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Ocean Science Discussions

Interactive comment on "Study on organic matter fractions in the surface micro layer in the Baltic Sea by spectrophotometric and spectrofluorometric methods" *by* Violetta Drozdowska et al.

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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

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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 (citation), (ii) terrestrial organic matter that enter seawater transported from a land with riverine outflow (natural and synthetic), (iii) natural oil leakages from the seabottom 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 (citation)“.

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 (citation), exchange of momentum between atmosphere and ocean by reducing the sea surface roughness (citation) 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)

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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; Ćosović 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.”

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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

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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 45âÚę . 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 aCDOM(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 aCDOM(ïĄň)), 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 Fig.1. Dependence between salinity and aCDOM(ïĄň), [m-1] for filtered and unfiltered samples from a) the SML and b) SS.

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

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Line 8: "smaller and smaller" is meaningless. Provide numbers and statistics for the decrease a sthe information is hard to extract from the figure

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 aCDOM(ïĄň) 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 aCDOM(ïĄň) in the SML are higher than in SS, while with increasing salinity the values of aCDOM(ïĄň) decrease with increasing salinity and the difference between the results of aCDOM(ïĄň) for the SML and SS decrease as well.

Fig.3 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 (r2 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 R2, 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 comparision of R.U. are not significantly different, but it requires statistical test and p values, which the authos 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, H0, is that the levels of sampling are meaningless (irrelevant), while the alternative hypothesis, H1, 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, H0. 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 , H0, 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 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).

Fig.4 Figure 4. (Figure 7.) 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.

Please also note the supplement to this comment:
http://www.ocean-sci-discuss.net/os-2017-4/os-2017-4-AC3-supplement.pdf

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Interactive comment on Ocean Sci. Discuss., https://doi.org/10.5194/os-2017-4, 2017.

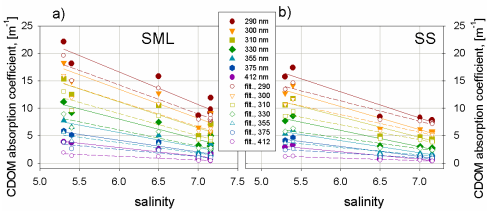

Fig.1. Dependence between salinity and $a_{CDOM}(\lambda)$, [m^{-1}] for filtered and unfiltered samples from a) the SML and b) SS.

Fig. 1. fig-1

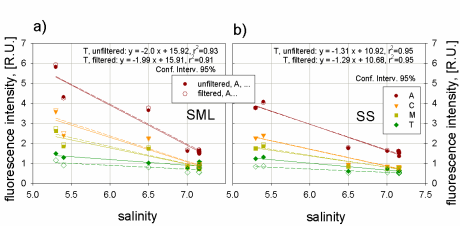

Fig. 2. Dependence between salinity and FDOM intensity at peaks, [R.U.] for filtered and unfiltered samples from a) the SML and b) SS.

Fig. 2. fig-2

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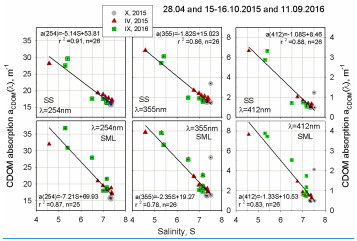

Figure 3. Dependences between salinity and CDOM absorption coefficient at several wavelengths.

Fig. 3. fig-3

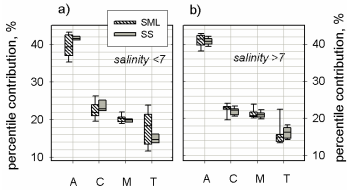

Figure 4. (Figure 7.) Dependence of percentage contribution of the main FDOM components in SML and SS as the box plots for (a) coastal waters (salinity <7) and (b) open sea (salinity >7).

Fig. 4. fig-4