Piotr Kowalczuk
Institute of Oceanology
Polish Academy of Sciences
Ul. Powstańców Warszawy 55
PL – 81 - 712 Sopot

May 17, 2017

Christian Stamm, Ph.D.
Associate Editor
Hydrology and Earth System Science

Attn: Review of the manuscript by Kaishan Song, Ying Zhao, Zhidan Wen, Chong Fang, and Yingxin Shang entitled "A systematic examination of the relationships between CDOM and DOC in inland waters in China" submitted to Hydrology and Earth System Science and coded hess-2017-179.

Dear Dr Stamm,

After reading the manuscript by Song et al., submitted to Hydrology and Earth System Science and coded hess-2017-179, I think that this study **should be consider** for publication in this journal after **major revision**.

General opinion

This study presented results of extensive field studies on relationships between absorption of Chromophoric Dissolved Organic Matter and Dissolved Organic carbon in different water bodies conducted in continental China in different climatic zones. Authors found overall very good correlation between DOC and CDOM absorption coefficient at selected wavelengths, 275 and 400 nm. They have showed that both values of the slope coefficient of the linear regression between considered variables and values of determination coefficient varied considerably between studied water bodies. Author have also proposed a solution to minimize those variations by groping data according to spectral index M, which gave quite uniformed results in respect of the calculated R2, but still there was a significant variability of in regression slope coefficient values. This study proved that application of simple optical measurements could be applied in accurate and reliable estimation of DOC content in fresh water bodies in continental China.

My overall good opinion on this manuscript is somehow hampered by two major flaws: the introduction is overlong with many repetitions especially in regarding remote sensing applications, and Author have written their results together with discussion and it is very difficult for reader to judge when Author presents their own results and when they discuss with published results.

I strongly recommend to reduce introduction to maximum 3-4 pages from current 5, reduce the implications to remote sensing in Introduction. This is particularly redundant because Author have not presented a link between their regression analysis and remote sensing reflectance – the geophysical variable that is physically measured by radiometers placed on

spaceborne or airborne platforms. I also strongly recommend that Author shall present their own results and later give their interpretation in Discussion.

Detailed comments.

Abstract

Page 1 Lines 12 - 13

"An algorithm has been developed to retrieve DOC via CDOM absorption (a_{CDOM}) at 275 and 295 nm for coastal waters, but it is still unclear for the relationship between DOC and a_{CDOM} in other types of waters."

This sentence has no support in presented results. Authors have derived regression relationship between $a_{CDOM}(275)$ and $a_{CDOM}(440)$ but did proposed any remote sensing algorithms in the way it usually developed by the ocean color remote sensing/ocean optics community. Consider to remove this sentence. Abstract shall described your own findings - and shall not contain discussion. When you mention spectral values of $a_{CDOM}(\lambda)$ – use the symbol l in parenthesis and than indicate specific wavelengths.

Page 2 Lines 28 – 30

Our results indicated the relationships between CDOM and DOC are variable for different inland waters, and therefore remote sensing models for DOC estimation through linking with CDOM absorption need to be tailored according to water types.

This sentence is not precise. Author developed empirical relationships between DOC and $a_{CDOM}(\lambda)$ but not proposed any remote sensing algorithm. Algorithm need to be developed for different water types and later tested and validated and finally optimized. Please rewrite this sentence. It would be OK in discussion as it points the future direction of your work. Abstract shall briefly and comprehensively present your results.

Introduction

Please reduce length of introduction significantly. Please try to use separate paragraphs to present current knowledge of CDOM biogeochemistry, optics and remote sensing applications to study part of the Earth carbon pool. Just one paragraph thread is sufficient. Avoid later repetitions.

Page 4 Lines 77 – 95

There are a lot overstatements or incorrect sentences in this paragraphs – examples below.

"CDOM is a major light-absorbing substance, which is responsible for much of the color in waters (Reche et al., 1999). "

First of all CDOM is not a substance – it is a heterogeneous mixture of water soluble organic compounds. CDOM have specific optical properties, it absorbs light in UV and visible spectral range and those optical properties change spectral properties and light intensity in water column. From physical point the water color, that can be sensed by human eye (or

radiometer) is a ratio between scattering coefficient and sum absorption and scattering coefficients. As CDOM absorption contributes strongly to total absorption coefficient and thus changes the $b(\lambda)/(a(\lambda)+b(\lambda))$ ratio, the visual effect of CDOM presence in water is change of color to yellowish (or brownish when CDOM concentration is high). That is why first definition of CDOM was "yellow substance".

Page 5 Lines 78 – 80

"The chemical structure and origin of CDOM can be characterized by its absorption coefficients ($a_{CDOM}(\lambda)$) and spectral slopes (De Haan and De Boer, 1987; Helms et al., 2008)."

CDOM absorption coefficient $a_{CDOM}(\lambda)$ cannot characterized CDOM chemical structure – first CDOM is a mixture of countless compounds, second CDOM absorption spectrum is featureless and monotonic and does not contain any spectral peaks that could be associated with specific compounds. Spectral slope of CDOM absorption spectrum is only an approximate proxy of the relative contribution of fulvic acids and humic acids in this mixture, see Carder et al 1999 for details. There many physical and microbial process influencing effective values of the spectral slope coefficient, so Author shall be caustions using such a definitive statements. All spectral indices cited in following sentences, like SUVA(254), SR etc shall be cited correctly as defined by their Author. Those spectral indices are only optical proxies correlated with sum physical (SR – molecular weight) or chemical (SUVA(254) – relative aromaticity) characteristics of CDOM.

Page 5 Lines 83 – 85

"…while the ratio of CDOM absorption at 250 to 365 nm (aCDOM(250/365), herein, M values) …"

This ratio shall be defined as $a_{CDOM}(250)/a_{CDOM}(365)$ - not $a_{CDOM}(250/365)$ – this a formal error – please correct throughout the whole manuscript text

"…to track the changes in DOM molecule weight (De Haan and De Boer, 1987; Zhang et al., 2010) and absorption intensity (Song et al., 2013)."

The ratio of two absorption coefficient at two different wavelengths tell nothing about intensity of the absorption process - it only give a relative information who much absorption is stronger(weaker) at one wavelengths relative to other wavelength. Magnitude of ratio by spectral values of absorption coefficients could be an effect of some reasons – according to De Haan and De Boer, 1987 – change in molecular weight). Please cite literature correctly.

Page 5 Lines 91 – 93

"It should be noted that $a_{CDOM}(440)$ is usually used by remote sensing community due to this wavelength is less affected by phytoplankton (Lee et 93 al., 2002)."

This sentence is a complete nonsense. The principle and highest phytoplankton pigments absorption is located at 443 nm. Therefore the effect of phytoplankton absorption on total absorption is highest here. The CDOM absorption in visible range have overlapps with

phytoplankton pigments absorption at 443, and this effect was introducing errors in ocean color remote sensing algorithms for retrieval of chlorophyll a concentration. In most cases chlorophyll a was overestimated by those algorithms that were not taking into account CDOM absorption at 443 nm. That was a reason for reporting $a_{CDOM}(443)$ in literature, and inclusion of this parameter particularly in semi0anlytical remote sensing algorithms.

Page 6 Lines 102 – 104

"With compositional change, the absorption feature of CDOM and its relation to DOC varies correspondingly, but the relationship between CDOM and DOC is far from solved (Gonnelli et al., 2013)."

CDOM is a complex mixture of heterogeneous organic compounds, each having individual optical properties. Therefore, the estimation of the universal bulk carbon-specific CDOM absorption coefficient, $a^*_{CDOM}(\lambda)$, defined as the ratio $a_{CDOM}(\lambda)$/DOC, seems almost unfeasible (Woźniak and Dera, 2007). Therefore value of $a^*_{CDOM}(\lambda)$ may change an order of magnitude in short spatial scale (e.g. Del Vecchio and Blough, 2004; Kowalczuk et al., 2010, Mar Chem 118, 22-36). .

Please consider to rewrite a whole paragraph between lines 77 – 105

Page 6 Line 119

"… for example the Finish Gulf (Kowalczuk et al., 2006) …"

Wrong citation. Paper by Kowalczuk et al., (2006) said nothing about relationship between $a_{CDOM}(350)$ and DOC. This relationship has been presented for Baltic Sea surface waters (not Gulf of Finland) in paper by Kowalczuk et al., (2010) (Oceanologia, 52(3), 431-471). Remove citation to Kowalczuk et al., 2006.

Page 7 Lines 131 – 134

" According to Fig.1, the proposed hypothesis suggests that the main source of …."

Repetition. Please try to keep different thread together, do not repeat things that you have said before.

Materials and Methods

Page 9 Line 178

" … converted to in situ salinity units (PSU) in the laboratory. "

The salinity in practical salinity scale has no units – it's a ratio of water electrical conductivity measured at given temperature and pressure to ratio of electrical conductivity of artificial sea water measure at standard temperature and pressure. This phrase shall be written as follow:

… converted to in situ salinity, expressed in practical salinity scale (PSU), in the laboratory.

Page 9 Line 190

“Chlorophyll-a (Chl-a) was extracted and concentration was measured using a Shimadzu UV-2050PC spectrophotometer (Song et al., 2013).”

Detailed method of spectroscopic measurements of chlorophyll a concentration shall be given, or at least a proper reference to equation that converts measurer absorbance of pigments extract to chlorophyll a concentration shall be cited. Song et al., are not authors of this method, it has been proposed first by Strickland and Parsons, 1972.

Results and discussion

The whole section shall be rewritten to two sections: Results - where Authors presents their own results, and Discussion – where Authors give interpretation of their results.

Page 11 Line 219

Chl-a concentrations (46.44±59.71 μg/L) changed from 0.28 to 521.12μg/L, with the mean of 46.44 μg/L.

Redundancy – you give the same value of averaged chlorophyll a concentration twice in the same sentence. Correct.

Page 14 Lines 285 – 287

Phytoplankton degradation may contribute relative large portion of CDOM and DOC in these water bodies (Zhang et al., 2010), due to the lower molecular weight, its absorption is different from that derived from terrestrial systems (Helms et al., 2008).

Wrong citation again. Helms et al., 2008 neither worked in fresh water bodies nor studied phytoplankton degradation products. They have focused on photobleaching effect on spectral slope and have established a spectral slope ratio as proxy for molecular weight. I do not see any information on spectral slope ratio in this paper – so why do you discuss with Helms et al., 2008. This paper does not present any CDOM absorption spectral slope data at all.

The same wrong citation to Helms et al., (2008) repeated on the same page at line 291.

Page 14 – 15, Lines 297 - 300

“As suggested by Brezonik et al. (2015) and Cardille et al. (2013), CDOM in the eutrophic waters or those with very short resident time may show seasonal variation due to algal bloom or hydrological variability, while CDOM in some oligotrhopic lakes or those with long resident time may show an opposite pattern.”

This is a part of discussion, but I do not know which part of results is discussed here. Authors did not spent a lot of time on trophic status of studied lakes. The chlorophyll a is mentioned only in one sentence at the beginning of Results section.

Page 15 Line 318

" … were found and less colored portion of DOC was presented in waters in semi-arid to arid regions … "

I did not found any data on $a_{CDOM}(\lambda)$/DOC relationship in this paper, neither in the text, tables nor figures. What Authors refer to?

Page 16 Line 339

" … which is consistent with the findings from Helm et al. (2008) …"

Wrong citation again. There is no single line in paper by Helms et al., (2008) on DOC vs. $a_{CDOM}(l)$ relationship.

Page 19 Line 397

" … ice and snow cover shielded out most of the solar radiation that might cause a series of biochemical process for CDOM contained in water …"

What specific processes Authors refer to? Citation need to support this statements, otherwise I suggest to delete it.

Page 20 Line 428

"This has important implication for remote sensing of DOC through the CDOM absorption as a bridge (Zhu et al., 2014; Kuster et al., 2015; Brezonik et al., 2015)."

What kind of bridge CDOM absorption is ?

Page 23 Line 491

"Most of the paired data sitting close to the regression line except some scattered ones."

Very bizarre sentence that contains no useful information. Delete it.

Conclusion

Delete first two sentences that refer to remote sensing. This paper is about DOC vs. $a_{CDOM}(\lambda)$ relationships in different water bodies not about remote sensing algorithms.

Page 24 Lines 514 – 516

The slope values of saline lakes and urban waters were close to unity, slope values of river water were highest (~ 3.1), and slope values of other water types were in between.

Repetition of results – consider to delete.

Acknowledgements

"Last but not the least, the authors 534 would like to thank the editor and two anonymous referees ….."

Has this manuscript been submitted to other journal and reviewed before current review?

Figure 3 and 5, 8, 9

Y axis legend on figure 3, 5, 8, 9

Is: $a_{CDOM}275$ (m-1), should be $a_{CDOM}(275)$ [m^{-1}] – please correct accordingly in all specified figures.

Figure 4

Add information to legend – what CDOM absorption coefficient, $a_{CDOM}(\lambda)$ is presented on 3 panel of Figure 4.

Figure 4

The same remark as for figures 3, 5, 8, 9 – correct Y axis legend to $a_{CDOM}(440)$ [m^{-1}]

Figure 7.

Figure 7 legend the ratio shall be defined as $a_{CDOM}(250)/a_{CDOM}(365)$ - not $a_{CDOM}(250/365)$. Panel a Y axis SUVA(254) dimension is [m^2 g^{-1}].

Figure 9

Scales on panel c graph shall be expressed in decimal logarithms log-log. The regression shall be fitted to power function – so it will be linear in log-log scale. See examples in paper by Kowalczuk et al., (2010) (Oceanologia, 52(3), 431-471).

Table 2

Add units to DOC and $a_{CDOM}(440)$ as in Table 1.

Best regards,

Piotr Kowalczuk