
690 CDOM/FDOM concentration with increasing salinity, both in SS and SML, [however the
values of the absorption and fluorescence indices indicate on the enrichment effect in in the](#)

[surface microlayer](#). ~~What is more~~ Moreover, a decreasing of DOM concentration with salinity occurs faster in SML than in SS. Analysis of absorption and fluorescence spectra allow the detection of subtle changes in the percentage composition of CDOM/FDOM components that revealed an increase of M and T (produced in-situ, in the sea) and a simultaneous decrease in A and C (terrestrial origin) with increasing salinity. Moreover the changes of the [dependence of a percentage composition and salinity](#) occur in SML more rapidly than in SS. The results suggest a higher rate of degradation processes in a surface microlayer ([Drozdowska et al., 2015; Timko et al., 2015](#)).

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In addition, the analysis of indices obtained from the values of the intensity of the absorption and fluorescence of the samples enabled tracking sources and processes, which have been subjected to investigated molecules, in SML and SS. The authors: (i) confirm that the processes of structural changes in molecules of HMW to LMW, due to effects of photo- and biodegradation, occur faster in SML than in SS ([Helmes et al., 2008](#)); (ii) organic molecules contained in a surface microlayer, SML, have a smaller molecular mass than SS, thus, SML and SS are characterized by different percentage distributions of the main FDOM components ([Helmes et al., 2008; Engel et al., 2017](#)); (iii) the fresh water of the Vistula River is the main driving force of allochthonous character of organic matter in coastal waters of Gulf of Gdansk.

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Summarizing, the distributions of light intensity reached over or behind the sea surface is modified effectively by the specific absorption and/or emission of a light by surfactants. The degradation processes of the organic molecules contained in SML and SS proceed at different rates. Hence, the DOM molecules included in the SML can specifically modify the physical processes associated with the sea surface layer. It should be necessary to continue

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a study on the physical properties of surface microlayer in other Baltic Sea sites and in less urbanized and more natural and pristine region, like Arctic.

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