The response to the reviewer #1 comment on manuscript by Meler at al., Ocean Sci. Discuss., doi:10.5194/os-2016-34,

Anonymous Referee #1

General comments

The paper presents very interesting work. Obviously, a lot of careful work has gone into this study and the assessment of model performance is detailed and thorough. It does, however, not become clear what the motivation for of this work is. What are potential applications for each of the presented models and where is the advantage over previously published work? What progress has been made?

Reply: We would like to thank Reviewer 1 for appreciation of our work. We will make effort to explain our motivation and implication of our research and proposed model in the broad context of the possible application in remote sensing, biogeochemistry and carbon cycle studies in enclosed marine basins and estuaries and fresh water lakes. The Reviewer #2 has similar remark therefore we have added a short paragraph in Introduction that fit our research in the broader aspects of applied environmental studies. Proposed new paragraph and references is included below:

"The CDOM absorption coefficient is a very reliable predictor of the dissolved organic carbon concentration in fresh and estuarine waters (Brezonik et al., 2015; Kutser et al., 2015; Toming et al., 2016), and therefore this optical parameter could be easily applied in various aspects of organic carbon biogeochemistry. The ocean color remote sensing offer new operational satellite missions based on medium ground resolution (of the order of 250 m) sensors, like the European Earth Observation Copernicus program Sentinel-3 OLCI mission, and the US Joint Polar Satellite System program VIIRS sensors. These radiometers are particularly suitable for remote sensing observations of inland water bodies and estuaries (Palmer et al., 2015; Kwiatkowska et al., 2016). The optical properties of CDOM, abundant in fresh and estuarine waters at high concentrations, shift the spectral maximum of the water transparency to solar radiation and water leaving radiance towards the longer wavelengths (Darecki et al., 2003; Morel and Gentili, 2009). In extreme cases, in humic boreal lakes, CDOM reduces the waterleaving radiance intensity in the visible spectrum almost to zero (Ficek et al., 2011; Ficek et al., 2012; Ylöstalo et al., 2014). To minimize this effect, the remote sensing algorithm for retrieving bio-optical and biogeochemical variables in optically complex waters has been based on spectral band combinations at longer wavelengths where CDOM absorption is low (e.g. Ficek et al., 2011). Therefore, models need to be developed that enable the complete CDOM absorption spectrum to be reconstructed. Detailed spectral information of CDOM absorption is required, for example, to calculate the spectral indices related to molecular weight, degree of photochemical transformation (Helms et al., 2008) or aromaticity (Weishaar et al., 2003). "

The references list has been updated with those cited in this paragraph.

Specific comments

1. Why was a linear function fitted to the data in Figure 2

Data presented on Figure 2 were showed in the semi – logarithmic scale (the $a_{\text{CDOM}}(400)$ on X-axis is shown in logarithmic scale, the spectral slope *S* is shown in linear scale). We have used the logarithmic function (equations 10, 11 and 12), to approximate relationship between $a_{\text{CDOM}}(400)$ and S, and therefore graphical representation of logarithmic function in a semi-logarithmic scale, is a straight line.

2. Slope values for the data set presented seem fairly high. What about the quality of the data used to establish the models developed here: is there a dependency of slope values on concentrations which is caused by artifacts due to limited data quality (the use of a short pathlength in combination with relatively low CDOM concentrations)? Low coefficients of determination for the calculation of slope values point towards issues here.

We disagree with the reviewer comment.

The Baltic Sea CDOM absorption data were analyzed twice with focus of on the spectral slope values and its dependency with CDOM absorption coefficient values.

The fist study published by Kowalczuk et al., (2206) presented the differences between spectral slope values calculated with different methods (linear vs. non-linear) and different spectral range used for slope calculations. We have proved in that paper that non-linear fitting methods returns higher slope values compared to linear fit log-transformed absorption data, and that the broader spectral range the smaller uncertainty is slope values would be achieved. The averaged spectral slope value $S_{300-600}$ (calculated with use of non-linear fitting method) presented in the paper by Kowalczuk et al., (2006) was 0.02334 nm⁻¹ (n = 1610, C.V. = 12%)

The second study, published by Kowalczuk et al., (2015), presented most complete to date statistical distribution of the spectral slope values in the function of salinity in the Baltic Sea. This statistical distribution has been derived upon 3636 measured $a_{\text{CDOM}}(\lambda)$ spectra and the spectral slope was calculated with use the same Matlab code and in the same spectral range as we used in the current submission Presented variability range of the spectral slope S, contained within 0.015 to 0.030, plus few point over the value of 0.030. We have also characterized the CDOM optical properties in end members: in the inflowing riverine fresh waters and in marine open Baltic Sea waters. The statistical description CDOM optical properties in open Baltic Sea waters presented in the paper by Kowalczuk et al., (2015) were as follow: salinity at the surface: 7.381 \pm 0.209, $a_{CDOM}(350) = 1.617 \pm 0.233 \text{ m}^{-1}$, and $S_{300-600} = 0.0232 \pm 0.0015$ nm⁻¹, (n = 673). The fresh water end member was characterized by following average and standard deviation values: salinity = 0.918 ± 0.546 ; $a_{\text{CDOM}}(350) = 8.705 \pm 2.842 \text{ m}^{-1}$ and spectral slope coefficient $S_{300-600} = 0.0185 \pm 0.0008 \text{ nm}^{-1}$, salinity = 0.918 ± 0.546 ; respectively (n = 30). The Baltic Sea data set used in the current submission were a subset of the data described by Kowalczuk et al. (2015). The same method for spectral slope calculation has been applied in to process the $a_{CDOM}(\lambda)$ in lakes. In the current manuscript we presented the spectral slope variability range within 0.007 up to 0.30, both in lakes and Baltic Sea, (see, Table 2). The CDOM absorption and spectral slope variability and averaged values were very close to those already reported by Kowalczuk et al., 2006 and 2015. The lower spectral slope values were observed in lake waters, which agrees with current the knowledge about the spectral properties of CDOM absorption (CDOM absorption in fresh water is larger and absorption spectra flatter). The observed inverse dependence of the spectral slope with increasing CDOM absorption has been explained in details in paper by Stedmon and Markager (2003) and explored further in the paper by Kowalczuk et al. (2006).

We were very conservative in while performing $a_{\text{CDOM}}(\lambda)$ data base re-analysis and only those spectral slope values were used in Kowalczuk et al. (2015) paper that were fitted with R^2 at

least 0.99. The re-analysis of CDOM absorption data based presented in paper by Kowalczuk et al., (2015), contained CDOM spectra measured with different brands of research grade spectrophotometers and different pathlengths used in measurements. We did not observed any statistical difference related to subset of data measured with different apparatus or different pathlengths. We can assure that 5 cm cuvette used in CDOM absorption measurement in open Baltic Sea water gave similar results as CDOM absorption spectra measured with use of 10 cm cuvettes. We quite confident in quality of our data and we do not see any issue related to low quality of data.

3. Direct comparison of the different models (presented here and previously published) might be easier if values were presented in separate tables for every statistic metric rather than each model. Similarly, Figure 10 could be re-arranged, so that each panel shows the outputs of all models for a single chlorophyll concentration which would enable a more direct comparison.

Reply: The figure 10 has been re-arranged according to reviewer suggestions.

4. Page 7: It would be helpful to add a short description and purpose of the different statistical metrics.

Reply: The following paragraph has been added to explain statistical metrics used in uncertainty analysis.

Linear metrics are represented by relative mean error and standard deviation were used to measure dispersion of results and asses the modes uncertainty. The relative mean error (Eq. 5a) is the average of all relative deviations between measured and calculated values and it quantified the systematic error. Standard deviation (Eq. 5b) is the dispersion around the average error due to random errors and it quantified the statistical error. Logarithmic metrics were used to better describe the uncertainty in the data ste varying in the range of several orders of magnitude. The standard error factor described how many times the error is deviated from the average value.

5. The structure, especially of the Discussion section (e.g. paragraph ll. 537.), should be revised as it is difficult to follow the argumentation at times. The Discussion contains paragraphs better suited in the Introduction and Results sections.

The revised manuscript structure will thoroughly corrected in terms of used argumentation and clarity. The whole manuscript will be edited to clarify the English usage, grammar and style.

Technical comments

The language needs to be tidied up thoroughly prior to publication. It distracts from the content.

Reply: We will send the revised manuscript to a English editor prior its submission to a journal editor office.

The symbols for CDOM absorption coefficients and abbreviation for chlorophyll a concentration are used inconsistently throughout the manuscript.

Reply: It has been amended.

Lines 177 – 180: Add reference for protocol used in this work.

Reply: It has been amended.

Line 188/ Eq. 4: Specify at which wavelength chlorophyll specific absorption coefficients calculated.

Reply: It has been amended.

Line 198: The term 'standard deviation' is slightly mis-leading in this context as Eq. 5b is used as descriptor of the overall error rather than variability in the data.

Line 203: Move symbol definitions to the top of the paragraph, i.e. line 197.

Reply: It has been amended.

Line 264: How are relative RMSE values calculated? If a parameter has a logarithmic distribution, simply dividing the RMSE by the mean value creates a potential bias.

Reply:

All optical parameters values were presented in logarithmic scale, because in this way the relationship between these parameters (which varies with respect to more than two or three orders of magnitude) are more visible. The linear metric were applied to untransformed values of optical and bio-optical parameters. Due to broad range of variability (spanning up to three orders of magnitude) we additionally used the logarithmic metric to reduce to bias due to occurrence of very high values in the data set, that could impact the linear metrics calculations.

Line 452: 'uncertainty level' - Which statistical metrics does this refer to?

Reply: "Uncertainty level" in this line is refer to arithmetic metric.

Line 519: This paragraph contains multiple subjective assessments of model performances. It would be helpful to add numbers to support the statements made.

Reply: We will revise the Discussion section to make our statements clear, and to assess the model performances on objective arguments.

The response to the reviewer #2 comment on manuscript by Meler at al., Ocean Sci. Discuss., doi:10.5194/os-2016-34,

Anonymous Referee #2

General comments

An interesting work in which a lot of effort for sampling, analysis and modeling has gone. The motivation for this work is not quite clear. Advantages should be more highlighted, combined with future prospects for its application.

Reply: We would like to thank Reviewer 2 for appreciation of our work. We will make effort to explain our motivation and implication of our research and proposed model in the broad context of the possible application in remote sensing, biogeochemistry and carbon cycle studies in enclosed marine basins and estuaries and fresh water lakes. The Reviewer #1 has similar remark therefore we have added a short paragraph in Introduction that fit our research in the broader aspects of applied environmental studies. Proposed new paragraph and references is included below:

"The CDOM absorption coefficient is a very reliable predictor of the dissolved organic carbon concentration in fresh and estuarine waters (Brezonik et al., 2015; Kutser et al., 2015; Toming et al., 2016), and therefore this optical parameter could be easily applied in various aspects of organic carbon biogeochemistry. The ocean color remote sensing offer new operational satellite missions based on medium ground resolution (of the order of 250 m) sensors, like the European Earth Observation Copernicus program Sentinel-3 OLCI mission, and the US Joint Polar Satellite System program VIIRS sensors. These radiometers are particularly suitable for remote sensing observations of inland water bodies and estuaries (Palmer et al., 2015; Kwiatkowska et al., 2016). The optical properties of CDOM, abundant in fresh and estuarine waters at high concentrations, shift the spectral maximum of the water transparency to solar radiation and water leaving radiance towards the longer wavelengths (Darecki et al., 2003; Morel and Gentili, 2009). In extreme cases, in humic boreal lakes, CDOM reduces the waterleaving radiance intensity in the visible spectrum almost to zero (Ficek et al., 2011; Ficek et al., 2012; Ylöstalo et al., 2014). To minimize this effect, the remote sensing algorithm for retrieving bio-optical and biogeochemical variables in optically complex waters has been based on spectral band combinations at longer wavelengths where CDOM absorption is low (e.g. Ficek et al., 2011). Therefore, models need to be developed that enable the complete CDOM absorption spectrum to be reconstructed. Detailed spectral information of CDOM absorption is required, for example, to calculate the spectral indices related to molecular weight, degree of photochemical transformation (Helms et al., 2008) or aromaticity (Weishaar et al., 2003). "

The references list has been updated with those cited in this paragraph.

Specific comments

Some structures should be revised, especially the discussion. Argumentation is often difficult to follow. Short and concise sentences might be easier. A little bit mixed up with other chapters, especially results.

Reply: The revised manuscript structure will thoroughly corrected in terms of used argumentation and clarity. The whole manuscript will be edited to clarify the English usage, grammar and style.

Fig 10 could be arranged according to chlorophyll a concentrations.

Reply: It has been amended.

To clarify and support statements add numbers (i), (ii), especially in the discussion section.

Reply: This remark is similar to comment by Reviewer #1. We will make effort during manuscript revision to make our statements clear, and to assess the model performances on objective arguments.

Technical comments

The language should be revised prior to publication. Reply: As we already stated the revised manuscript will corrected by professional English editor.

Sentences are often too long, resulting in confusion.

Reply: The English usage, grammar and style will be corrected by professional English editor.

Formulas should be consistent; the same goes for the description of existing parameters. Symbols and abbreviation are used inconsistently in manuscript, e.g. chl a, CDOM. This should be revised prior to publication.

Reply: It has been amended.

Lines 175ff: Add reference.

Reply: It has been amended.

Line 182ff: Eq 4: At which wavelength was it calculated?

Reply: It has been amended.

Line 203-212: not consistent with others, try to rearrange.

Reply: It has been amended.

matter in the Baltic Sea and Pomeranian Lakes 2 Justyna Meler^{a*}, Piotr Kowalczuk^a, Mirosława Ostrowska^a, Dariusz Ficek^b, Monika 3 Zabłocka^a, Agnieszka Zdun^a 4 ^a Institute of Oceanology Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 5 Sopot, Poland 6 ^b Institute of Physics, Pomeranian University of Słupsk, Bohaterów Westerplatte 64, 76-200 7 Słupsk, Poland 8 9 corresponding author: <u>jmeler@iopan.pl</u> 10 Keywords: Baltic Sea; Pomeranian lakes; Chromophoric Dissolved Organic Matter; three 11 alternative models of CDOM absorption; light absorption; ocean optics, 12 13 Abstract 14 This study presents three alternative models for estimatingon of the absorption properties of 15 Chromophoric Dissolved Organic Matter, $a_{CDOM}(\lambda)$. For this analysis we used a database 16 containing 556 absorption spectra measured in 2006 - 2009 in different regions of the Baltic 17 Sea (open and coastal waters, the Gulf of Gdańsk and the Pomeranian Bay), at river mouths, 18 in the Szczecin Lagoon and also in three lakes in Pomeranian (lakes in Poland), - Lakes 19 Obłęskie, Łebsko and Chotkowskie. Observed The variability range of the CDOM absorption 20 coefficient at 400 nm, $a_{\text{CDOM}}(400)$, contained lay within 0.15 – 8.85 m⁻¹. The variability in 21

Parameterization of the light absorption properties of chromophoric dissolved organic

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 $a_{\text{CDOM}}(\lambda)$ was parameterized with respect to the three orders of magnitude-variability over 22 <u>three orders of magnitude</u> in the chlorophyll μ concentration Chla (0.7 – 119 mg m⁻³). The 23 <u>c</u>Chlorophyll a concentration and CDOM absorption coefficient, $a_{CDOM}(400)$ were correlated, 24 and a statistically significant, non-linear empirical relationship between theese parameters 25 was derived (R^2 =0.83). Based on On the basis of the observed co-variance between these 26 parameters, we derived two empirical mathematical models that enabled to project design the 27 CDOM absorption coefficient dynamics in natural waters and reconstruct the completed 28 updated complete CDOM absorption spectrum in the UV and visible spectral domains. The 29 input variable in the -first model was the chlorophyll a concentration, used the chlorophyll a 30 concentration as the input variable. The second model used the and in the account (400), as the 31 input variable second one it was a_{CDOM}(400), Both models were fitted to a power function, 32

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and the <u>a</u> second_-order polynomial function was used as the exponent. Regression coefficients for derived-these formulas were determined for wavelengths from 240 to 700 nm at 5 nm intervals-. Both approximations reflected the real shape of the absorption spectra with <u>a</u> low <u>level of uncertainty</u>. Comparison of these approximations with other models of light absorption by CDOM proved-demonstrated that-that our proposed parameterizations were <u>better superior</u> (bias from -1.45% to 62%, RSME from 22% to 220%) for estimationg CDOM absorption in the optically complex waters of the Baltic Sea and <u>Pomeranian</u> lakes. **Formatted:** No underline, Font color: Auto, English (U.S.)

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40 **1. Introduction**

All natural waters contain optically significant constituents that determines their 41 inherent optical properties, i.e. the: absorption coefficient, scattering coefficient and beam 42 attenuation coefficient. The total absorption coefficient in the ultraviolet and visible spectral 43 44 range of the electromagnetic radiation spectrum, is almost entirely determined by four main groups of absorbents: water molecules, organic and inorganic suspended particulate matter 45 46 (SPM), and Chromophoric Dissolved Organic Matter (CDOM). The quantityative and 47 qualitative properties of these absorbents significantly affect the quantity-amount and spectral distribution of light in the aquatic environment. The absorption of pure water, as measured by 48 Pope and Fry (1997), is almost constant in natural waters and may can be omitted in further 49 from the following analysis because it does not contribute to a the variability of in the total 50 51 absorption coefficient. Changes in spectral values of the pure sea water absorption are almost entirely determined by the concentration and the composition of sea salt ions and dissolved 52 gases; they and is are mostly pronounced mostly in the UV-A and UV-B spectral regions 53 below 300 nm (Woźniak and Dera, 2007). Spectral properties (values and spectral shape) and 54 the mutual proportions of light absorption coefficients by CDOM, $(a_{CDOM}, (\lambda))$, $-b_{T}$ 55 phytoplankton pigments, $(a_{\rm ph}(\lambda))$, organic detritus and mineral particles $(a_{\rm NAP}(\lambda))$, determine 56 57 the spectral shape and magnitude of the total absorption spectrum as well as affectings both the inherent and the apparent optical properties of natural waters (Woźniak and Dera, 2007). 58

The Chromophoric Dissolved Organic Matter (CDOM) is the uncharacterized fraction of the dissolved organic matter pool consisting from of a heterogeneous mixture of water. soluble organic compounds that have the ability to absorb light (Nelson and Siegel, 2002). The effect of the CDOM absorption is mostly visible in the UV and blue spectral range of electromagnetic radiation, where the CDOM contribution to the total non-water absorption could reach can be as much as 90%, even in the clearest natural waters found in South Pacific

Subtropical Gyre south of Easter Island, (Morel et al., 2007; Bricaud et al., 2010; Tedetti et 65 al., 2010). The CDOM absorption band overlaps also overlaps with the primary 66 67 phytoplankton pigment absorption band in the blue part of the spectrum; this leads to contributing to significant errors of standard algorithms for retrievals of chlorophyll a, 68 69 especially in coastal ocean - and shelf waters and semi-enclosed seas (Darecki and Stramski, 2004; Siegel et al., 2005). Therefore, appropriate quantitative and qualitative descriptions of 70 the optical properties of CDOM is are crucial in for the ocean color remote sensing of aquatic 71 environments. 72

73 The CDOM absorption coefficient is a very reliable predictor of the dissolved organic carbon concentration in fresh and estuarine waters (Brezonik et al., 2015; Kutser et al., 2015; 74 Toming et al., 2016), and therefore this optical parameter could be easily applied in various 75 aspects of organic carbon biogeochemistry. The ocean The new ocean color remote sensing 76 77 offer new operational satellite missions based on medium ground resolution (of the order of 250 m) sensors, like the European Earth Observation Copernicus program Sentinel-3 OLCI 78 mission, and the space sensors of the European Earth Observation Copernicus program and 79 the US Joint Polar Satellite System program VIIRS sensors. These of the US Joint Polar 80 Satellite System program, offered the medium ground resolution (in of the order of 250 m) 81 radiometers, which would are particularly be suitable for remote sensing observations of 82 inland water bodies and estuaries (Palmer et al., 2015; Kwiatkowska, et al., 2016). The optical 83 84 properties of CDOM, abundant in fresh and estuarine waters at high concentrations, shift the spectral maximum of the water transparency to solar radiation and water leaving radiance 85 towards the longer wavelengths (Darecki et al., 2003; Morel and Gentili, 2009). In extreme 86 cases, in humic boreal lakes, the CDOM reduces the water-leaving radiance intensity in the 87 visible spectrum almost to null-zero (Ficek et al., 2011; Ficek et al., 2012; Ylöstalo et al., 88 2014). To minimize this effect, the remote sensing algorithm for retrievingals of the bio-89 90 optical and biogeochemical variables in optically complex waters has been were based on 91 spectral bands combinations at longer wavelengths where CDOM absorption is low (e.g. Ficek et al., 2011). Therefore, there is a need for development of models need to be developed 92 93 that that would enable to reconstruct the complete CDOM absorption spectrum to be reconstructed. The dDetailed spectral information of CDOM absorption is required, for 94 example to calculate the spectral indices related to molecular weight, degree of 95 photochemical transformation (Helms, et al., 2008) or aromaticity (Weishaar et al., 2003). 96

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CDOM plays-also plays various ecological roles in aquatic environments: even small concentrations strongly absorb UV radiation, protecting organisms from its destructive action. Higher levels of CDOM absorptions limits the amount of radiation available for photosynthesis, and consequently reducing the primary production of organic matter in that water (Górniak, 1996; Wetzel, 2001). CDOM plays an important part in the various biological processes taking place in water bodies: it can affect the species composition, number and size of plankton organisms (Arrigo and Brown, 1996; Campanelli et al., 2009), and in oligotrophic lakes can promote the growth of bacterioplankton (Moran and Hodson, 1994). Several authors have pointed out that CDOM is a potential source of reactive oxygen forms in aquatic ecosystems, which has a considerable influence on a variety of biological processes (Whitehead and de Mora, 2000; Kieber et al., 2003).

CDOM absorption decreases exponentially towards longer wavelengths and can be described by the exponential function (Jerlov, 1976, Bricaud et al., 1981,Kirk 1994):

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$$a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0)e^{-S(\lambda_0 - \lambda)}$$

1 where: $a_{\text{CDOM}}(\lambda)$ is the light absorption coefficient for a given wavelength λ , λ_0 is the 2 reference wavelength; and S is the slope of the spectrum within a given wavelength interval.

113 The CDOM accumulates in the surface Baltic Sea waters as a combined effect of a 114 very high large inflow of fresh water from rivers, and the limited exchange of waters with the 115 North Sea and the very high productivity of in this marine basin, that sea (Kowalczuk et al., 116 2006). The Ssystematic studies over the last two decades on the optical properties in the of 117 Baltic Sea waters and its adjoining acent fresh water systems, i.e. -coastal lagoons and 118 Pomeranian lakes, have provided yielded evidence that the CDOM is the principal absorbent 119 of solar radiation and the main factor governing their optical properties (Kowalczuk 1999; 120 Kowalczuk et al., 2005a; 2006; 2010; Ficek et al., 2012; Ficek 2013).

We have performed analyses using a combined data set of optical properties of marine 121 122 and lacustrine water samples, treating the data as a single, pooled set. Other optical properties of lacustrine waters displayed a resemblance to resembled marine waters in the Baltic Sea 123 124 waters, despite the observed differences in the trophic status of theese water bodies. According to In accordance with Choiński (2007), the lakes waters were divided into ultra-125 oligotrophic, oligotrophic, mesotrophic, eutrophic, hypereutrophic and dystrophic. The 126 trophicity $\frac{1}{2}$ was determines d by from the concentration of chlorophyll a, the water 127 transparency (determined measured by using a Secchi disk), and the concentration of biogenic 128

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factorsnutrients, e.g. nitrogen and phosphorus (Carlson, 1977; Kratzer and Brezonik, 1981).
The ranges of concentrations of chlorophyll and trophicity-defining nutrients defining
trophicity awere higher wider in lakes than in marine sea waters. In our modelling approach
we have assumed that lakes ecould ould be treated as a natural extension of coastal, lagoon
and river mouth waters.

The main objective of the present work was to derive three alternative parameterizations scenarios of the relationships between the CDOM absorption coefficient in the Baltic and Pomeranian lakes waters and physical or biogeochemical variables. The motivation for developing ment of these models was to estimate a the complete spectrum of the CDOM light absorption coefficients by using different input parameters: *i*) in the first scenario the known chlorophyll *a* concentrations in the first scenario, *ii*) in the second scenario known values of the CDOM absorption coefficient at 400 nm, $a_{CDOM}(400)$, in the second scenario, *iii*) and in the third scenario known values of $a_{CDOM}(400)$ and known nonlinear relationships between CDOM absorption coefficient and the spectral slope coefficient S in the third scenario. Developed These models can be used to improve the accuracy of ocean colour remotes sensing algorithms for retrievingal of environmental variables in the Baltic Sea, adjacent estuaries river mouths, and lagoons and fresh-water lakes.

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146 **2. Material and methods**

147 2.1 Sampling area

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Water samples for determining ation of optically significant water constituents 148 concentrations were collected from August 2006 to November 2009 in the southern Baltic and 149 150 in three lakes in the Pomeranian Lake District (Poland) during the long-term observation 151 program of inherent and apparent optical properties for calibrationg and validationg of ocean colour satellite imagery products, conducted run by the Institute of Oceanology, Polish 152 Academy of Sciences, Sopot, Poland, (IOPAN). The lLocations of the 116 measuring stations, 153 154 where empirical data were gathered (a total of 413 data sets) during 16 cruises of r/v Oceania 155 on the Baltic weare shown on Figure 1, and the cruises details is are given in the Table 1. R The research cruises were organized so as to capture the dynamics of natural seasonal 156 157 variability occurring in temperate waters: i) at the end of the winter, before the onset of the spring phytoplankton bloom, when wind-driven mixing, the vertical convective thermohaline 158 circulation, reduced biological activity and reduced riverine outflow all result in clearer 159 surface waters; *ii*) in spring, when the spring phytoplankton bloom coincides with the 160

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| 161 | maximum freshwater runoff from the Baltic Sea watersheddrainage basin; iii) and at the end |
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| 162 | of summer, when at the peak of secondary phytoplankton blooms peak and the period of |
| 163 | maximal thermal stratification of waters reaches its maximum extent. The geographical |
| 164 | coverage of the samples included the Gulf of Gdańsk, the Pomeranian Bay, the Szczecin |
| 165 | Lagoon, Polish coastal waters and the open sea (the Baltic Proper). The coastal sites in the |
| 166 | Gulf of Gdańsk and the Pomeranian Bay are under the direct influence of two major river |
| 167 | systems, the Vistula and the Odra, respectively, which drain the majority of Poland. |
| 168 | Additionally, samples were collected twice a month on-at the sampling station at-on the Sopot |
| 169 | pier (Gulf of Gdańsk), from which 66 sets of data were obtained. Field observations were also |
| 170 | carried out from April 2006 to November 2009 on-at monthly intervals a month-(except the |
| 171 | months when the lake surfaces of the lake wasere covered with ice) ion three Pomeranian |
| 172 | lakes (Łebsko, Chotkowskie and Obłęskie) from which 77 data sets were obtained. Selected |
| 173 | These lakes are enclosed water bodies with only small rivers flowing in and out of them. Lake |
| 174 | Łebsko is a specific case, however: it is a coastal lake, and connected directly to the sea by a |
| 175 | short channelanal, Part of the land around Lake Lebsko area-immediately adjacent to the |
| 176 | channel anal-can, on occasion, be inundated when large backflows of sea water enter the lake. |
| 177 | The lake's water level can then rise by 50-60 cm (Chlost and Cieśliński, 2005). Such a |
| 178 | situation obviously affects the composition and properties of the lacustrine water. Similar |
| 179 | effects, resulting from the great variability of water properties, can be expected at the points |
| 180 | where rivers flow into lakes. The lacustrine water in these areas is thus modified by the river |
| 181 | water. |

182 2.2 Samples processing

183 Discrete samples of water were taken from the surface layer of the southern Baltic and the three Pomeranian lakes with use of thea Niskin bottle. The samples for spectroscopic 184 185 measurements of CDOM light absorption were filtered twice underwent a two-step filtration 186 process:- The first filtrationonce was through acid-washed Whatman glass fibere filters (GF/F, nominal pore size 0.7 µm)-, then The water was then passed through acid-washed Sartorius 187 0.2 µm pore cellulose membrane filters to remove fine-sized particles. Spectrophotometric 188 scans of CDOM absorption spectra were performed_done_with use the a_Unicam UV4-100 189 double beam spectrophotometer in the 240-700 nm spectral range; these instruments were 190 installed both-in the land base-laboratory and on board of the research ship-in the 240 700 nm 191 spectral range. The cuvette path_length was 5 cm and the-MilliQ water was used as the 192

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193 reference for all measurements. The absorption coefficient $a_{\text{CDOM}}(\lambda)$ was calculated using the 194 following equation:

| 195 | $a_{\rm CDOM}(\lambda) = 2.303 \cdot A(\lambda)/L, \tag{2}$ | | Formatted: English (U.S.) |
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| | | \square | Formatted: English (U.S.) |
| 196 | where: $A(\lambda)_{\overline{i}}$ is the optical density, and L is the optical path length in meters; and the factor | | Formatted: English (U.S.) |
| 107 | 2 303 is the natural logarithm of 10 | Ń | Formatted: English (U.S.) |
| 157 | | | Formatted: English (U.S.) |
| 198 | A nonlinear least squares fitting method using a the Trust-Region algorithm | | Formatted: English (U.S.) |
| 100 | implemented in Matlah R2000 was applied (Stedmon et al. 2000 Kowalczuk et al. 2006 | | Formatted: English (U.S.) |
| 200 | 2015) to coloridate the CDOM characterian anestrum clans coefficient S in the enestrel and | | |
| 200 | 2015) to calculate <u>the</u> CDOM absorption spectrum slope coefficient , 5, in the spectral range | | |
| 201 | 300-600 nm spectral range using the following equation: | | Formatted: English (U.S.) |
| | $-S(\lambda - \lambda)$ | | Formatted: English (U.S.) |
| 202 | $a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0)e^{-S(\lambda_0 - \lambda)} + K \tag{3}$ | | |
| 202 | where: λ_{i} is 350 nm and K is a background constant that allows for any baseling shift caused | | |
| 205 | where τ_0 is 550 min, and K is a background constant that anows for any baseline shift caused | | Formatted: English (U.S.) |
| 204 | by residual scattering by <u>due to</u> fine size particle fractions, micro-air bubbles or colloidal | | Formatted: English (U.S.) |
| 205 | material present in the sample, refractive index differences between sample and the reference, | / | Formatted: Not Highlight |
| 206 | or attenuation not due to CDOM. The parameters $a_{\text{CDOM}}(350)$, $S_{\overline{s}}$ and K were estimated | | Formatted: English (U.S.) |
| 207 | simultaneously via by non-linear regression using Equation 3 (Kowalczuk et al. 2006) | | Formatted: English (U.S.) |
| 207 | sinuitaneousiy via py non-intear regression using Equation 5 (Rowalczuk et al., 2000). | | Formatted: English (U.S.) |
| 208 | The chlorophyll <i>a</i> concentration was determined with useby -pigment extraction method. The | | Formatted: English (U.S.) |
| 209 | pPigments contained within the suspended particles were collected by filtration of passing the | | Formatted: English (U.S.) |
| 210 | water complex onto through 47 mm Whatman glass fiber filters (GE/E) under a low vacuum | | Formatted: English (U.S.) |
| 210 | water samples onto unodin 47-min whatman grass-riber rifers (Or/F) under <u>a low vacuum</u> | | Formatted: English (U.S.) |
| 211 | and extracted 24 hours in 96% ethanol at room temperature for 24 hours (Wintermans & and | | Formatted: Not Highlight |
| 212 | De Mots, 1965, Marker et al., 1980). The cehlorophyll a, Chla, concentration, Chla, was | | Formatted: English (U.S.) |
| 213 | determined spectrophotometrically with a Unicam UV4-100 spectrophotometer. (Unicam | | Formatted: English (U.S.) |
| 215 | determined specificionical and the specific photometer (official, | | Formatted: English (U.S.) |
| 214 | Ltd). In this method the optical density (absorbance) of the pigment extract in ethanol at 665 | | Formatted: Font: Not Italic |
| 215 | nm was corrected for <u>the</u> background signal in the near infrared (750 nm): $\Delta OD =$ | | Formatted: English (U.S.) |
| 216 | OD(665 nm) - OD(750 nm); the absorbance was converted to the chlorophyll a concentration. | | Formatted: English (U.S.) |
| 217 | using an equation involving the volumes of filtered vector (V) [dm ³] and athenol extract | | Formatted: English (U.S.) |
| 217 | using an equation involving the volumes of intered water (v_w) [uni]; and entation extract | | Formatted: English (U.S.) |
| 218 | (V_{EtOH}) [cm], a 2cm <u>cuvette</u> path length of <u>cuvette</u> (l), and the <u>chlorophyll</u> specific | \vee | Formatted: English (U.S.) |
| 219 | absorption coefficient of chlorophyll \underline{a} in 96% ethanol $[dm^3 (g cm)^{-1}]$ (for the 665 nm) | | Formatted: Not Highlight |
| 220 | [Strickland and Parsons 1972; Stramska et al., 2003]: | | Formatted: English (U.S.) |
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 $Chla = (10^3 \cdot \Delta OD \cdot V_{EtOH}) / (83 \cdot V_w \cdot l)^{-1}.$

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| 222 | During the field-surveys-work, temperature and salinity profiles were measured with |
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| 223 | and SeaBird SB36 CTD probe to provide the background physical conditions during to |
| 224 | sampling. |

The collected data obtained were analyzed by the useing of a statistical package and 225 226 data visualization software (SigmaPlot 8.1). As the dDynamic range of variability of analyzed 227 the optical parameters values exceeded 3three orders of magnitude, therefore logarithmic transformation was applied which allowed for a better presentation of their dynamics changes 228 and to analyze statistically analyze collected the data-set accordingly. FThe following 229 230 arithmetic and logarithmic statistical metrics were used to assess the uncertainty of developed 231 <u>the</u> empirical relationships and models $(X_{i,M})$ measured values; $X_{i,C}$ estimated values (<u>the</u> 232 subscript *M* stands for 'measured'; subscript *C* stands for 'calculated')):

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| α atomotord domation (atotictical arror) of c (UNINE root moon callero | standard deviation | (statistical arror) | of c (DMS) | E root m | |
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• mean logarithmic error:
$$\langle \varepsilon \rangle_g = 10^{\left[\langle \log(x_{i,C}/x_{i,M}) \rangle \right]} - 1$$
 (6).
• standard error factor: $x = 10^{\sigma \log}$ (7).

statistical logarithmic errors: $\sigma_+ = x - 1$ $\sigma_- = \frac{1}{x} - 1$ (8)

 $\langle \log(X_{i,C}/X_{i,M}) \rangle$ - mean of $\log(X_{i,C}/X_{i,M})$;

 σ_{\log} - standard deviation of the set $\log(X_{i,C}/X_{i,M})$.

The linear metrics are represented by the relative mean error, and the standard 241 deviation wasere used to measure the dispersion of results and assess the model's uncertainty. 242 The relative mean error (Eq. 5a) is the average of all relative deviations between measured 243 and calculated values and it-quantifiesd the systematic error. SThe standard deviation (Eq. 5b) 244 245 is the dispersion around the average error due to random errors and it-quantifiesd the statistical error. Logarithmic metrics weare used to better describe the uncertainty in the data 246

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stet varying in the range of over several orders of magnitude. The standard error factor
describesd how many times the error is deviatesd from the average value.

249 **3. Results**

250 251 3.1 Variability of *analysed_the* parameters and empirical relationship between CDOM absorption and spectral slope coefficient.

Table 2 lists the Vyariability range and average values of selected optical parameters 252 253 measured in the study area and used for formulating the empirical model; the light absorption coefficients by CDOM at two wavelengths: (375 and 400 nm); $-a_{CDOM}(375)$ and $a_{CDOM}(400)$; 254 spectral slope S, and chlorophyll a concentrations, Chla., measured in the study area and used 255 256 for formulation of empirical model have been presented in the Table 2. The minima in of the variability ranges of $a_{\text{CDOM}}(375)$, $a_{\text{CDOM}}(400)$ and Chla, were noted reached a minimum in sea 257 watersin marine waters. The minimalum values of CDOM absorption coefficients in 258 259 lacustrine waters were almost an one order of magnitude higher than in marine sea waters, indicating a significant accumulation of CDOM in fresh waters. The maximalum values of 260 $a_{\text{CDOM}}(375)$, $a_{\text{CDOM}}(400)$ and *Chla* were observed recorded in fresh waters; these maximal 261 262 values were approximately two time twice as high as higher than those values of the respective parameters in marine sea waters. Consequently, the average values of the CDOM 263 absorption coefficients: $(a_{CDOM}(375), a_{CDOM}(400))$ and chlorophyll a concentrations, were 264 higher in fresh waters compared to marine than in sea waters. -The reverse trend is observed 265 266 was reversed in the case of the CDOM absorption spectrum slope coefficient, S_{τ} and its variability range: both of the minimal maximum and maximal minimum spectral slopes, 267 values were lower in the lakes than those observed in the marine sea waters. The average 268 269 value of the spectral slope coefficient was higher in marine sea waters than in lake waters. These two data sets, measured in the the Baltic Sea waters and Pomeranian lakes, were 270 statistically significantly different, as indicated by the results of simple analysis of variance: 271 $(p-p = -3.4, -10^{-38})$. However, their variability ranges were such, that the data from the two 272 273 different aquatic environments were overlapped, ing creating a coherent data set, that could be analyszed togetherjointly. Our principle assumption for when the derivation of deriving the 274 CDOM absorption model was that, the optical properties of lacustrine waters could be treated 275 276 as if they were an extension of estuarine and marine sea waters.

The spectral slope coefficient was inversely and non-linearly related with to the
CDOM absorption coefficient. The highly absorbing samples were spectrally flatter

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| 279 | (characteriszed by <u>a lower</u> S value). Different functional types were used to model this | | Formatted | |
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| 280 | relationships: hHyperbolic (Stedmon and Markager, 2001, Kowalczuk et al., 2006), and or | | | |
| 281 | logarithmic (Kowalczuk et al., 2005b) functional types were used to model this relationship. | | | |
| 282 | For consistency with Kowalczuk (2001), we have used the log-linear fit to describe the | | | |
| 283 | relationship between $a_{\text{CDOM}}(400)$ and S. The distribution of the spectral slope in the as a | | | |
| 284 | function of the CDOM absorption coefficient in the Baltic Sea (black dots) and Pomeranian | // | | |
| 285 | lakes (green dots) has been presented is shown o in the F igure 2a. The black line <u>re</u> presents <u>the</u> | / | | |
| 286 | log-linear dependence (Equation 9) cobtained by Kowalczuk (2001), overlaiding on our data set: | | Formatted: English (U.S.) | |
| | | | (- | |
| 287 | $S = log[1.038 a_{CDOM}(400)^{-0.022}].$ (9) | | Formatted | |
| 288 | The old realation his worksed satisfactorily for part of the Baltic Sea data set | | Formatted | |
| 289 | $(R^2 = 0.76)$ - but it does not cover a large group of CDOM absorption coefficients values larger | | | |
| 200 | then $> 5 \text{ m}^{-1}$. The values of $q = -(400) > 5 \text{ m}^{-1}$ were measured in the lakes and in | | | |
| 290 | $\frac{1}{1}$ $\frac{1}{2}$ $\frac{1}$ | | | |
| 291 | estuarine waters, as well as and in the Szczecin Lagoon and where the waters of the Vistula | | | |
| 292 | and Odra mouth infiguoung into the southern Baltic. We have derived a new formulea to | | | |
| 293 | determine the $a_{\text{CDOM}}(400)/S$ relationship that covered the whole range of the $a_{\text{CDOM}}(400)$ | // | | |
| 294 | observed recorded in both the Baltic Sea and in Pomeranian lakes waters. The new formulea | | | |
| 295 | was is marked shown oin Figure 2-a as a red curve and is described by Equation 10-: | | Formatted: English (U.S.) | |
| 296 | $S = 0.0213 - 0.003 \ln[a_{CDOM}(400)]. \tag{10}$ | | Formatted | |
| | | | Formatted: English (U.S.) | |
| 297 | The new $a_{\text{CDOM}}(400)$ /S relationship has been found is much better constrained and explainsed | 1 | Formatted | |
| 298 | much more variance ($R^2 = 0.79$) with less uncertainty (RMSE = 0.1%) compared to the one | // | | |
| 299 | presented given by Kowalczuk (2001). | | Formatted: English (U.S.) | |
| 200 | Detailed analysis of the spectral slope distribution of spectral slope in the as a function | | Cormottod | |
| 201 | $c_{\text{f}} = (400)$ indicated that the date set could be divided in with respect to colinity into two | | ronnatteu | <u> </u> |
| 202 | of $u_{\text{CDOM}}(400)$ indicated that the data set could be divided $\frac{1}{1000}$ with respect to samily into two | | | |
| 302 | subsets. samples characterized by saminty $\frac{1}{10000000000000000000000000000000000$ | | | |
| 303 | those with samily $\frac{1}{2}$, which include waters from fiver mouths, lakes and the | | | |
| 304 | Szczecin Lagoon. The relationship between $a_{\text{CDOM}}(400)$ and S derived for the respective data | | | |
| 305 | substets weare presented ion Figure 2-b and the functional formulaes weare given by | | (| |
| 306 | Equations 11 (salinity > 5) and Equation 12 (salinity < 5): | | Formatted: English (U.S.) | |
| 307 | $S = 0.0206 - 0.004 \ln[a_{\text{CDOM}}(400)]$ (11) | | Formatted | |
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| 308 | $S = 0.0196 - 0.0009 \ln[a_{\text{CDOM}}(400)].$ (12) | | Formatted: English (U.S.) | |
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| 309 | The suggested Proposed approximations of the $\mu_{CDOM}(400)/S$ relationships in the two salinity | 1 | Formatted | |
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| 310 | ranges we have re characterised by the a higher explained variance ($R^2 = 0.78$ for Equation 11, | | | |
| 311 | and lower $R^2 = 0.22$, for Equation 12), respectively. In both cases, the estimation uncertainties | /// | | |
| 312 | <u>-y</u> : RSME = 0.08% for Equation 11, and RSME = 0.09% , for Equation 12, respectively, _ | // | | |
| 313 | were lower compared to than the approximation presented by given by Equation 10. | | Formatted: English (U.S.) | |
| 314 | 3.2. A model for approximating on of the CDOM light absorption spectrum from the empirical | | Formatted | |
| 315 | dependence on with the chlorophyll a concentration. | | Formatted: English (U.S.) | |
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| 316 | The principle bio-optical assumption on interdependencies among optically significant | 1 | Formatted | |
| 317 | water constituents in global-the world ocean was formulated by Morel and Prieur (1977), who | | | |
| 318 | introduced the concept of the Case 1 waters, where the variability iof those constituents wais | | | |
| 319 | to far-a considerable extent correlated with the variability of in the phytoplankton biomass | | | |
| 320 | expressed as chlorophyll <i>a</i> concentration. The Case 1 waters we were mostly open oceanic | | | |
| 321 | waters and upwelling regions at along western continental margins. The marine basins sea | | | |
| 322 | areas where these is assumption were was not fulfilled, we were considered treated as Case 2 | | | |
| 323 | waters; mostly semi-enclosed and shelf seas and coastal oceans, where there wewere sources | | | |
| 324 | of riverine waters. It was assumed that changes in the magnitude of optically significant water | | | |
| 325 | constituents in the Case 2 waters were independent. This concept was critically reassessed by | | | |
| 326 | Siegel et al. (2005), who reanalyzed the global ocean colour imagery data set. They, and | | | |
| 327 | demonstrated proved-that, although in open ocean-the bio-optical assumption iwas still valid | | | |
| 328 | in the open ocean, there were significant dependences between chlorophyll p and other | | | |
| 329 | optically significant water constituents at regional scales in along oceanic continental | | | |
| 330 | margins. Even though the CDOM was not thought to be correlated with chlorophyll a | | | |
| 331 | concentrations in Case 2 waters, there were examples showing that such a relationships were | | | |
| 332 | was possible (Ferrari and Tassan, 1992; Vodacek et al., 1997). In the-Baltic waters such | | | |
| 333 | analyses were carried out by Kowalczuk and Kaczmarek (1996) and Kowalczuk (1999). | | | |
| 334 | These authors demonstrated that the correlation between the concentration of chlorophyll <i>a</i> | | | |
| 335 | and the CDOM absorption coefficient was observed were correlated. The positive correlation | | | |
| 336 | between light absorption by CDOM and chlorophyll <i>a</i> concentration has been confirmed with | | | |
| 337 | new data available, from both in marine sea and fresh waters. The elear clearly increasing | | | |
| 338 | trend of increase of the CDOM absorption level with increasing phytoplankton biomass has | | | |
| 339 | been presented on is shown in Figure 3. The dependence between $a_{\text{CDOM}}(400)$ coefficient and | | | |
| 340 | the concentration Chla obtained by Kowalczuk (2001) has been overlaind on the new, | | Field Code Changed | |
| 341 | currently reported updated empirical data set, in Figure 3. It is evident that the | > | Formatted | |

| 342 | $a_{\text{CDOM}}(400)/Chla$ relationship reported by Kowalczuk is applicable to only some of the Baltic | | Formatted | |
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| 343 | Sea data, in the chlorophyll <i>a</i> -concentration range $0.8 < Chla < 10$ mg m ⁻³ . The old, previous | / | | |
| 344 | power function relationship did not reproduced correctly the $a_{\text{CDOM}}(400)$ values for high | | | |
| 345 | chlorophyll <i>a</i> concentrations, and CDOM absorption data measured in estuaries in river | /// | | |
| 346 | mouths and lakes were lying lay above the model curve. We have proposed a new | // | | |
| 347 | statistically significant relationship between the $a_{CDOM}(400)$ and Chla which was that is | | | |
| 348 | described by a second-degree polynomial ($R^2 = 0.83$, RMSE = 28%, n = 541, p<0.0001). | | Formatted: English (U.S.) | |
| 3/10 | The same function has been applied to reconstruct the complete CDOM absorption | | Formatted | |
| 350 | spectrum in the spectral range from 245 to 700 nm with 5 nm resolution- (Equation 13): | / | Formatted: English (U.S.) | |
| 330 | spectrum in the spectral range from 245 to 700 min with 5 min resolution; (requation 15), | | | |
| 351 | $a_{\text{CDOM}}(\lambda) = 10^{(A(\lambda)(\log Chla)^2 + B(\lambda)\log Chla + D(\lambda))},$ (13) | | Formatted | |
| | | | Formatted: English (U.S.) | |
| 352 | where $A(\lambda)$ [m ⁻² mg ⁻²], $B(\lambda)$ [m ⁻² mg ⁻¹] and $\overline{D}(\lambda)$ [m ⁻¹] are the regression coefficients. | \langle | Formatted: English (U.S.) | |
| 353 | The spectral distribution of the regression coefficients and determination coefficient | | Formatted | |
| 354 | have been are presented oin Figure 4 and their values weare included in Table A in Appendix | \square | | |
| 355 | A. Both regression coefficients $A(\lambda)$ and $B(\lambda)$ showed exhibited a relatively small spectral | | | |
| 356 | variation in the UV and part of the visible spectral range. The biggest changes in regression | | | |
| 357 | coefficients spectra have been were noted above 580 nm, where a significant increase of the | | | |
| 358 | in $A(\lambda)$ was to a large extent has been relatively compensated with by a decrease of the in β | | | |
| 359 | $B(\lambda)$. Solution Spectral distribution of regression coefficient A, indicates a potential β | | | |
| 360 | influence of the phytoplankton pigments absorption on the CDOM absorption spectrum, as its | | | |
| 361 | maximum, situated around 675 nm, overlaps with the longwave maximum of the chlorophyll | | | |
| 362 | a absorption spectrum. This effect is visible apparent only at longer wavelengths, because the | | | |
| 363 | principale chlorophyll a maximum at 440 nm, is masked by CDOM absorption, especially at | | | |
| 364 | in very turbid estuarine and fresh water, where the highest values of CDOM absorption were | | | |
| 365 | recorded. The free term $D(\lambda)$ spectrum, decreasesing monotonically with increased | | | |
| 366 | wavelength, resembles theat of the logtransformed CDOM absorption coefficient spectrum | | | |
| 367 | corresponding to the average CDOM absorption spectrum at a chlorophyll <i>a</i> concentration of | | | |
| 368 | 1 mg m ⁻³ -, as shown oin Figure 4-c. The spectral distribution of the determination coefficient | | | |
| 369 | values R ² (<u>, presented on Figure 4-d)</u> , shows demonstrated that, the model based on the | | | |
| 370 | dependency between the CDOM absorption coefficient and the chlorophyll p concentration, | | | |
| 371 | explained more than 80% of the variability in $a_{\text{CDOM}}(\lambda)$ in the UV and VIS, and that this | | | |
| 372 | variability was controlled governed by phytoplankton biomass production. The model's | | | |
| 373 | performance deteriorated at wavelengths longer than 550 nm. | | Formatted: English (U.S.) | |
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| 374 | The results of the model uncertainty analysis result for selected wavelengths have | Formatted |
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| 375 | been-are summarized in Table 3 and presented-illustrated oin Figure 5. Comparison between | |
| 376 | estimated vs. and measured $a_{\text{CDOM}}(\lambda)$ values at selected wavelengths (260, 350, 440, 500, 550, | |
| 377 | 600 nm) from the range 240 - 700 nm range weare shown on the first six upper panels of | |
| 378 | Figure 5 (a-f). Histograms of the ratios of between estimated and to measured values at the | |
| 379 | same wavelengths, weare presented oin the lower six Figure 5 panels of Figure 5 (g-1). The | |
| 380 | deterioration of model performance with increasing wavelength has been is evident. The | |
| 381 | overall uncertainty expressed by arithmetic statistics and logarithmic statistics wajes | |
| 382 | satisfactory up to 500 nm, and but then both systematic and statistical estimation errors | |
| 383 | increasedd rapidly at longer wavelengths. The arithmetic systematic error has increased from | |
| 384 | 1.47% at 260 nm to 19.54% at 600 nm, and the arithmetic statistical error has increased from | |
| 385 | 17.03% at 260 nm , to 79.13% at 600-respectively. Logarithmic uncertainty metrics indicated | |
| 386 | that, the standard error factor estimated for the entire spectral range from 240 to 700 nm of | |
| 387 | light absorption coefficients varieds from 1.19 to 2.66. This meanst that the statistical | |
| 388 | logarithmic error variesd from -62% to +165%. The logarithmic systematic errors throughout | |
| 389 | in-the all-240 - 700 nm range doid not exceed 3%. | Formatted: English (U.S.) |
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| 390 | 3.3. An empirical model for approximating on of the CDOM light absorption spectrum based | () |
| 391 | on <u>the empirical dependence on with</u> the CDOM absorption coefficient value at 400 nm, | |
| 392 | $a_{\text{CDOM}}(400)$ | Formatted: English (U.S.) |
| 393 | The exponential model for CDOM absorption requires information on two input | Formatted |
| 394 | parameters: the magnitude of CDOM absorption at the reference wavelength and the spectral | |
| 395 | slope-value. However, the monotonicity property of the CDOM absorption spectrum | //// |
| 396 | determines ensures a the high level of interdependence between y of absorption coefficients. | |
| 397 | values across considered the spectral range in question, so that and allows omit the detailed | |
| 398 | information on the spectral slope can be omitted. The second model that we have developed is | |
| 399 | based on the dependence of light absorption by CDOM at any given wavelength and the | |
| 400 | CDOM absorption coefficient at wavelength 400 nm. Many authors treat this wavelength as a | |
| 401 | reference for CDOM absorption using the exponential Equation 1 (e.g. Kowalczuk et al., | |
| 402 | 2005a; Woźniak and Dera, 2007). It was also recommended by Sathyendranath et al. (1989) | |
| 403 | to distinguishing between absorption by dissolved organic matter absorption from that caused | |
| 404 | by phytoplankton. In optically complex waters (the Baltic Sea and the lakes), a_{CDOM} (400), | Field Code Changed |
| 405 | makes up the <u>a large</u> proportion of the total absorption of light in water, (Kowalczuk, 2001; | Formatted |
| 406 | Ficek, 2013). | Formatted: English (U.S.) |
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| 407 | The interdependencye of spectral CDOM absorption values has been was assessed by | 1 | Formatted | |
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| 408 | Kowalczuk (2001), who analyszed the linear cross-correlation matrix between $a_{\text{CDOM}}(\lambda)$ | | | |
| 409 | values measured at different wavelengths. The linear interrelationship between $a_{\text{CDOM}}(\lambda)$ | | | |
| 410 | deteriorated with increasing spectral distance from the reference wavelength both-towards | //// | | |
| 411 | both shorter and longer wavelengths. To better reflect the non-linear property of the CDOM | | | |
| 412 | absorption spectrum we have used the a second order polynomial model based on log. | | | |
| 413 | transformed $a_{\text{CDOM}}(\lambda)$ values as the input variable. The cellulations were performed in the | | | |
| 414 | spectral range 240 – 700 nm spectral range, with a 5 nm resolution. The statistical analyses | | | |
| 415 | yielded the formula: | | Formatted: English (U.S.) | |
| | | | Competing d | |
| 416 | $a_{\text{CDOM}}(\lambda) = 10^{(M(\lambda)(\log(a_{\text{CDOM}}(400))^{-} + N(\lambda)\log(a_{\text{CDOM}}(400)) + O(\lambda))}, \qquad (14)$ | | Formatted: English (U.S.) | <u> </u> |
| 417 | where $M(\lambda)$ [m] $N(\lambda)$ [dimensionless] and $Q(\lambda)$ [m ⁻¹] are the peremeterization coefficients | | Enumentad | |
| 417 | where $M(\lambda)$ [iii], $N(\lambda)$ [dimensionless] and $O(\lambda)$ [iii] are the parameterization coefficients shown graphically illustrated in Figure 6. Their values for the 240 – 700 nm range are listed in | 1 | ronnatteu | J |
| 410 | Table R (in Appendix A) | | Enumentade English (U.S.) | |
| 419 | | | |) |
| 420 | The spectral shapes of the regression coefficients $M(\lambda)$, $N(\lambda)$ and the free term $O(\lambda)$. | | Formatted | |
| 421 | which that were derived for the empirical model that used using the $a_{\text{CDOM}}(400)$ value as an | | | |
| 422 | independent variable, were quite similar to the spectral shapes of the regression coefficient | | | |
| 423 | and the free term of the model based on chlorophyll <i>a</i> concentration. The regression $M(\lambda)_{\tau}$ | | | |
| 424 | and $N(\lambda)$ were also characterized by maxima located in the red part of the light-spectrum. | // // | | |
| 425 | Similarly As in to the first presented model, the spectral shape of the free term $O(\lambda)$ | / /// | | |
| 426 | resembled the log-transformed CDOM absorption spectrum. The spectral distribution of the | /// | | |
| 427 | determination coefficient R ² indicated that the approximation of $a_{CDOM}(\lambda)$ values based on the | | | |
| 428 | magnitude of the CDOM absorption at the reference wavelength was much more accurate | | | |
| 429 | than approximation-that based on chlorophyll a concentration. The R^2 values were over ≥ 0.9 | | | |
| 430 | in the ultraviolet part of the spectrum approaching 1, near the reference value, and but | | | |
| 431 | dropped felt down to below < 0.8 at 560 nm. | | Formatted: English (U.S.) | |
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| 432 | Ine result of the uncertainty analysis of the second model uncertainty analysis result | 1 | Formatted | <u> (</u>) |
| 433 | for at the same wavelengths as previously used, have been are summarized in at Table 4 and | | | |
| 434 | presented to Figure /. Comparison between the estimated vs. and measured $a_{\text{CDOM}}(\lambda)$ values | | | |
| 435 | at six selected wavelengths were shown are compared on the tirst six upper six panels of | | | |
| 436 | Figure / (a-t)-, and h-Histograms of the ratio between estimated and measured values at the | / | | |
| 437 | same wavelength were presented are shown on the lower six panels of Figure 7 panels (g-l). | | | |
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The deterioration of model performance with increasing wavelength hwas been much smaller 438 than in the case of the CDOM absorption spectrum approximation based on the chlorophyll a 439 440 concentration. The overall uncertainty expressed by arithmetic statistics and logarithmic statistics was much better up to 550 nm. Similarly, to As in the first model, both systematic 441 442 and statistical estimation errors increased at longer wavelengths. The arithmetic systematic error has-increased from 0.38% at 260 nm to 16.64% at 600 nm, and the arithmetic statistical 443 error has-increased from 9.11% at 260 nm, to 67.45% at 600 nm-respectively. Logarithmic 444 uncertainty metrics indicated that, the standard error factor estimated for the entire spectral 445 range from 240 to 700 nm of light absorption coefficients varieds from 1.09 to 1.76. This 446 meanst that the statistical logarithmic error variesd from -43% to +75%. The systematic errors 447 448 in the 240 - 700 nm interval did not exceed 2%

3.4 Two-parameterical model for estimating of CDOM absorption in the Baltic Sea and Pomeranian Lakes

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Two alternative one-parameter models of CDOM absorption were presented in the previous sections, which that enabled estimation of $\rho_{\text{CDOM}}(\lambda)$ values to be estimated with relatively low small errors. For comparison, we have analyzed the two-parameter model, developed by Kowalczuk et al. (2006) for the Baltic Sea waters.; This statistical model for estimating on of the CDOM absorption coefficient at 375 nm; $\rho_{\text{CDOM}}(375)$ at in surface waters was based on the seasons and the chlorophyll *a* concentration, which that acted as a proxy for the autochthonous production of CDOM. We have used the non-linear relationship between the CDOM absorption coefficient $\rho_{\text{CDOM}}(375)$ and the spectral slope to derive S, and used it later for then to reconstruct the CDOM absorption spectrum reconstruction using the classical exponential model (Equation 1).

The dependence between slope-S and $a_{\text{CDOM}}(375)$, coefficient obtained by Kowalczuk 461 et al. (2006) hwas been overlaind on the currently reported empirical data set reported here, 462 463 Figure 8), The $S/a_{CDOM}(375)$ relationship reported by Kowalczuk et al., (2006) is applicable to most of the Baltic Sea, estuaries river mouth and lakes data in-within the $a_{\text{CDOM}}(375)$ range 464 from 1.5 to-14.16 m⁻¹. -Thatis hyperbolic relationship did not reproduced correctly reproduce 465 the S values for $a_{\text{CDOM}}(375) < 1.5 \text{ m}^{-1}$. however, SThe spectral slopes measured in open and 466 coastal Baltic waters were lying lay below the model curve. We have proposed a similar 467 hyperbolic, statistically significant, relationship between the S and $a_{\text{CDOM}}(375)$ which could 468 better fit to-the present current data set. The determination coefficient of the updated 469

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hyperbolic function was very high: $R^2 = 0.86$, RMSE = 0.08%, n = 541, p<0.0001. The new 470 471 empirical relationship between the spectral slope S_{7} and $\mu_{CDOM}(375)$ is given by formula (15):

$$S = 0.01722 + \frac{0.0057}{0.0407 + a_{\text{CDOM}}(375)}$$
(15)

The new formulae was applied Equation 1 to calculate the CDOM absorption 473 spectrum in the spectral range between 240 - and 700 nm. The results of the uncertainty 474 analysis result of the exponential model, which that used the spectral slope variable estimated 475 476 from the approximation given by Equation 15, have been are summarized in Table 5. For comparison, we have also done-carried out an uncertainty analysis of the exponential model 477 with the spectral slope variable estimated from the S and $a_{\text{CDOM}}(375)$ relationships presented 478 479 given by Kowalczuk et al. (2006). Thise uncertainty analysis has revealed that the two-480 parameter estimateion of the CDOM absorption spectrum was less accurate than thet two first one-parameters models. The spectral values of CDOM absorption estimated forom the 481 482 exponential relationship and spectral slope parameterization with use-using the empirical formulas of Kowalczuk et al. (2006) and the present one current empirical formulas-were 483 systematically overestimated in the UV and underestimated in the visible spectral range. The 484 systematic and statistical errors were-increasinged towards the red part of the spectrum. The 485 highest uncertaintiesy, that exceededing 30% in the systematic error and 20% in the statistical 486 error, were noted at wavelengths longer than < 500 nm. The uUse of the present current 487 empirical spectral slope parameterization enabled estimation of $a_{CDOM}(\lambda)$ values to be 488 estimated with relatively lower-smaller errors, compared to the results given obtained by the 489 same approach with use of using the Kowalczuk et al. (2006) slope parameterization of 490 491 Kowalczuk et al. (2006),

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492 4. Discussion

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The Presented dataset presented here is a was subset of the almost 25 year longs timer series of bio-optical data collected in-by IOPAN in the Baltic Sea. This subset matched the observations conducted measurements obtained in the 2006 2009 in Pomeranian lakes in 2006 - 2009 by Ficek et al., (2012) and Ficek (2013). Analysed-These data were characterized by exhibit a large wide range of dynamic variability range, that which in some cases exceedsed three orders of magnitude. The sSea waters and lake water datas were pooled and 498 499 analyzed jointlyjoint data set, despite some certain differences in the compositions of the optically active components of in these waters. We have treated the lakes as a natural 500

501 extension of marine waters with optical properties resembling the properties of estuaries.

502 Chlorophyll a concentrations and μ_{CDOM} (λ) values of varied by 3 over three orders of magnitude: the *Chla* variability range was found from 0.72 to 119 mg m⁻³-, and a_{CDOM} -(375) 503 varied from 0.41 to 14.16 m⁻¹ and, μ_{CDOM} (400) varied from 0.15 to 8.85 m⁻¹, respectively. 504 <u>The s</u>pectral slope $S_{300-600}$ in Baltic Sea and lakes was found in the ranged from 0.007 — to 505 0.03 nm⁻¹. <u>RThe variability ranges of variability of analyzed these parameters corresponded to</u> 506 the data-figures given presented in earlier works on the optical properties in the of Baltic Sea 507 waters (Babin et al. 2003, Kowalczuk 1999, Kowalczuk et al. 2005a, 2006, 2010, 2015) or 508 and Pomeranian lakes (Ficek et al. 2012; Ficek 2013). Ficek (2013) reported that in 509 Pomeranian lakes Chla concentrations can may be even as high as 336 mg m⁻³ in Pomeranian 510 511 lakes.

512 <u>4.1 Assessment of the accuracy of one parameter models for for approximating the CDOM</u> 513 <u>light absorption spectrum</u>

The fFirst two presented models, each based on a single independent variable, were 514 characterized by a similar arithmetic systematic error. The arithmetic systematic errors 515 calculated for the model which used <u>Chla</u> the chlorophyll a concentration as the independent 516 variable (Eq. 13) were in-of the order of 1.5 - 7% in the UV and the visible spectral range to 517 500 nm. The arithmetic systematic error calculated for the model which used the using 518 $a_{\text{CDOM}}(400)$ as the independent variable (Eq. 14) were in-of the order of 0.2 -2.2 % in the same 519 spectral ranges. Based on the arithmetic metrics presented listed in Tables 3 and in Table 4 for 520 521 model (14), we could concluded that the $a_{CDOM}(400)$ independent variable model was characterized by had a lower smaller uncertainty and higher spectral values of the 522 523 determination coefficient. Likewise, the standard error factor in the *Chla*-based model wais higher than in the one based on the $a_{\text{CDOM}}(400)$ dependence. 524

Comparison of the data presented in Tables 3, 4 and 5 showed, ed that the accuracy of 525 526 estimation accuracy have deteriorated at wavelengths longer than 550 nm. One possible explanation is tThe precision of the CDOM measurements might offer a possible explanation. 527 The use of 5 cm cuvettes allowed enabled the reliable detection of CDOM absorption 528 detection at $\mu_{\rm CDOM}(\lambda)$ larger than $\leq 0.046 \text{ m}^{-1}$. The spectrophotometer's detection limit has 529 been-was usually reached usually at wavelengths longer than <- 550 nm in samples collected 530 in of open Baltic Sea waters. Therefore, the modeled values were usually compared to 531 532 measured values, that were heavily impacted by measurements errors accuracy. One of the 533 possible way of increasing the spectrophotometric accuracy of CDOM absorption

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534 measurements would rely on involve increasing the cuvettse path length (the maximum cuvettes path length used in most desktop spectrophotometers does would not exceed 10 cm). 535 However, using usage of long measurements path lengths, offered available in optical waveguide spectrophotometer systems (0.2 - - 2 meters) (D'Sa et al., 1999; Miller et al. 2002), in optically complex waters such as the Baltic Sea and fresh-water lakes, would severely impact the radiometric sensitivity of any spectrophotometer in the UV spectral range. 539

There were A number of regional studies have presentinged the dependence between 540 chlorophyll a concentration, Chla, and CDOM absorption, $a_{\rm CDOM}(\lambda)$, similar using a 541 542 parameterization similar to that described by Equation 13 (Ferrari and Tassan, 1992, Tassan 1994, Vodacek et al. 1997, Morel et al. 2007, Morel and Gentili 2009, Bricaud et al. 2010, 543 Organelli et al. 2014). We have-compared the $a_{CDOM}(\lambda)/Chla$ relationship that we derived by 544 us-with some of the elected relationships between CDOM absorption coefficients $\mu_{CDOM}(\lambda)$ 545 and Chla developed derived by different various authors for different water types. Selected 546 model outputs were overlaiding on the observed distribution of $a_{\text{CDOM}}(\lambda)$ in the as a function of 547 Chla; (presented on Figure 9). In all cases, Tthese relationships in all cases were 548 549 approximated by power functions, and assumed different rates of increase of the $a_{\text{CDOM}}(\lambda)$ value with increasing Chla (Tassan, 1994; Morel et al., 2007; Morel and Gentili 2009; 550 551 Bricaud et al. 2010). The rRelationships developed derived by other authors, were not found 552 unsuitable for estimating CDOM absorption in the Baltic Sea waters and lakes waters. The Empirical relationships derived developed by Tassan, (1994), Morel et al., (2007), Morel and 553 554 Gentili (2009) and Bricaud et al. (2010) all underestimated the CDOM absorption in the 555 Baltic Sea. Such a large mismatchgreat discrepancy between estimated and observed CDOM absorption values eertainly will-have resulted from the fact that these relationships were 556 developed for clearn oceanic waters, where the contribution of dissolved organic material to 557 the total light absorption light-was lower-less than in the Baltic Sea and the concentration of 558 *Chla* did not exceed 40 mg m⁻³. For example, Bricaud et al. (2010) have based their empirical 559 model on measurements from mesotrophic waters around the Marquesas Islands to 560 hyperoligotrophic waters in the subtropical gyre and eutrophic waters in the upwelling area 561 west off the Chilean coast (South Pacific). Reported The Chla concentrations they reported 562 spanned more than two orders of magnitude (0.017 to 1.5 mg m⁻³) in the surface layer, values 563 of ;- the spectral slope; S; values contained lay within the range of 0.007 - 0.032 nm⁻¹ range; 564 and while observed the $a_{CDOM}(440)$ values were from 0.0003 to 0.038 m⁻¹. Morel et al. (2007) 565 566 carried out measurements in hyperoligotrophic waters in the South Pacific gyre (near Easter

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Island), where observed Chla concentrations were within ranged from of 0.022 to 0.032 mg 567 m⁻³ in the surface layer. Tassan (1994) reported two relationships between $a_{CDOM}(\lambda)$ and *Chla* 568 569 (one for Gulf of Naples waters and second for the Adriatic Sea), and then used these relationships for estimation of to estimate CDOM absorption coefficients values at different 570 ranges of Chla concentrations (0.25 do 40 mg m⁻³). Morel and Gentili (2009) tested developed 571 a satellite ocean color algorithm they derived for enabling determiningation of the CDOM 572 573 absorption and the Chla concentrations from satellite imagery in of Mediterranean waters, where *Chla* varied within the range from 0.01 to 0.5 mg m⁻³. The eutrophic Baltic Sea waters 574 575 and supertechutrophic lakes waters were characterized by significantly higher Chla concentrations. The total absorption in our study area wereas dominated by the absorption of 576 <u>CDOM organic dissolved substances</u> (Woźniak et al., 2011; Ficek et al., 2012); therefore, 577 observed measured $a_{CDOM}(\lambda)$ values per unit of chlorophyll a concentrations were almost 578 twice as much high in the Baltic Sea and Pomeranian lakes, as compared to those observed in 579 580 Pacific Ocean and Mediterranean and Adriatic Sea watersoceanic waters in the Pacific and marine water in the Mediterranean and Adriatic. These findings underline thed need for to 581 582 derive development of regional algorithms and bio-optical models, because one-those derived for developed in other regions did do not account fored the constant, and very high 583 background in CDOM absorption persistently prevalent in the Baltic Sea and fresh waters in 584 the temperate climatic zone. 585

The uncertainty analysis showed proved that, both the mathematical, single 586 independent variable CDOM absorption estimates ions-presented in this paper performed 587 better, than the classical exponential model, with variable slope parameterized with the 588 589 relationship derived by Kowalczuk et al. (2006) and its modification presented given in Equation 15-. The two-parameters exponential model significantly underestimated $\mu_{\rm CDOM}(\lambda)$ 590 at longer wavelengths. The sS tandard error factor x wais lower in the Kowalczuk et al. (2006) 591 model and our modification of this model than in approximations (13) and (14). But the 592 systematic errors, both arithmetic and logarithmic, weare much higher. For example, in the 593 models by Kowalczuk et al. (2006) for the 440 nm wavelength, the arithmetic systematic error 594 tookakes an average value of -16% and the average logarithmic systematic error takes average 595 value was -17%, while whereas with using the formula (13), we had $\frac{1}{100}$ we had $\frac{1}{100}$ whereas $\frac{1}{100}$ with $\frac{1}{100}$ we had $\frac{1}{100}$ with $\frac{1}{100}$ w 596 the with formula (14) 0.4% and 0.003%, respectively. Morel and Gentili (2009) and Morel et 597 598 al. (2010) derived a two-component model for description of describing the CDOM 599 absorption properties, and they modeling led the spectral slope values using its empirical

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relationship with the chlorophyll *a* concentration. These models were based on data sets collected in clear oceanic waters, so their applicability to Baltic Sea conditions would probably be questionable, as it was in the case of the $a_{CDOM}(\lambda)/Chla$ relationships.

<u>4.2 Assessment of the accuracy of two parameters models for for approximating the CDOM</u> <u>light absorption spectrum</u>

Finally, we have compared the performance in the retrieval of the CDOM absorption spectrum in the Baltic Sea conditions of two three standard exponential models broadly used in optical oceanography: *i*) model the one by Bricaud et al. (1981) with spectral slope $S_{375-500}$ and CDOM absorption reference wavelength $\lambda_0 = 375 \text{ nm}_{\frac{1}{2}i} ii)$ model the one by Babin et al. (2003) with spectral slope; $S_{350-500}$ and CDOM absorption reference wavelength $\lambda_0 = 443$ nm); and *iii*) the model by Kowalczuk et al. (2006). The modelled spectra weare presented oin Figure 10, together with measured CDOM absorption spectra and those calculated from the one-parameter models expressed by Equations 13 and 14 for determined measured *Chla* concentrations. EThe empirical model developed for the Baltic Sea and inland waters (-Equations 13 and 14), based on locally observed variabilitiesty in biogeochemical and optical variables, adequately reflected the measured light absorption coefficients in the spectral range 240-600 nm. The model based on the dependence of the chlorophyll μ concentration, Equation 13, fitted best the $a_{CDOM}(\lambda)$ from 240 to 600 nm, and could be applied in-to a variety of water bodies with contrasting trophic status. From this point of view, it has outperformed to-the models derived by Bricaud et al. (1981) or and Babin et al. (2003), which were developed either-for oligotrophic or mesotrophic oceanic waters, and European coastal waters, respectively, The Mmodel by Kowalczuk et al. (2006) underestimated values of $\mu_{\text{CDOM}}(\lambda)$ for *Chla* concentrations below <- 5 mg m⁻³ (see Figure 10). For *Chla* greater than >- 2 mg m⁻³ (see Figure 10). 20 mg m^{-3} the shapes of all the modeled spectra for-were similar.

<u>20 mg m the shapes of an <u>the modeled spectra</u> tor were similar</u>

In order to compare the performance of two parameters models developed by Bricaud et al., (1981) and Babin et al., (2003) above mentioned models, we adapted them to the empirical data set presented in this study within the spectral range from 240 to 700 nm, and then we have applied the same statistical metrics to assess their uncertainty. The cCalculated errors for selected wavelengths weare listed in Table 6 for selected wavelengths. The systematic errors in arithmetic statistics were higher for the models by ouput-Bricaud et al. (1981) and Babin et al. (2003) compared to the errors calculated for the parameterizations Formatted: English (U.S.)

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Formatted: English (U.S.) 632 given by Equations 13 and 14. The systematic errors calculated for the CDOM absorption model by Babin et al., (2003) were significantly higher in-at all the selected-wavelengths 633 634 compared to those presented listed in Tables 3 and 4. The CDOM absorption could be estimated by using the empirical model based on the a the $a_{CDOM}(\lambda)/Chla$ dependency 635 relationship with the a systematic error of 3.13 % at $\lambda = 350$ nm, whereas the model by Babin 636 et al., (2003) model estimated the CDOM absorption at the same wavelength with a 637 systematic error of -33.70%. CThe calculated statistical errors of the estimates with use of 638 639 using the models by the Bricaud et al. (1981) and Babin et al. (2003) models were very large 640 compared to the results obtained with models expressed by Equations 13 and 14. Whereas the standard error factors are quite good for Bricaud's model (from 1 to 2.43), they are much 641 higher for Babin's model (from 1.045 to 3.58). However, in both cases, the systematic errors 642 643 weare significant : -59% to 144-and 79% to +400%, respectively.

644 **5.** Conclusions

We have-demonstrated that CDOM absorption wawas non-linearly-correlated non-645 <u>linearly</u> with chlorophyll a concentration in over a broad range of variability range spanning 646 over-three orders of magnitude in marine-waters of the Baltic Sea, its estuaries, coastal 647 lagoons and in the fresh water lakes characterised by of different throphic status. The A 648 second,—order polynomial approximation of the relationship between chlorophyll a_{i} 649 concentration and $a_{\text{CDOM}}(400)$ could be was used to with respect to in both marine sea and 650 fresh water, and was much more accurate than the one derived for Baltic Sea waters by 651 Kowalczuk (2001). This relationship has also proved demonstrated that the optical and bio-652 653 optical properties of marine sea and fresh waters could be regardsed as an continuum in regard of CDOM absorption and chlorophyll a concentration. We have had derived models 654 655 for estimatingon of the CDOM light absorption by spectrum in the spectral range 240-700 nm non-linearly from chlorophyll a concentrations Chla or from coefficients of light absorption 656 by CDOM for wavelength 400 nm ($a_{\text{CDOM}}(400)$). For comparison, we have also, tested the 657 658 classical exponential model for approximation g the CDOM absorption spectrum, where the spectral slope coefficient was determined from the nonlinear relationship between the spectral 659 660 slope coefficient and values of a_{CDOM}(375). The result of the uncertainty analysis results proved showed that, the one-parameterie, second, order polynomial function of the 661 chlorophyll a concentration, Chla, enabled estimation of spectral values of the CDOM 662 absorption coefficient, $a_{CDOM}(\lambda)$ to be estimated with just a slightly lower accuracy than, its 663 estimateion based on a second order polynomial function of the CDOM absorption 664

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| 665 | coefficient at wavelength 400 nm $a_{\text{CDOM}}(400)$. The models presented here, Presented models, | |
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| 666 | optimized for the specific optical and bio-optical conditions of the Baltic Sea and fresh water | |
| 667 | bodies-specific optical and bio optical conditions, were characterized with had significantly | |
| 668 | lower estimation errors of estimations compared to the widely used CDOM absorption models | |
| 669 | proposed-developed by other authors. The CDOM absorption models presented in this study, | |
| 670 | could can be used for improving ements of remote sensing algorithms designed for retrieving | |
| 671 | als of various optical and bio-optical parameters needed required for characterizing ation and | |
| 672 | monitoring of the state and functioning of the Baltic Sea and Pomeranian lakes ecosystems. | Formatted: English (U.S.) |
| 673 | Validation of these models showed that they can be reliably applied in monitoring surveys, | |
| 674 | when a rapid, approximation \underline{of} the light absorption spectrum is needed. | Formatted: English (U.S.) |
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 Table 1. Dates, numbers of samples ceollected and parameters measured during cruises and private field experiments made carried out for this study.

| Dates of cruises | Number of | Parameters measured | Region |
|-------------------|-----------|--|---|
| | samples | | |
| 24-31 Aug 2006 | 20 | agrow(A) Chla CTD | southern Baltic Proper, Gulf of Gdańsk |
| 27-51 Aug. 2000 | 20 | $\mu_{\text{CDOM}}(k), Chu, C1D_{k}$ | soulien Datte Proper, Gun of Guansk |
| 24-29 Sept. 2006 | 12 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{A}$ | southern Baltic Proper, Gulf of Gdańsk |
| 18-28 Oct. 2006 | 30 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}$ | southern Baltic Proper, Gulf of Gdańsk, |
| | | | Pomeranian Bay |
| 21-31 March 2007 | 36 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\star}$ | southern Baltic Proper, Gulf of Gdańsk, |
| | | | Pomeranian Bay, Szczecin Lagoon |
| 21-31 May 2007 | 38 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\lambda}$ | southern Baltic Proper, Gulf of Gdańsk |
| 20-28 Oct. 2007 | 26 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}$ | southern Baltic Proper, Gulf of Gdańsk |
| | | | |
| 01-11 March 2008 | 29 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\bullet}$ | southern Baltic Proper, Gulf of Gdańsk, |
| l | | | Pomeranian Bay |
| 11-18 April 2008 | 22 | $\rho_{\rm CDOM}(\lambda), Chla, {\rm CTD}$ | southern Baltic Proper, Gulf of Gdańsk |
| 06-14 May 2008 | 23 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\star}$ | southern Baltic Proper, Gulf of Gdańsk |
| 01-09 Sept. 2008 | 26 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\lambda}$ | southern Baltic Proper, Gulf of Gdańsk, |
| | | | Pomeranian Bay, Szczecin Lagoon |
| 25-29 Nov. 2008 | 18 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}$ | Gulf of Gdańsk |
| 04-12 March 2009 | 14 | $a_{\rm CDOM}(\lambda), Chla, {\rm CTD}$ | Gulf of Gdańsk, Gotland Basin |
| • | | | · · · · · · · · · · · · · · · · · · · |
| 15-21 April 2009 | 29 | $\mu_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\Lambda}$ | southern Baltic Proper, Gulf of Gdańsk |
| 20-28 May 2009 | 34 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\Lambda}$ | southern Baltic Proper, Gulf of Gdańsk, |
| | | | Pomeranian Bay, Szczecin Lagoon |
| 07-16 Sept. 2009 | 35 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}$ | southern Baltic Proper, Gulf of Gdańsk |
| 06-10 Oct. 2009 | 21 | $a_{\text{CDOM}}(\lambda), Chla, \text{CTD}_{\star}$ | southern Baltic Proper, Gulf of Gdańsk |
| Dec. 2006 – Sept. | 66 | $a_{\rm CDOM}(\lambda), Chla_{\rm A}$ | Sopot Pier |
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| April – Dec. 2007 | 10 | $\rho_{\rm CDOM}(\lambda), Chla_{\rm A}$ | Lake Łebsko |
|--------------------|-----|--|------------------|
| April – Sept. 2008 | 8 | $a_{\text{CDOM}}(\lambda), Chla_{\lambda}$ | Lake Łebsko |
| June – Oct. 2009 | 9 | $a_{\text{CDOM}}(\lambda), Chla$ | Lake Łebsko |
| March – Dec. 2007 | 10 | $\rho_{\rm CDOM}(\lambda), Chla_{\rm A}$ | Lake Chotkowskie |
| Feb. – Sept. 2008 | 8 | $a_{\text{CDOM}}(\lambda), Chla$ | Lake Chotkowskie |
| April – Nov. 2009 | 8 | $\mu_{\rm CDOM}(\lambda), Chla$ | Lake Chotkowskie |
| March – Dec. 2007 | 9 | $\mu_{\rm CDOM}(\lambda), Chla_{\lambda}$ | Lake Obłęskie |
| Feb. – Sept. 2008 | 8 | $a_{\text{CDOM}}(\lambda), Chla_{\lambda}$ | Lake Obłęskie |
| May – Nov. 2009 | 7 | $\mu_{\rm CDOM}(\lambda), Chla_{\rm A}$ | Lake Obłęskie |
| All data | 556 | | |

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| ible 2. Rar | nge of variability of the spectral slope $S_{300-600}$, the coefficients of light absorption |
|-------------|--|
| by C | CDOM for wavelengths $\lambda = 375$ nm and 400 nm, a_{CDOM} (375) and a_{CDOM} (400), |
| and | concentrations of chlorophyll a, Chla, calculated for the empirical data-analysed |
| here | 3. |
| | |

| area variability $S_{300-600}$ [nm ⁻¹] altic 0.014 - 0.03 0.022 0.0021 |
|---|
| $S_{300-600} \text{ [nm}^{-1]}$ waltic 0.014 - 0.03 0.022 0.0021 |
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| |
| 10007 - 0.02 - 0.017 - 0.0030 |
| ll <u>0.007 – 0.03</u> 0.021 0.0022 |
| $\mu_{\rm CDOM}(375) [{\rm m}^{-1}]$ |
| altic 0.41 – 7.92 1.61 1.17 |
| ukes 211-1416 711 336 |
| |
| ll 0.41 – 14.16 2.06 2.17 |
| <i>а</i> _{ссом} (400) [m ⁻¹] |
| altic 0.15 – 4.79 0.997 0.73 |
| ikes, 1.28 – 8.85, 4.47, 2.07, |
| |
| ll 0.15 – 8.85 1.35 1.41 |
| \mathcal{L} |
| altic 0.72 - 76.94 8.77 11.61 |
| ikes 1.48 – 118.97 39.11 34.15 |
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| Table 3. Re | lative errors of the | emp | irical model ex | (pres | sed given | by forn | nula | (13) <u>for</u> |
|-------------|----------------------|-----------------|----------------------------|--------|-----------|---------|------|-----------------|
| det | erminingenabling | the- | determination | of | -spectral | values | of | CDOM |
| ab | sorption coefficient | s ($a_{\rm C}$ | $DOM(\lambda)$) at select | cted v | vavelengt | ths. | | |

| Wavelength [nm] | Arithmetic | statistics | | Logarithmic st | atistics |
|-----------------|----------------------|---------------------------|------------|----------------|---|
| | systematic | statistical | systematic | standard | statistical error |
| | error | error | error | error factor | |
| | (ɛ) [%] _▲ | σ _ε [%] | (ɛ) g[%] | <i>x</i> , | σ ₊ [%], σ ₋ [%], |
| 260 | 1.47 | 17.03 | 0.00 | 1.19 | 19.06 -16.01 |
| 350 | 3.13 | 25.16 | -0.01 | 1.29 | 29.01 -22.49 |
| 440 | 4.01 | 29.37 | -0.01 | 1.33 | 32.71 -24.65 |
| 500 | 6.54 | 39.43 | 0.01 | 1.42 | 42.45 -29.80 |
| 550 | 11.03 | 55.07 | 0.00 | 1.57 | 57.40 -36.47 |
| 600 | 19.54 | 79.13 | -0.09 | 1.83 | 83.43 -45.48 |

Table 4. Relative errors of <u>the empirical model expressed given</u> by formula (14) <u>enabling for</u> <u>determining the determination of spectral values of CDOM absorption coefficients</u> $(a_{\text{CDOM}}(\lambda))$ at selected wavelengths.

| Wavelength [nm] | Arithmetic | statistics | | Logarithmic st | atistics | |
|-----------------|-----------------------------|--------------------|------------|----------------|--|--|
| | systematic | statistical | systematic | standard | statistical error | |
| | error | error | error | error factor | | |
| | (ε) [%] _▲ | σ _ε [%] | (ɛ) g [%] | x _ | σ ₊ [%a _∗ [%] _∗ | |
| 260 | 0.38 | 9.11 | 0.00 | 1.09 | 8.94 -8.21 | |
| 350 | 0.20 | 6.43 | -0.01 | 1.07 | 6.86 -6.42 | |
| 440 | 0.42 | 9.51 | 0.00 | 1.09 | 9.39 -8.59 | |
| 500 | 2.21 | 22.11 | 0.01 | 1.23 | 23.01 -18.71 | |
| 550 | 6.24 | 37.86 | 0.00 | 1.42 | 41.79 -29.47 | |
| 600 | 16.61 | 67.45 | -0.01 | 1.76 | 75.88 -43.14 | |

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878 879 880 **Table 5.** Relative errors of the empirical models expressed given by formulas dependence (15) and (1) for determining enabling determination of spectral values of CDOM absorption coefficients ($a_{CDOM}(\lambda)$) at selected wavelengths.

| Wavelength [nm] | Arithmetic | statistics | | Logarithmic sta | atistics |
|-----------------------|------------------|---------------------------|------------|-----------------|---|
| | systematic | statistical | systematic | standard | statistical error |
| | error | error | error | error factor | |
| | (ɛ) [%] ₄ | σ _ε [%] | (ɛ) g[%] | x _ | σ ₊ [%] _^ σ ₋ [%] _^ |
| 260 | 2.81 | 14.14 | 1.82 | 1.15 | 15.33 -13.29 |
| 350 | 3.69 | 4.46 | 3.59 | 1.04 | 4.49 -4.30 |
| 440 | -14.74 | 14.13 | -15.86 | 1.18 | 17.53 -14.92 |
| 500 | -31.15 | 22.06 | -34.44 | 1.37 | 36.54 -26.76 |
| 550 | -43.73 | 31.25 | -50.93 | 1.67 | 67.41 -40.27 |
| 600 | -36.05 | 50.48 | -50.16 | 2.01 | 101.01 -50.25 |
| Kowalczuk et al. 2006 | | | | | |
| 260 | 9.32 | 11.48 | 8.62 | 1.13 | 13.02 -11.52 |
| 350 | 5.14 | 4.70 | 5.04 | 1.05 | 4.68 -4.47 |
| 440 | -18.16 | 13.96 | -19.29 | 1.18 | 17.90 -15.18 |
| 500 | -35.34 | 21.93 | -38.71 | 1.38 | 38.23 -27.66 |
| 550 | -47.27 | 27.17 | -53.46 | 1.65 | 64.71, -39.29, |
| 600 | -41.25 | 46.17 | -54.77 | 2.05 | 104.97 -51.21 |

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Table 6. Relative errors of <u>the models of Bricaud et al. (1981)</u> and Babin et al. (2003) models for determiningenabling determination of spectral values of CDOM absorption coefficients ($a_{CDOM}(\lambda)$) at selected wavelengths.

| Wavelength [nm] | Arithmetic | statistics | | Logarithmic st | atistics | |
|-------------------|------------------|---------------------------|------------|----------------|--------------------|------------------|
| | systematic | statistical | systematic | standard | statistic | al error |
| | error | error | error | error factor | | |
| | (ε) [%] ⊾ | σ _ε [%] | (ɛ) g[%] | <i>x</i> , | σ ₊ [%] | σ ₋ [%] ₄ |
| Bricaud et al. | A | | | | | |
| 1981 | -35.74 | 20.98 | -38.79 | 1.36 | 35.97 | -26.46 |
| 2.00 | -6.95 | 3.64 | -7.02 | 1.04 | 3.98 | -3.82 |
| 260 | 11.10 | 8.51 | 10.78 | 1.08 | 7.95 | -7.37 |
| 350 | 14.24 | 19.13 | 12.82 | 1.17 | 16.72 | -14.32 |
| 440 | 11.21 | 30.85 | 7.70 | 1.28 | 27.77 | -21.74 |
| 440 | 51.80 | 90.23 | 33.10 | 1.64 | 64.00 | -39.03 |
| 500 | | | | | | |
| 550 | | | | | | |
| 600 | | | | | | |
| Babin et al. 2003 | | | | | | |
| 260 | -58.45 | 27.26 | -65.30 | 1.78 | 77.78 | -43.75 |
| 350 | -33.70 | 13.85 | -35.08 | 1.23 | 22.59 | -18.43 |
| 440 | -4.69 | 4.10 | -4.78 | 1.04 | 4.45 | -4.26 |
| 500 | 12.87 | 18.23 | 11.40 | 1.18 | 17.77 | -15.09 |
| 550 | 26.12 | 42.51 | 19.30 | 1.40 | 40.12 | -28.63 |
| 600 | 92.38 | 137.52 | 55.82 | 1.95 | 95.05 | -48.73 |





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0.035 0.035 R²=0.79, p<0.0001 (N=541) b а R²=0.78, p<0.0001 (N=391) R²=0.22, p<0.0001 (N=150) 0.030 0.030 Spectral slope S₃₀₀₋₆₀₀ [nm⁻¹] Spectral slope $S_{300-600}$ [nm⁻¹] 0.025 0.025 0.020 0.020 0.015 0.015 Baltic Sea salinity >5 • • Lakes salinity <5 0.010 0.010 10 0.1 0.1 10 1 1 $a_{CDOM}(400) \, [\text{m}^{-1}]$ $a_{CDOM}(400) \, [\text{m}^{-1}]$ 890 1

889

| 891 | Figure 2. Relationship between the spectral slope $S_{300-600}$ and the coefficient of light |
|-----|--|
| 892 | absorption by CDOM for wavelength 400 nm, $a_{\text{CDOM}}(400)_{4}$ in the semi-log |
| 893 | scale (a) in the Baltic (black dots) and lakes (green dots). The black curve is |
| 894 | the approximation obtained by Kowalczuk (2001), the red line represents, the |
| 895 | approximation expressed given by Equation 10; (b) for samples with salinity |
| 896 | $\frac{1}{10000000000000000000000000000000000$ |
| 897 | (samples from lakes, river mouths, the Szczecin Lagoon). The blue line |
| 898 | represents the approximation given, expressed by Equation (11), and the cyan |
| 899 | line the approximation given by Equation (12). |
| | |

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Formatted: No underline, Font color: Auto, English (U.S.) 900 Formatted: English (U.S.) Formatted: English (U.S.) 10 Baltic o lakes Kowalczuk 2001 this study $a_{CDOM}(400) \, [\mathrm{m}^{-1}]$ 1 0.1 10 100 1 Chla [mg m⁻³] 901 Figure 3. Dependence between coefficients of light absorption by CDOM $\rho_{CDOM}(400)$ and 902 Formatted: No underline, Font color: Auto, English (U.S.) chlorophyll *a* concentration. The black line shows the approximation obtained by 903 Kowalczuk (2001) and the red line shows the second-degree polynomial 904 **Formatted:** No underline, Font color: Auto, English (U.S.) 905 approximation second degree polynomial ion the log-log scale. Formatted: No underline, Font color:

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(green dots) for selected wavelengths: (a) 260 nm; (b) 350 nm; (c) 440 nm; (d) 500 nm; (e) 550 nm; (f) 600 nm. The solid line represents the function $a_{\text{CDOM}}(\lambda)_{\text{cal}} =$

 $a_{\text{CDOM}}(\lambda)_{\text{m}-}$. And <u>T</u> the probability density distribution of the ratio of calculated

 $a_{\text{CDOM}}(\lambda)_{\text{cal}}$ to measured $a_{\text{CDOM}}(\lambda)_{\text{m}}$ light absorption coefficients for selected

wavelengths: (g) 260 nm; (h) 350 nm; (i) 440 nm; (j) 500 nm; (k) 550 nm; (l) 600

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927 928 929

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Figure. 8. The relationship between the spectral slope coefficient S, and $a_{CDOM}(375)$ in the 933 Baltic (black dots) and lakes (green dots). The bBlack line indicates the model of 934 Kowalczuk et al. (2006), and the red one indicates our new approximation (15). 935



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Table A. Model parameters for light absorption by CDOM (13) for the wavelength range 240

- 700 nm shown for intervals of 5 $\rm nm_{\scriptscriptstyle A}$

| wave- | A | В | D | R ² | wave- | A | В | D | R ² |
|--------|------------------------------------|------------------------------------|--------------------|----------------|--------|------------------------------------|------------------------------------|--------------------|----------------|
| length | | | | | length | | | | |
| 0 | [m ⁵ mg ⁻²] | [m ² mg ⁻¹] | [m ⁻¹] | | 0 | [m ⁵ mg ⁻²] | [m ² mg ⁻¹] | [m ⁻¹] | |
| [nm] | | | | | [nm] | | | | |
| | | | | | | | | | |
| 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| | | | | | | | | | |
| 240 | 0.200 | -0.104 | 1.286 | 0.78 | 475 | 0.262 | 0.027 | -0.857 | 0.79 |
| 245 | 0.207 | -0.110 | 1.250 | 0.79 | 480 | 0.272 | 0.002 | -0.880 | 0.77 |
| 250 | 0.211 | -0.114 | 1.221 | 0.80 | 485 | 0.255 | 0.057 | -0.956 | 0.79 |
| 255 | 0.214 | -0.115 | 1.195 | 0.81 | 490 | 0.263 | 0.024 | -0.959 | 0.77 |
| 260 | 0.216 | -0.114 | 1.166 | 0.81 | 495 | 0.264 | 0.028 | -1.003 | 0.76 |
| 265 | 0.218 | -0.110 | 1.131 | 0.81 | 500 | 0.275 | 0.010 | -1.038 | 0.76 |
| 270 | 0.220 | -0.107 | 1.090 | 0.82 | 505 | 0.277 | 0.005 | -1.059 | 0.76 |
| 275 | 0.222 | -0.101 | 1.041 | 0.82 | 510 | 0.265 | 0.032 | -1.105 | 0.75 |
| 280 | 0.230 | -0.102 | 0.990 | 0.83 | 515 | 0.290 | -0.003 | -1.147 | 0.74 |
| 285 | 0.233 | -0.095 | 0.931 | 0.83 | 520 | 0.292 | -0.013 | -1.177 | 0.72 |
| 290 | 0.237 | -0.088 | 0.865 | 0.83 | 525 | 0.304 | -0.050 | -1.178 | 0.73 |
| 295 | 0.243 | -0.080 | 0.795 | 0.83 | 530 | 0.310 | -0.055 | -1.221 | 0.73 |
| 300 | 0.249 | -0.074 | 0.727 | 0.83 | 535 | 0.313 | -0.047 | -1.275 | 0.70 |
| 305 | 0.253 | -0.066 | 0.660 | 0.83 | 540 | 0.307 | -0.045 | -1.292 | 0.70 |
| 310 | 0.258 | -0.061 | 0.599 | 0.83 | 545 | 0.320 | -0.054 | -1.345 | 0.70 |
| 315 | 0.260 | -0.055 | 0.541 | 0.83 | 550 | 0.344 | -0.110 | -1.354 | 0.68 |
| 320 | 0.261 | -0.047 | 0.487 | 0.83 | 555 | 0.344 | -0.101 | -1.398 | 0.66 |
| 325 | 0.261 | -0.040 | 0.435 | 0.84 | 560 | 0.337 | -0.065 | -1.470 | 0.64 |
| 330 | 0.258 | -0.027 | 0.382 | 0.84 | 565 | 0.341 | -0.087 | -1.468 | 0.67 |
| 335 | 0.257 | -0.019 | 0.332 | 0.84 | 570 | 0.337 | -0.091 | -1.491 | 0.62 |
| 340 | 0.260 | -0.020 | 0.286 | 0.84 | 575 | 0.314 | -0.040 | -1.537 | 0.65 |
| 345 | 0.262 | -0.018 | 0.238 | 0.84 | 580 | 0.291 | 0.036 | -1.641 | 0.65 |
| 350 | 0.266 | -0.024 | 0.196 | 0.83 | 585 | 0.462 | -0.307 | -1.597 | 0.65 |
| 355 | 0.265 | -0.018 | 0.150 | 0.83 | 590 | 0.382 | -0.195 | -1.612 | 0.60 |
| 360 | 0.268 | -0.022 | 0.108 | 0.83 | 595 | 0.367 | -0.095 | -1.//6 | 0.65 |
| 305 | 0.205 | -0.012 | 0.059 | 0.03 | 605 | 0.405 | 0.198 | 1.000 | 0.61 |
| 370 | 0.263 | -0.002 | 0.008 | 0.83 | 605 | 0.444 | -0.251 | -1.886 | 0.52 |
| 3/5 | 0.200 | -0.007 | -0.035 | 0.03 | 615 | 0.480 | 0.200 | -1.903 | 0.57 |
| 205 | 0.200 | -0.004 | 0.121 | 0.03 | 615 | 0.510 | 0.450 | 1.070 | 0.57 |
| 200 | 0.261 | 0.009 | 0.174 | 0.03 | 02U | 0.520 | 0.227 | 2 1 10 | 0.40 |
| 205 | 0.200 | 0.014 | 0.214 | 0.03 | 620 | 0.510 | 0 = 20 | 2.110 | 0.30 |
| 395 | 0.201 | 0.012 | 0.240 | 0.03 | 625 | 0.584 | 0.471 | 2.015 | 0.40 |
| 400 | 0.250 | 0.009 | 0.204 | 0.02 | 640 | 0.553 | 0.424 | -2.0/5 | 0.44 |
| 405 | 0.255 | 0.022 | -0.294 | 0.03 | 645 | 0.585 | -0.434 | -2.110 | 0.53 |
| 410 | 0.261 | 0.008 | -0.326 | 0.83 | 045 | 0.600 | -0.487 | -2.069 | 0.51 |

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| 415 | 0.252 | 0.032 | -0.379 | 0.83 | 650 | 0.682 | -0.567 | -2.115 | 0.59 |
|-----|-------|--------|--------|------|-----|-------|--------|--------|------|
| 420 | 0.248 | 0.037 | -0.418 | 0.82 | 655 | 0.572 | -0.371 | -2.096 | 0.64 |
| 425 | 0.255 | 0.021 | -0.451 | 0.82 | 660 | 0.512 | -0.099 | -2.375 | 0.67 |
| 430 | 0.257 | 0.016 | -0.486 | 0.82 | 665 | 0.301 | 0.387 | -2.524 | 0.72 |
| 435 | 0.258 | 0.015 | -0.529 | 0.82 | 670 | 0.446 | -0.024 | -2.320 | 0.66 |
| 440 | 0.253 | 0.028 | -0.577 | 0.82 | 675 | 0.319 | 0.264 | -2.428 | 0.69 |
| 445 | 0.258 | 0.019 | -0.614 | 0.81 | 680 | 0.305 | 0.224 | -2.352 | 0.66 |
| 450 | 0.251 | 0.036 | -0.662 | 0.80 | 685 | 0.360 | 0.072 | -2.297 | 0.62 |
| 455 | 0.262 | 0.011 | -0.688 | 0.80 | 690 | 0.452 | 0.103 | -2.314 | 0.60 |
| 460 | 0.271 | -0.005 | -0.723 | 0.80 | 695 | 0.191 | 0.466 | -2.481 | 0.67 |
| 465 | 0.253 | 0.048 | -0.795 | 0.81 | 700 | 0.243 | 0.310 | -2.412 | 0.62 |
| 470 | 0.267 | 0.014 | -0.815 | 0.80 | | | | | |

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Table B. Parameters of the model of light absorption by CDOM (14) for the wavelength

range 240 - 700 nm, shown for intervals of 5 nm $_{\rm \star}$

| wave- | M | N | 0 | R ² | wave- | M | N | 0 | R ² |
|--------|------------------------------------|------------------------------------|--------------------|----------------|--------|------------------------------------|------------------------------------|--------------------|----------------|
| length | [m ⁵ mg ⁻²] | [m ² mg ⁻¹] | [m ⁻¹] | | length | [m ⁵ mg ⁻²] | [m ² mg ⁻¹] | [m ⁻¹] | |
| [nm] | | | | | [nm] | | | | |
| 1. | 2. | 3 | 4 | 5 | 1. | 2. | 3 | 4 | 5. |
| | | | | | | | | | |
| 240 | 0.337 | 0.444 | 1.360 | 0.92 | 475 | -0.300 | 1.184 | -0.572 | 0.95 |
| 245 | 0.356 | 0.445 | 1.323 | 0.94 | 480 | -0.195 | 1.129 | -0.613 | 0.95 |
| 250 | 0.369 | 0.450 | 1.294 | 0.95 | 485 | -0.211 | 1.159 | -0.657 | 0.95 |
| 255 | 0.372 | 0.455 | 1.269 | 0.95 | 490 | -0.217 | 1.147 | -0.682 | 0.93 |
| 260 | 0.375 | 0.463 | 1.243 | 0.96 | 495 | -0.226 | 1.163 | -0.720 | 0.93 |
| 265 | 0.376 | 0.474 | 1.213 | 0.96 | 500 | -0.218 | 1.163 | -0.756 | 0.92 |
| 270 | 0.370 | 0.490 | 1.177 | 0.96 | 505 | -0.176 | 1.138 | -0.787 | 0.92 |
| 275 | 0.363 | 0.511 | 1.136 | 0.96 | 510 | -0.187 | 1.150 | -0.823 | 0.90 |
| 280 | 0.355 | 0.535 | 1.091 | 0.96 | 515 | -0.206 | 1.183 | -0.867 | 0.89 |
| 285 | 0.348 | 0.562 | 1.042 | 0.96 | 520 | -0.188 | 1.174 | -0.901 | 0.88 |
| 290 | 0.340 | 0.596 | 0.988 | 0.97 | 525 | -0.140 | 1.137 | -0.929 | 0.87 |
| 295 | 0.332 | 0.633 | 0.930 | 0.97 | 530 | -0.139 | 1.149 | -0.969 | 0.88 |
| 300 | 0.317 | 0.672 | 0.873 | 0.97 | 535 | -0.182 | 1.186 | -1.005 | 0.86 |
| 305 | 0.300 | 0.709 | 0.819 | 0.97 | 540 | -0.148 | 1.158 | -1.033 | 0.86 |
| 310 | 0.283 | 0.743 | 0.767 | 0.98 | 545 | -0.197 | 1.215 | -1.082 | 0.83 |
| 315 | 0.265 | 0.771 | 0.718 | 0.98 | 550 | -0.092 | 1.150 | -1.116 | 0.82 |
| 320 | 0.247 | 0.794 | 0.673 | 0.98 | 555 | -0.025 | 1.119 | -1.155 | 0.79 |
| 325 | 0.229 | 0.813 | 0.628 | 0.98 | 560 | -0.097 | 1.192 | -1.204 | 0.77 |
| 330 | 0.212 | 0.833 | 0.584 | 0.98 | 565 | -0.157 | 1.195 | -1.217 | 0.78 |
| 335 | 0.195 | 0.851 | 0.541 | 0.98 | 570 | -0.126 | 1.174 | -1.243 | 0.76 |
| 340 | 0.185 | 0.865 | 0.497 | 0.99 | 575 | -0.081 | 1.154 | -1.282 | 0.73 |
| 345 | 0.174 | 0.880 | 0.454 | 0.99 | 580 | 0.036 | 1.130 | -1.355 | 0.74 |
| 350 | 0.167 | 0.890 | 0.411 | 0.99 | 585 | 0.187 | 1.101 | -1.434 | 0.74 |
| 355 | 0.154 | 0.902 | 0.370 | 0.99 | 590 | 0.227 | 1.022 | -1.444 | 0.70 |

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| 360 | 0.139 | 0.913 | 0.328 | 0.99 | 595 | 0.267 | 1.075 | -1.543 | 0.70 |
|-----|--------|-------|--------|------|-----|--------|-------|--------|------|
| 365 | 0.119 | 0.928 | 0.286 | 0.99 | 600 | 0.420 | 1.009 | -1.601 | 0.68 |
| 370 | 0.089 | 0.950 | 0.244 | 0.99 | 605 | 0.774 | 0.876 | -1.742 | 0.59 |
| 375 | 0.089 | 0.955 | 0.200 | 1.00 | 610 | 0.771 | 0.937 | -1.804 | 0.61 |
| 380 | 0.073 | 0.965 | 0.157 | 1.00 | 615 | 0.719 | 1.020 | -1.873 | 0.60 |
| 385 | 0.050 | 0.979 | 0.115 | 1.00 | 620 | 0.656 | 0.924 | -1.827 | 0.54 |
| 390 | 0.030 | 0.990 | 0.076 | 1.00 | 625 | 0.853 | 0.918 | -1.969 | 0.55 |
| 395 | 0.014 | 1.001 | 0.035 | 1.00 | 630 | 1.122 | 0.784 | -2.016 | 0.55 |
| 400 | 0.000 | 1.000 | 0.000 | 1.00 | 635 | 1.238 | 0.704 | -2.069 | 0.50 |
| 405 | -0.029 | 1.015 | -0.038 | 1.00 | 640 | 1.078 | 0.787 | -2.061 | 0.50 |
| 410 | -0.046 | 1.021 | -0.075 | 1.00 | 645 | 1.293 | 0.784 | -2.060 | 0.54 |
| 415 | -0.063 | 1.033 | -0.115 | 1.00 | 650 | 1.090 | 0.999 | -2.088 | 0.61 |
| 420 | -0.092 | 1.042 | -0.151 | 1.00 | 655 | 0.620 | 1.229 | -1.952 | 0.68 |
| 425 | -0.122 | 1.060 | -0.190 | 0.99 | 660 | 0.130 | 1.655 | -2.029 | 0.71 |
| 430 | -0.123 | 1.059 | -0.228 | 0.99 | 665 | -0.868 | 2.149 | -1.893 | 0.76 |
| 435 | -0.125 | 1.063 | -0.269 | 0.99 | 670 | 0.075 | 1.468 | -1.922 | 0.67 |
| 440 | -0.210 | 1.111 | -0.307 | 0.98 | 675 | -0.590 | 1.782 | -1.839 | 0.70 |
| 445 | -0.221 | 1.118 | -0.346 | 0.98 | 680 | 0.268 | 1.233 | -1.910 | 0.61 |
| 450 | -0.297 | 1.161 | -0.382 | 0.97 | 685 | -0.316 | 1.508 | -1.839 | 0.65 |
| 455 | -0.312 | 1.171 | -0.419 | 0.96 | 690 | 0.117 | 1.321 | -1.951 | 0.59 |
| 460 | -0.314 | 1.177 | -0.458 | 0.96 | 695 | -0.832 | 1.847 | -1.843 | 0.68 |
| 465 | -0.275 | 1.169 | -0.503 | 0.96 | 700 | -0.453 | 1.610 | -1.882 | 0.67 |
| 470 | -0.302 | 1.190 | -0.540 | 0.95 | | | | | |

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