

***Interactive comment on “Spatio-seasonal variability of chromophoric dissolved organic matter absorption and responses to photobleaching in a large shallow temperate lake” by María Encina Aullo-Maestro et al.***

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Response to Reviewers – Aulló-Maestro et al. Biogeosciences Discuss., doi:10.5194/bg-2016-329, 2016 Anonymous Referee #1 General comments. This paper documents variability in DOM along a longitudinal transect in Lake Balaton during 2014. The authors report that DOM concentrations generally ranged from 8 to 16 mgC/L in surface waters (which is relatively high), with values above 10 mgC/L mostly in the eastern end of the lake which receives inflow from a large wetland. They also report four optical properties of the DOM (absorbance, spectral slope coefficient, SUVA

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and E2/E3) as potential indices of DOM source or internal processing (especially photodegradation). Unfortunately, the choice of wavelengths for some of the optical measurements was not optimal, thus limiting comparison with other systems and studies.

We agree with the reviewer that this can limit the comparison with other systems and studies, however, and as justified after in the text, this paper is strongly motivated by the understanding of the changes on the inherent optical properties of CDOM particularly with reference to the implications for remote sensing. In this framework, remote sensing studies often use 412 nm or 440 nm (Carder et al. 1989; Nelson et al. 1998; Schwarz et al. 2002) to describe CDOM absorption because information in the UV cannot be obtained from space. For this reason, and to ensure consistency with previous publications, our results are more strongly based on absorption in the blue rather than the UV.

Although the paper reports apparently new information about Lake Balaton, there are several matters in the text, tables and figures that will require re-thinking and major revision.

We wish to thank the reviewer for this very thorough and constructive review. We agree with most of the suggestions and have therefore modified the text according to them. We think they have greatly enhanced the quality of the paper.

Specific comments. 1. Abstract. Line 35. The data on Fig 9c and 9d are not convincing evidence that UV irradiation caused any change in the absorbance of “autochthonous” DOM. Omit sentence R1. The sentence has been omitted as suggested 2. Abstract. Omit last two sentences. Nothing new here. R2. The sentence has been omitted as suggested 3. Lines 70-73. Unclear sentence. What nutrients are we talking about? Re-think and re-write. R3. We agree it sounded like an incomplete sentence and have therefore rephrased it to now read as: “CDOM can be remineralised by bacteria acting as a source of inorganic nutrients (Buchan et al. 2014), which is important for phytoplankton nutrition” 4. Line 93. The wavelength 440nm is not commonly used

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for CDOM. 440nm is routinely used for Chl-a because it is the absorbance maximum for that pigment. The preferred wavelength for CDOM is in the UV, usually less than 370nm. Choice of 440 (blue) rather than UV needs to be justified. R4. As justified later in the text (lines 196–198) and explained before, the fact of this study being strongly motivated by the understanding of the changes on the inherent optical properties of CDOM particularly with reference to the implications for remote sensing and to ensure consistency with previous publications, our results are based on CDOM absorption measurements at 440 nm. 5. Line 95. The spectral slope coefficient recommended by Helms et al (2008) and by Fichot and Benner (2012) is calculated over the UV range 275-295 nm. But in Balaton, the authors used a very different range (350-500 nm). Choice of this range needs to be justified given that the authors cite Helms et al and Fichot and Benner. R5. We agree our choice needs to be justified and as modified in the text (line 201-203): “This range of calculation was consistent with Babin et al. 2003 and Matsuoka et al. 2012 amongst others and is more relevant to remote sensing studies than the use of wavelength ranges that extend into the UV spectrum”. 6. Line 113-120. Not true. There is a relatively rich literature on DOM in temperate lakes. Literature search needed. R6. Modified in text as suggested (lines 114-115): “There is a relatively rich literature on DOM in temperate lakes (e.g., Zhang et al. 2011; Read & Rose 2013; Müller et al. 2014) but few studies have focused on large shallow lakes like Lake Balaton with a strongly continental climate and hence our understanding of the variability in CDOM optical properties in these systems is comparatively poorer. 7. Lines 124-127. For objective #1, add “over the course of one year.” Done For objective #3, since there were no direct measurements of the underwater light field (e.g.Kd PAR, or spectral Kd), this is not a bona fide objective. R7. We agree the fact of not providing measurements of the underwater light field makes objective 3 unreachable and this has therefore been deleted. 8. Line 174-175. One year of data is not sufficient to document a representative seasonal cycle. Caveat needed. R8. A clarification has been written specifying the seasonal variability was recorded and studied over the course of seven months (March to September 2014). 9. Line 180.

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A 0.7um filter will not remove small phytoplankton, bacteria or large organic colloids. Explain why 0.2um filters were not used, and what the consequences of including small particulates might be. R9. In response to the reviewer's suggestion, the use of 0.7 um filters has been justified in the text (lines 178-183). They were selected for DOC measurements because of their compatibility with other measurements in POC (interesting in partitioning dissolved and particulate), chl- a, TSM, PC etc. Due to their larger nominal pore size, GF/F are expected to allow higher number of bacteria, viruses and colloids, which are not considered dissolved to pass through. This could lead to an overestimation of the DOC in the water samples. However, the differences due to filter are expected to be small and its importance is lessened given that DOC was only used to correlate with aCDOM. Also due to their design GF/F normally retain particles smaller than is mentioned by the manufacture. 10. Lines 211-212. Helms et al (2008) recommended S275-295 as an indicator of in situ DOM photoprocessing for future DOM studies (not E2:E3). That needs to be acknowledged. R10. We agree with the reviewer and this text has been deleted to avoid confusion. 11. Section 2.5. CDOM photodegradation. Except for Comment #13 (below), this is a very interesting and well planned experiment. Kudos. R11. We very much appreciate the reviewer's comments on the merits of the CDOM bleaching experiment. 12. Lines 226-234. In nature, autochthonous DOM is more likely the exudates from live phytoplankton rather than dead cell remains (which would be colonized by microbes and sink out). Since exudates would be in the supernatant not the pellet, the method of grinding and digesting the pellet needs to be justified. R12. We partially agree with the reviewer, cell exudates are an important source of autochthonous CDOM but other natural processes such as grazing by zooplankton, (Levine et al. 1999) or the presence of viruses causing the lysis of phytoplankton cells (Suttle et al. 1990) can also result in release of CDOM. The process of pelleting, cleaning and breaking cells helped to mimic the effect of these processes and also ensure sufficient CDOM was produced for our experimental needs. The optical properties of the resulting CDOM were in line with expectations for autochthonous material. In the text we will comment on that fact

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the physical breaking cells has the potential to release cellular material that might not be excreted the optical properties of the material produced was consistent with that for autochthonous CDOM. Moreover, this material can also be released by cell lysis due to grazing or viruses in the natural environment (Levine et al. 1999, Suttle et al. 1990) 13. Section 3.1. Seasonal variability. Caveat needed to acknowledge that seasonal changes were characterized for only 1 year, and may not represent the “average” seasonal cycle across multiple years with different weather patterns R13. As suggested by the reviewer, it has been stressed in the text that seasonal changes were only measured for one year and therefore may not represent the typical seasonal cycle observed over longer time periods. 14. Line 263. Rephrase sentence. With the exception of STO. Basin 1, the data on Fig 2 do not indicate high CDOM variability across most of the lake. In 5 of the 6 basins, DOC and a(440) were relatively stable. R14. We agree with the reviewer that this was unclear, and the sentence has been clarified. 15. Line 286. The evidence for two peaks in DOC on Fig 2 is weak at best. Rephrase. R15. We accept the reviewer’s comment here and have revised the text here accordingly. There is evidence of two peaks at the inflow (summer and autumn) with the latter coinciding with the timing of peaks elsewhere. However, the evidence is weak for more than one elsewhere. 16. Line 296. Add “during July when interbasin differences were likely to be highest.” R16. Accepted and modified as suggested. 17. Lines 303 to 308. This paragraph needs to be re-thought. The range of S<sub>cdom</sub> across stations is actually quite wide in the scheme of things for natural waters. Compare to Helms et al (2008) and other studies where S<sub>cdom</sub> gradients have been reported. R17. We appreciate the reviewer’s comment about the significance of these results and have modified the text to better emphasise the significance of the variability observed in SCDOM. 18. Line 318. Re-think. Concluding that DOC varied more than these two optical properties seems a consequence of scaling rather than a property of the variable. Comparison of CVs or Z-scores is needed here R18. Reviewer 1 is correct and actually DOC showed greater variability through the system than for SCDOM (CV = 0.053) but smaller than for aCDOM (440) (CV = 2.065). Sentence

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has been correct accordingly to this. 19. Section 3.3. Photodegradation experiment. This section needs to be re-written. The results shown on Figure 9 indicate that UV irradiation had a significant effect only on the absorbance of allochthonous cdom. This result is consistent with the data on Fig 10a. That’s all that one can say with confidence about the photodegradation experiment. There is no discernible effect on S<sub>cdom</sub> or on “autochthonous” cdom in these data. R19. We agree with the reviewer and the sentence referring to autochthonous CDOM has been deleted. 20. Section 4. Discussion. This section has some overstatement, speculation and misinterpretation that needs to be removed. R20. We agree with the reviewer with some over-reaching statements and misinterpreted results and have therefore removed several statements along the section and toned down others a. L 356-363. Actually, DOM across most of the lake is relatively constant (Fig 2&5c), as observed in other large lakes. High DOM in Balaton was restricted to stations near the inflow from a high DOM river. R20A. In studies of other large lakes, such stations were likely not sampled because they skew the data and contribute little to the total lake mass of DOM. We appreciate the reviewer’s comments and agree that the variability observed in the western basin was not observed over the rest of the lake. However, the influence of the DOM entering the lake from the River Zala at times stretches across the western basin, which equates to an area of approximately 100 km<sup>2</sup>. The high concentrations of DOM observed in the west are therefore not an insignificant component of the total lake DOM. Moreover, the high input of DOM will certainly influence biological processes in the highly productive western part of the lake. We have amended the text here to emphasise that marked variability was confined to the western part of the lake b. L364-374. It is an exaggeration to say that aCDOM and DOC varied seasonally throughout the system. This was only true for Basin I. In the other 4 basins, aCDOM and DOC were relatively constant throughout the year (FIG 2) R20B. The text here has been toned down in line with the reviewer’s comments c. L413-424. Photomineralization would not affect S<sub>cdom</sub>, it would only affect DOM concentration. But photobleaching can have a large effect on S<sub>cdom</sub> (e.g. Helms et al, 2008), and the data for Lake Balaton shown on figs 9

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and 10 suggest that the humics are the fraction of DOM that is being bleached. R20C. This sentence has been revised such that it no longer implies that mineralisation influences SCDOM and rather emphasises that the effect is on the DOM pool more broadly d. L457. Again, microbes mineralize (respire) DOM or turn it into biomass rather than bleaching it R20D. We agree with the reviewer and the text has been modified as suggested e. L471-480. This is an over-interpretation of the results shown on Fig 9. It is unsupported speculation. Omit paragraph R20D. Paragraph has been omitted as suggested f. L481-491. This is also over-interpretation and speculation. In fig 9c, there was no difference between the irradiated “autochthonous” samples and the dark controls. In 9b, there were no controls. Omit paragraph R20F. Paragraph omitted as suggested g. L492-500. The low fluorescence signal from “autochthonous” DOM is likely due to its low concentration. Re-write R20G. We agree with reviewer’s 1 suggestion and the sentence has been re-written h. L 505-519. Absent measurements of the underwater light field in the lake, it is speculation to propose light limitation by DOM in such a shallow, well-mixed and eutrophic lake. Ten percent of incident solar irradiance is generally sufficient to support strong phytoplankton growth, and the authors would need to show that attenuation by DOM was sufficient to reduce downwelling light penetration below that level in the epilimnion. Re-write paragraph R20H. High DOC in the western basin certainly impacts the quality and quantity of light available for photosynthesis but the authors acknowledge we cannot demonstrate that light limitation of primary production occurs near the inflow of the River Zala from the data presented in this paper. We have revised the text to reflect this. 21. Table 1. Change notation to (mean±SD). Specify date range in heading R21. Table 1 has been modified as suggested 22. Table 2. Are these data for July 2013 or July 2014 (or both)? If both, how was interannual variation accounted for. Specify dates in heading R22. Specifications have been made on Table 2 as suggested 23. Fig 2. Check the trace for aCDOM(440). It behaves weirdly during autumn in some of the plots. Needs to be fixed R23. Graphs have been corrected as suggested 24. Fig 5. Add “measurements made in July...” to legend. R24. Changes have been made to legend

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of figure 5 as suggested by Reviewer 1 25. In Fig 5c the 5 DOC categories exaggerate actual spatial variability. The three highest categories are separated by less than 1 mgC/L, while the low category spans more than 8 mg.C/L. The category indicated by a yellow X is highly questionable (zero DOC? I don’t think so). Re-think this. R25. Reviewer’s 1 comment made us realise some typographical error involved in the figure preparation and have been corrected 26. Fig 9. Panel 9d is superfluous. Omit R26. We agree with reviewer’s comment and the panel has been deleted

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/bg-2016-329/bg-2016-329-AC1-supplement.pdf>

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