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Interactive Comment

# Interactive comment on "Towards a merged satellite and in situ fluorescence ocean chlorophyll product" by H. Lavigne et al.

#### H. Lavigne et al.

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General comments:

Point 1. Word significant (used in the paper numerous times) should be accompanied with some statistical method that is showing the significance of the comparison. For example, Figure 7, I can see that there are differences between method presented here and Boss et al [2008] method. How significant those differences are, I could see only if authors compare these two datasets, and use a specific statistical method (t-test or something similar) to show the significance of these differences.

Authors response: We agree with the referee. In most of the cases, we used improperly the word "significant" instead of "relevant" or "important". To avoid any misunderstand-





ing, we replaced, in the new version of manuscript, "significant" with synonyms, or we rephrased entirely the sentence. We additionally introduced the results of statistical tests when it was required for the discussion. We changed the text accordingly.

P11911 line 2 : "a significant scatter" was replaced by "an important scatter" P11911 line 29 : "less significant than expected" was replaced by "less relevant than expected" P11915 line 18: "significant differences" was replaced by "Important differences" P11915 line 20: "is significantly lower" was replaced by "is lower" P11915 line 24: "a significant scatter", this expression was totally removed. P11918 line 11: "significantly different results" was replaced by "different results" P11918 line 16; "could significantly improve" was replaced by "could improve"

Results of statistical tests:

p11906 line 8 : "Increasing temporal and spatial resolutions does not significantly modify the similarity between the HPLC and satellite estimations (tests of similarity on absolute percent difference: 8-day  $\pm 0.25^{\circ}$  with 8-day  $\pm 0.1^{\circ}$  pvalue=0.86; 8-day  $\pm 0.25^{\circ}$ with 1-day  $\pm 0.25^{\circ}$  pvalue=0.66)." p11916 line 6 : "does not significantly enhance the performance". This sentence refers to the statistical test developed above.

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Point 2. I see that authors are using a  $\pm$ 30% cutout line when comparing their results with the remote sensing chlorophyll. Is that 30% a random number or it has something to do with the fact that remote sensing derived chlorophyll has a 30% uncertainty level. If it does, it would be nice to state that somewhere in text; it makes your case stronger.

Authors response: We agree with the referee. The  $\pm$ 30% cutout line should represent the accepted uncertainty level of ocean color satellite [Chl-a] data. In the new version of the manuscript, the  $\pm$ 30% cutline was modified to  $\pm$ 35%, and two references were added to support this number (McClain, 2009; Moore et al., 2009). A new sentence was also added: "The 35% threshold value has been used because it is the accepted

averaged error of the satellite chlorophyll, McClain, 2009; Moore et al., 2009."

Specific comments

Point 3. 11901-11. Total Chlorophyll-a is not a pigment. It is a pigment sum. "...in all autotrophic marine organisms." This is not true. What about chemolithoautotrophs? I presume you meant photoautotrophs. I would recommend re-writing this sentence. This is an opening an opening sentence and it should have a strong statement and lead reader into the story.

Authors response: We agree with referee #3, and we changed the text accordingly: "In the ocean, Chlorophyll-a concentration (named "Chl-a" and corresponding here to the sum of chlorophyll-a, divinyl chlorophyll-a and chlorophyllide-a) is considered as a good, although not optimal, proxy for phytoplankton biomass (i.e. Cullen, 1982; Strickland, 1965)."

Authors response: We modified the text as suggested.

Authors response: We agree with referee. We modified the sentence to: "Although it is the most abundant biological oceanic measurement, [Chl-a] observations are, however,

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Point 4. 11901-16. Word Total is un-needed. Total chlorophyll-a has been previously defined (line 11) as Chl-a, so no need for word total.

Point 5. 11901-18. "...as with several other biological parameters," I would be free to say that most, if not all biological parameter measurements are scarce, and probably the most abundant biological oceanic measurement that is available is Chl-a.

scarce, particularly in comparison with the number of physical observations available (i.e. temperature and salinity)."

Point 6. 11902-3 This whole paragraph is poorly written. Especially since one of techniques mentioned here (fluorometry) is a base for in-situ measurement of chlorophyll fluorescence. Maybe a mention of one of the numerous reviews and comparison between these three techniques, that would make the reader realize why is the HPLC technique important.

Authors response: We agree that the difference between benchtop fluorometry techniques and in-situ fluorescence was not clear in the submitted version of the manuscript. The whole paragraph has been therefore reformulated and additional references have also been introduced: "The conventional and historical approach to measure [Chl-a] in the ocean is to filter water samples collected at different depths, which are further analysed using three principal benchtop methods: fluorometry (Holm-Hansen et al., 1965), spectrophotometry (Lorenzen, 1967) and chromatography (Mantoura and Llewellyn, 1983). The three techniques have different accuracy and precision. A general consensus indicates that the most accurate method is High Performance Liquid Chromatography (HPLC, Gieskes and Kraay, 1983, Hooker et al., 2009), which provides the concentrations of a large spectrum of phytoplankton accessory pigments in addition to Chl-a."

Point 7. 11902-8&9 "...which additionally provides the concentrations of a large spectrum of phytoplankton accessory pigments in addition to Chl-a." Un-needed repetition. Authors response: We removed the word "additionally".

Point 8-a. 11906-8. and Table 1 "Increasing temporal and spatial resolutions does not C6188

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significantly modify the similarity between the HPLC and satellite estimations. However, the number of match-ups strongly decreased." As I read this table, it is true that increase in temporal resolution results with the decrease in number of matchups. However, I would not agree with authors that increase in spatial resolution (from 0.25 to 0.1) but keeping the same temporal resolution (8- days) causes the strong decrease number of matchups (80.5 to 77.5). This is a table that is showing nicely that Boss et al [2008] approach is lowering down the regression strength, however from the results presented in table 1, I really see no reason for not using 8 day/0.1 deg boxes.

Authors response: We agree with the referee suggestions. Consequently, the matchup protocol is changed in the new version of manuscript (boxes of 8-day/ $0.1^{\circ}$ ). This modification led to the modification of most tables (see the new version of tables in annexe) and figures, although the overall method performances changed only slightly.

Point 8-b. It would be interesting to see how would the overall results look like if the spatial resolution is increased, and how does the increase/decrease in size of the pixel impact the overall matchup performance.

Authors response: The comparison of the two matchup protocols (8days/0.1° boxes, new version of Table 3, see the annexe document, and 8days/0.25°, previous version Table 4) indicates that the increase of the spatial size of the boxes does not improve the overall performances of our method. This result was expected, because we didn't observe a significant improvement of the satellite matchup (i.e. satellite estimations versus in-situ HPLC observations, Table 1), when spatial and temporal resolution are improved. We estimated then that this sensitivity analysis, although correct, does not bring any additional information to the manuscript and we decided to not further develop it in the text.

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Point 9. 11906 - 12. "For the three stations, only the HPLC and fluorescence data available for the 1998–2007 period were retained (i.e. the period of activity of the

SeaWiFS ocean color sensor)." This should me mentioned in the beginning of the Data section.

Authors response: We agree with the referee. We replaced the first sentence of the Data section: "In situ data from the long-term time-series data sets of stations BATS (Michaels and Knap, 1996, in the Sargasso Sea), DYFAMED (Marty et al., 2002, in the North Western Mediterranean Sea) and HOT (Karl and Lukas, 1996, in the North Pacific) were used over the 1998-2007 period (i.e. the period of activity of the SeaWiFS ocean color sensor)."

Point 10. 11907-11 .. or fluorometric...

Authors response: We agree and changed the text accordingly.

Point 11-a. 11908 -12. Non-photochemical quenching is a serious issue when it comes to fluorescence. I am of an opinion that it is something that is should be mentioned in the introduction to this paper.

Authors response: We agree with the referee. We added a new paragraph in the Introduction section: "This is particularly relevant in the surface layers, because of the non photochemical quenching (NPQ) of fluoresence. NPQ occurs when, in response to supra-optimal light irradiation, phytoplankton triggers photo-protection mechanisms, inducing a drastic decrease of the fluorescence to chlorophyll ratio (Kolber and Falkowski, 1993). The final effect of NPQ is a decrease of fluorescence at the surface, not paralleled by a Chl-a diminution (Xing et al., 2011; Sackman et al., 2008; Cullen and Lewis, 1995)."

Point 11-b. Authors here use correction proposed by Xing et al, however - this paper has not been published yet and I am not familiar with the details of this correction. I am, on the other hand familiar with the work of Sack-

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man et al [2008], and one developed for North Atlantic Bloom Experiment 2008 (see http://data.bcodmo.org/NAB08/Chlorophyll\_Calibration-NAB08.pdf) where auxiliary data are used to make this correction successful.

Authors response: We agree with the referee that our method of NPQ correction (based on the work of Xing et al, paper recently sent back to the editor after having been conditionally accepted in L & O methods) is simpler compared to more complex approaches, which are based on auxiliary data and on a more accurate modeling of NPQ mechanism (Sackman et al., 2008). However, specifically for the Sackman et al. 2008 method, the NPQ correction is not applicable, because the optical back scattering profiles as well as the daytime and nighttime fluorescence profiles are missing in our data set tests. Additionally, our rationale was to develop a method applicable with a minimum of auxiliary data other than fluorescence profiles and satellite ocean color [Chl-a] estimations. We decided then to maintain the rough NPQ correction of Xing et al. to keep as large as possible the range of applicability of our fluorescence correction method. We however mentioned that more elaborated methods for guenching correction exist, although they require more ancillary information than the Xing et al. approach we proposed. A sentence has been therefore introduced in the Method (3.2 parameters computation) section: "The most complex approaches (i.e. Sackmann et al., 2008) provide fluorescence corrections on the basis of (1) other proxies for phytoplankton (i.e. optical backscattering) or (2) nightlight fluorescence profiles which are not supposed to be affected by NPQ."

Point 11-c. Authors are stating that highest value encountered within the mixed layer was used as a reference point and for extraction to the surface. There are several reasons why such a simple correction is making me uncomfortable. Primarily, it is based on assumption that mixed layer is constantly mixed – vertical distribution of the phytoplankton in the mixed layers can be non-uniform and variable (from Sackman et al [2008] paper and personal experience). What if the increasing vertical pattern of the chlorophyll fluorescence (as a function of depth) is a reflection of the either changing

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abundance of the phytoplankton, changing community structure or just simple acclimation to the lower irradiance levels?

Authors response: We strongly agree with the referee that mixed and mixing layers could show different depths and that, consequently, phytoplankton distribution in the mixed layer could be irregular. In such a situation, we agree that the Xing et al. NPQ correction method, which assumes a uniform vertical distribution of the phytoplankton in the mixed layer, might omit important variable features which could therefore lead to erroneous reconstruction of the vertical [Chl-a] distribution. However, we still believe that the Xing et al., NPQ correction method in the process of fluorescence correction deserved to be implemented. Firstly, the impact of the NPQ effect on the overall method performances should be low, and a wrong parameterization of the quenching correction would induce only a relatively small error compared to other sources of error that methods introduce (i.e. satellite [Chl-a] estimation, determination of Chl-a integrated content. ...). To verify this assumption we compared "satellite-corrected" [Chl-a] with HPLC, on the overall dataset (BATS, DYFAMED and HOT), with and without the Xing et al. NPQ correction. We obtained a median ratio of "satellite-corrected" to HPLC [Chl-a] of 1.02 with Xing et al. NPQ correction (1.04 without any NPQ correction), a median percent difference of 31.4% (33.2% without NPQ correction) and a correlation coefficient between "satellite-corrected" and HPLC [chl-a] estimations of 0.68 (0.65 without NPQ correction). We interpret this effect by the combination of two factors. (1) We suppose that the number of data points of the fluorescence profile relevant for NPQ correction is relatively low compared to the number of points contained in the 1.5 Ze layer. (2) The use of integrated fluorescence content over the 1.5 Ze, instead of the surface fluorescence records only to correct the fluorescence profile, should strongly minimize the effect of the quenching correction. Although the overall impact of NPQ correction is low, we believe the application of the NPQ correction is still relevant, especially for surface data points. Indeed, the implementation of the Xing et al., method significantly reduces, for surface [Chl-a] estimations, the effect of NPQ (observed by an underestimation of "satellite-corrected" [Chl-a] estimations compared to HPLC). Us8, C6185–C6200, 2012

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ing only the 776 pairings of matchup points located in mixed layer of the three data sets tested, we obtained a median ratio of "satellite-corrected" to HPLC data of 0.93 if the quenching correction was previously applied and 0.78 if it was not. A Student test to compare "satellite-corrected" with HPLC ratios in the two conditions (i.e. with and without quenching correction) reveals that the positive effect of the Xing et al. NPQ correction is significant (pvalue < 0.01).

Point 11-d. How does one distinguish between "quenched" profiles and "nonquenched" profiles when one does not use other measurements to ground truth it?

Authors response: The Xing et al. NPQ correction is not based on the research of quenching affected profiles. The correction is applied on every profile. Every time the vertical distribution of fluorescence in the mixed layer is not uniform, the fluorescence profile will be modified by the quenching correction.

Point – 11e. I have done a fast calculation using your approach and came up with up to 8% error in MLD integrated chlorophyll for highly mixed open ocean waters.

Authors response: Although the point raised by the referee is pertinent, we considered this impact a second order effect compared to the total error on the method (35%) and to the other sources of error (see point 11-c). However, we agree with the referee that a more detailed discussion is required to better clarify the NPQ issues (see point 11-f).

Point 11-f.I am aware that this is not the paper focused on chlorophyll quenching correction, but it is an important part of the story and I would like to see more elaboration on methods, potential errors, etc.

Authors responses: In the new version of the manuscript, the NPQ issue is presented in the Introduction section (see point 11-a). The points examined before (Points 11-b, c and d) are now discussed in the Method section, with a whole paragraph dedicated to the proposed NPQ correction:

"Before computing the  $\alpha$  and  $\beta$  parameters, fluorescence profiles were corrected for

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non photochemical quenching (NPQ). Although NPQ represents a serious issue for the fluorescence calibration (Cullen and Lewis, 1995), methods exist to evaluate, and if possible correct, the NPQ impact on the Chl/fluorescence ratio (Sackmann et al., 2008; Xing et al., 2011). The most complex approaches (i.e. Sackmann et al., 2008) provided fluorescence corrections on the basis of (1) other proxies for phytoplankton (i.e. optical backscattering) or (2) nightlight fluorescence profiles which are not supposed to be affected by NPQ. Here, we applied the method of Xing et al. (in revision), which only requires mixed layer depth as input parameters to provide an NPQ correction. This method consists in extrapolating up to the surface the highest fluorescence value encountered within the mixed layer, identified after a smoothing of the profile (median filter) to reduce the noise in fluorescence data. Although the Xing et al. (in revision) method is less sophisticated than other approaches, its large range of applicability (i.e. only mixed layer depth is required as auxiliary parameter) better matches with the rationale of our approach, which is to develop a robust method to merge satellite and fluorescence profiles. Additionally, the use of the whole 1.5 Ze layer instead of only surface records to correct fluorescence allows for a minimization of the error which would be induced by a wrong NPQ parameterization. To assess the relevance of the Xing et al. (in revision) NPQ correction in the present merging method, we used the 776 pairings of matchup points located in mixed layer for the three data sets tested, obtaining a median ratio of "satellite-corrected" to HPLC data of 0.93 if the Xing et al. (in revision) NPQ correction was previously applied and 0.78 if it was not. A Student test to compare "satellite-corrected" with HPLC ratios in the two conditions (i.e. with and without guenching correction) reveals that the positive effect of the Xing et al. (in revision) NPQ correction was significant (p value < 0.01)."

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Point 12.11910-7 What kind of linear regression was used here? Type I or Type II. That would be nice to see. Also - for the sake of significance of these results - I would recommend stating p-values of each of these linear correlations, not only when you

#### need it to make a point (like in line 26 on page 11916)

Authors responses: We used type I regression. In the new version of manuscript it will be mentioned. All the p-values involved in regressions used to evaluate the performances of our method are lower than 10<sup>(-16)</sup>. Our interpretation is that, in the context of linear regression models, p-values are used to determine if the slope between variables x and y is significantly different from 0. We compared two datasets ("satellite-corrected" and HPLC) which should be equivalent, therefore it is normal that p-values should be very low. Hence, we believe that p-values are not very informative to evaluate the performance of our method. On page 11916 line 26, two different variables (i.e. raw fluorescence and [Chl-a]) are compared in the regression. We believe that this situation is different from the validation process, and that, in this case p-value can be informative.

Authors response: We agree with the referee and we modified the text accordingly. "The scattering of data for the three stations is relatively homogenous for values higher than 0.05 mg m-3 along the 1:1 line"

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Point 13.11910-24 here authors are stating that scattering of the data around the 1:1 line is relatively homogeneous, and later in discussion (11914 - line 6) they state that dispersion of datapoint under 0.05 mg m-3. Maybe mentioning here that scattering was relatively homogenous on values higher than 0.05 mg m-3.

Point 14. 11910-22 Paragraph starting here, discussing on the results presented in the Table 4. It seems to me that DYFAMED is an outlier, when compared with the rest of the dataset (HOTS and BATS). Although this paper is focusing mostly on performance of the correction approach, it would be interesting to see some "real" discussion here. For example, authors are stating that r2 is highest in DYFAMED since largest range of

chlorophyll was observed. But - other performance measurements (MPD and SIQR) are much worse for DYFAMED than for HOTS and BATS. Is it maybe because DY-FAMED is seeing largest phytoplankton biodiversity, therefore there are some other drivers of Chl F variability that could drive this error higher? It would be interested to say something later in discussion.

Authors response: We agree with the referee that the DYFAMED station is likely an outlier compared to HOTS and BATS. To discuss this point we added a new paragraph in the new version of the manuscript: "Not surprisingly, r2 is higher when large ranges of [Chl-a] are observed (i.e. DYFAMED). From performances statistics, however, the DYFAMED station appears likely different from BATS and HOTS, which showed similar performances. An explication of this difference could be ascribed to the phytoplankton variability, which at DYFAMED is characterized by a marked seasonality, determining a large phytoplankton biodiversity (Marty et al. 2002). Additionally, a strong interannual variability is observed at DYFAMED, with irregular succession of blooming and non-blooming years (Bosc et al., 2004). All the above could induce a higher variability of the [Chl-a] to fluorescence ratio which likely influences the performances of our approach."

Authors response: In the new version of manuscript this paragraph was totally rewritten (see also point 4 of response to referee #1). "The impact of the error of satellite observations on the "satellite-corrected" profiles is different for the three test stations analyzed (Table 4). At DYFAMED and BATS, the error of the "satellite-corrected" profiles (when compared with HPLC estimations) is largest when the difference between satellite and HPLC surface values are greater than "Ćś35% (Table 4, the 35% threshold value has been used because it is the accepted averaged error of the satellite chlorophyll, McClain, C. R., 2009; Moore et al., 2009). Conversely, at the HOT station, the

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Point 15. 11911 - 8-18. This paragraph doesn't read clearly. I suggest re-writing since the main points are getting lost.

final error appears to be hardly affected by the accuracy of the satellite observations."

## Point 16. 11914-4 to 7 First sentences - I don't understand - please re-write. Second sentence, maybe cite figure 1, just so reader can follow it clearly.

Authors response: The first sentence was re-written: "HPLC to "satellite-corrected" data spreading is also reduced, with most of the points concentrated along the 1:1 line" A reference to figure 1 was added in the second sentence.

Point 17. 11915-20 As stated in general comments - if authors use word significant, make sure that statistics are present here - fact that average difference was 0.15 mg m-3 is an interesting finding but does not have any statistical significance.

Authors response: We agree and replaced the word "significant" by "important" in this case (see also Point 1)

Point 18. 11916-3. I really don't understand what is more relevant within certain localized areas? I suggest re-writing this sentence to make sense to the reader.

Authors response: As also suggested by referee #1, we rephrased the whole paragraph: "Compared with HPLC references, "satellite-corrected" fluorescence profiles are globally unbiased, presenting an r2 of about 67% and a median error of about 31%. These errors (Figs. 1, 3 and 4, Table 4) are certainly affected by the uncertainty of satellite [Chl-a] measurements. Our analysis demonstrated that when the error of satellite [Chl-a] is lower than 35% (i.e. the estimated averaged accuracy of ocean color mission, McClain, 2009), our method performs better. However, several studies indicated that ocean color [Chl-a] observations could have error greater than 35%, in particular over certain localised areas (i.e. the Mediterranean Sea, D'Ortenzio et al. 2002, 8, C6185–C6200, 2012

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the Antarctic or the Equatorial Atlantic, Gregg and Casey, 2004). In these situations, particular attention should be dedicated to the interpretation of our "satellite-corrected" profiles."

Point 19. Table 1 needs a number (n) of HPLC/sat matchups.

Authors responses: We agree with the referee, and we added to table 1 the number (N) of matchups.

Point 20. Table 3, I am not sure if this is really needed here since it is a duplicate of the data shown in [Uitz et al., 2006]

Authors response: The same comment was made by referee #1 and #2, we removed table 3 in the new version of manuscript and mentioned Table 4 from Uitz et al., (2006).

Point 21. Figure 1. - panel d - keep the limits of the x and y axis the same in all the panels. Loglog space is not an easy format to think in, keeping all the axis same will allow reader to explore results easier.

Authors response: We agree and modified the figure 1 accordingly in the new version of manuscript (see figure in attachment).

Bosc, E., Bricaud, A. and Antoine, D.: Seasonal and interannual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of SeaWiFS observations, Global Biogeochem. Cycles, 18, 17 PP., doi:200410.1029/2003GB002034, 2004. 8, C6185–C6200, 2012

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New references in the manuscript:

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W. and Strickland, J. D. H.: Fluorometric Determination of Chlorophyll, Ices J. Mar. Sci., 30(1), 3–15, doi:10.1093/icesjms/30.1.3, 1965.

Hooker, S.B., Van Heukelem, L., Thomas, C.S., Claustre, H., Ras, J., Schülter, L., Clementson, L., Van der Linde, L., Eker-Develi, E., Berthon J.-F., Barlow, R., Sessions, H., Ismail, H. and Perl, J.: The third SeaWiFS HPLC Analysis Round-Robin Experiment (SeaHARRE-3). NASA technical Memorandum 2009-215849, Greenbelt: NASA Goddard Space Flight Center.

Lorenzen, C. J.: Determination of Chlorophyll and Pheo-Pigments: Spectrophotometric Equations, Limnol. Oceanogr., 12(2), 343–346, 1967.

Mantoura, R. F. C. and Llewellyn, C. A.: The rapid determination of algal chlorophyll and carotenoid pigments and their breakdown products in natural waters by reverse-phase high-performance liquid chromatography, Anal. Chim. Acta, 151(0), 297–314, doi:10.1016/S0003-2670(00)80092-6, 1983.

Please also note the supplement to this comment: http://www.biogeosciences-discuss.net/8/C6185/2012/bgd-8-C6185-2012supplement.pdf

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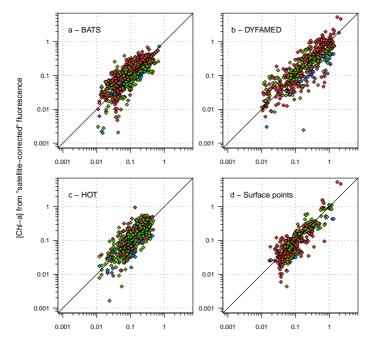


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[Chl-a] from HPLC

Fig. 1.