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Discussions

Interactive comment on "A systematic examination of the relationships between CDOM and DOC in inland waters in China" *by* Kaishan Song et al.

Kaishan Song et al.

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Interactive comment on "A systematic examination of the relationships between CDOM and DOC in inland waters in China" by Kaishan Song et al.

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May 17, 2017 Christian Stamm, Ph.D. Associate Editor Hydrology and Earth System Science

Attn: ReviewofthemanuscriptbyKaishanSong,YingZhao,ZhidanWen,ChongFang, 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 ïňĄeld 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 coefiňĄcient at selected wavelengths, 275 and 400 nm. They have showed that both values of the slope coefiňĄcient of the linear regression between considered variables and values of determination coefiňĄcient 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 signiïňĄcant variability of in regression slope coefiňĄcient 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 ïňĆaws: 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 difiňĄcult 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 reïňĆectance – the geophysical variable that is physically measured by radiometers placed on spaceborne or airborne platforms. I also strongly recommendthat Author shall present their own results and later give their interpretation in Discussion.

Responses: The authors thank for the positive comments on the overall quality of the manuscript, particularly for the data set. Also, the authors thank for Professor Kowalczuk pointing out the two major flaws, which we have addressed in the revised manuscript by shortening or removing some unnecessary parts relevant to remote sensing application in the Introduction section; further, we will separate Results section with Discussion section in the revised manuscript.

Detailed comments.

Abstract

Page 1 Lines 12 – 13 "An algorithm has been developed to retrieve DOC via CDOM absorption (aCDOM) at 275 and 295 nm for coastal waters, but it is still unclear for the relationship between DOC and aCDOM in other types of waters." Thissentencehasnosupportinpresentedresults.Authorshavederivedregressionrelationshipbetweena CDOM(275)andaCDOM(440)bu optics community. Consider to remove this sentence. Abstract shall described your own ïňĄndings - and shall not contain discussion. When you mention spectral values of aCDOM(ïAËŻËĞn) – use the symbol l in parenthesis and then indicate speciïňĄc wavelengths.

Responses: The authors thank for the instructive and specific comments, we removed this sentence in the revised manuscript. The very instructive comment for presentation of aCDOM by including specific wavelengths was incorporated throughout the manuscript during the revision.

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 aCDOM(ïAËŻËĞn) but not proposed any remote sensing algorithm. Algorithm need to be developed for different water types and later tested and validated and ïňĄnally optimized. Please rewrite this sentence. It would be OK in discussion as it points the future direction of your work. Abstract shall brieïňĆy and comprehensively present your results.

Responses: The authors thank for the thoughtful comments, we rewrote this sentence in the revised manuscript to avoid misunderstanding with remote sensing of DOC through the linkage with CDOM, we will try the best to achieve a concise and comprehensive abstract in the revised manuscript.

Introduction Please reduce length of introduction signiïňĄcantly. 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 sufiňĄcient. Avoid later repetitions.

Responses: The authors thank for the comments, the Introduction section was separated into current knowledge of CDOM biogeochemistry, optics and remote sensing applications. Thanks again for the suggestions that really make the Introduction presented more logically.

Page 4 Lines 77 – 95 There are a lot overstatements or incorrect sentences in this paragraphs – examples below. "CDOMisamajorlight-absorbingsubstance,whichisresponsibleformuchofthecolor 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 speciïňĄc 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 (orradiometer) is a ratio between scattering coefïňĄcient and sum absorption and scattering coefïňĄcients. As CDOM absorption contributes strongly to total absorption coefïňĄcient and thus changes the b(ïAËŻËĞn)/(a(ïAËŻËĞn)+b(ïAËŻËĞn)) 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 ïňĄrst deïňĄnition of CDOM was “yellow substance”. Responses: The authors thank for the very detailed comments, which really help for clarifying the role that CDOM plays in water color remote sensing, or the water leaving radiance by optically active constituents. Your kind suggestions were absorbed and incorporated in the revised manuscript, and some of the inappropriate statements were rephrased.

Page 5 Lines 78 – 80 “The chemical structure and origin of CDOM can be characterized by its absorption coefïňĄcients (aCDOM(λ)) and spectral slopes (De Haan and De Boer, 1987; Helms et al., 2008).”

CDOM absorption coefïňĄcient aCDOM(ïAËŻËĞn) cannot characterized CDOM chemical structure – ïňĄrst 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 speciïňĄc 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 inïňĆuencing effective values of the spectral slope coefïňĄcient, so Author shall be cautious using such a deïňĄnitive statements. All spectral indices cited in following sentences, like SUVA(254), SR etc shall be cited correctly as deïňĄned 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.

Responses: The authors really thank for the reviewer’s very instructive comments. These helpful suggestions or comments were adopted in the revised manuscript.

Page 5 Lines 83 – 85 “...while the ratio of CDOM absorption at 250 to 365 nm (aCDOM(250/365), herein, M values) ...” ThisratioshallbedeïňĄnedasaCDOM(250)/aCDOM(365)-notaCDOM(250/365)–this a formal error – please correct throughout the whole manuscript text.

Responses: The authors thank for the instructive comments. The authors replaced “aCDOM(250/365)” with “aCDOM(250)/aCDOM(365)” throughout the revised manuscript.

“...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 coefïňĄcient 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 coefïňĄcients could be an effect of some reasons – according to De Haan and De Boer, 1987 – change in molecular weight). Please cite literature correctly.

Responses: The authors really thank for the reviewer’s very instructive comments. The right citations were provide in the revised manuscript.

Page 5 Lines 91 – 93 “It should be noted that aCDOM(440) is usually used by remote sensing community due to this wavelength is less affected by phytoplankton (Lee et 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 aCDOM(443) in literature, and inclusion of this parameter particularly in semi0anlytical remote sensing algorithms.

Responses: This comments is very instructive, that really help me understand the underlying reason why aCDOM(443) was reported in remote sensing community. Thanks again for the reviewer's valuable comments.

Page 6 Lines 102 – 104 "With compositional change, the absorption feature of CDOM and its relation to DOC variescorrespondingly,buttherelationshipbetweenCDOMandDOCisfarfromsolved (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 carbonspeciïňĄc CDOM absorption coefïňĄcient, aâAËŻËİOCDOM(λ), deïňĄned as the ratio aCDOM(λ)/DOC,seemsalmostunfeasible(Woz′niakandDera,2007). Thereforevalue of aâAËŻËİOCDOM(λ) 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).

Responses: The authors really thank for the instructive comments, which has been incorporated in the revised manuscript, and these references recommended by the reviewer were also adopted during the manuscript revision.

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

Responses: Again, the authors thank for the comment, and the whole paragraph was rewritten in the revised manuscript, and all the reviewer's comments for the whole paragraph listed above were also incorporated during rewriting of this part.

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 aCDOM(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.

Responses: The authors thank for the very specific comment, the right study site and

right reference literature were incorporated in the revised manuscript.

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.

Responses: The authors thank for the valuable comments, these repetitions were avoided in the revised manuscript.

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 artiïňĄcial 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.

Responses: The authors really appreciated the valuable suggestion, which has been adopted in the revised manuscript.

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 measure absorbance of pigments extract to chlorophyll a concentration shall be cited. Song et al., are not authors of this method, it has been proposed ïňĄrst by Strickland and Parsons, 1972. Responses: The authors thank for the instructive comments, and the proper citation was added in the revised manuscript.

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

pretation of their results.

Responses: The authors for the instructive comments, as aforementioned, this section was divided into Results and Discussion sections in the revised manuscript.

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.

Responses: The authors for the instructive comments, the redundancy was avoided in the revised manuscript by deleting "with the mean of 46.44 μg/L".

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.

Responses: The authors thank for the comments. There might a misunderstanding for the reference, here the authors try to say that phytoplankton degradation may change the spectral slope due the change of molecular weight for some components of the

mixture compounds. The wrong citation was removed, and the proper ones were added in the revised manuscript.

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.

Responses: The authors really appreciated this comments. This sentence was removed since it did not have a strong link with the current study, and we did not pay much attention to the impact of eutrophication on CDOM absorption characteristics.

Page 15 Line 318 " ... were found and less colored portion of DOC was presented in waters in semi-aridto arid regions ... "

I did not found any data on aCDOM(ïAËŻËĞn)/DOC relationship in this paper, neither in the text, tables nor ïňĄgures. What Authors refer to?

Responses: The authors thank for this comments, and sorry for the misleading. In the first submitted version, the relationship between DOC and CDOM were analyzed based on the SUVA254 classification, which has connection with aCDOM(ïAËŻËĞn)/DOC relationship, this part was not full removed from the previous version, that caused the misunderstanding. We remove this sentence in the revised manuscript, thanks again for the valuable comments.

Page 16 Line 339 " ... which is consistent with the ïňĄndings from Helm et al. (2008) ..." Wrong citation again. There is no single line in paper by Helms et al., (2008) on DOC vs. aCDOM(l) relationship.

Response: The authors thank for the comment, there might a misunderstanding for the expression. Here the author did not state the relationship between DOC and CDOM, rather, we tried to say that CDOM in head waters tend to have high molecular weights, thus lower spectral slope values, which has nothing to do with the relationship between CDOM-DOC. To avoid misunderstanding, we rephrased this sentence in the revised manuscript.

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

Response: Thanks for the comment, this sentence was deleted in the revised manuscript.

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 ?

Response: Thanks for the comment, we rephrased this sentence in the revised manuscript to make it clear. Here, the authors try to say that CDOM is a optically active constituent that can be remotely sensed, but not DOC. Remote sensing of DOC is based on the relationship between DOC-CDOM, thus CDOM absorption is a bridge for DOC estimate through remotely sensed data.

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.

Response: Thanks for the comment, this sentence was deleted in the revised manuscript.

Conclusion Delete ïňĄrst two sentences that refer to remote sensing. This paper is

about DOC vs. aCDOM(ïAËŻËĞn) relationships in different water bodies not about remote sensing algorithms.

Response: The authors really thank for the very valuable comments, the first two sentences were removed as suggested.

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 (âĹij 3.1), and slope values of other water types were in between.Repetition of results – consider to delete.

Response: The authors really thank for the very valuable comments, theserepetitive statements were removed in the revised manuscript.

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?

Response: thanks for the comment, yes, this manuscript was submitted to HESS in 2016, and the handling editor (Professor Stamm) suggested to resubmit to HESS, thus the previous acknowledgements were kept.

Figure 3 and 5, 8, 9 Y axis legend on ïňĄgure 3, 5, 8, 9 Is: aCDOM275 (m-1), should be aCDOM(275) [m-1] – please correct accordingly in all speciïňĄed ïňĄgures.

Response: The authors really thank for the very valuable comments, Figure 3, 5, 8, and 9 were reproduced with the suggested labels.

Figure 4 Add information to legend – what CDOM absorption coefïňĄcient, aCDOM(ïAËŻËĞn) is presented on 3 panel of Figure 4.

Response: The authors really thank for the very helpful comments, CDOM absorption coefficient wavelength of three panels in Figure 4 were added in the revised manuscript.

Figure 6 The same remark as for ïňĄgures 3, 5, 8, 9 – correct Y axis legend to aC-

DOM(440) [m-1] Figure 6.

Response: The authors really thank for the very valuable comments, the Y axis legend for Figure 6 wascorrected in the revised manuscript.

Figure 7 legend the ratio shall be deïňĄned as aCDOM(250)/aCDOM(365) - not aCDOM(250/365). Panel a Y axis SUVA(254) dimension is [m2 g-1].

Response: The authors really thank for the very valuable comments, all your kind suggestions were incorporated in the revised manuscript.

Figure 9 Scales on panel c graph shall be expressed in decimal logarithms log-log. The regression shall be ïňĄtted to power function–so it will be linear in log-logscale. See examples in paper by Kowalczuk et al., (2010) (Oceanologia, 52(3), 431-471).

Response: Thanks for the valuable comments, panel c of figure 9 was reproduced as suggested.

Table 2 Add units to DOC and aCDOM(440) as in Table 1.

Response: Thanks for the suggestion, units for DOC and aCDOM(440) were added in Table 2.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-179, 2017.