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Comment

Interactive comment on “Characterization of the bio-optical anomaly and diurnal variability of the particulate matter, as seen from the scattering and backscattering coefficients, in ultra-oligotrophic eddies of the Mediterranean Sea” by H. Loisel et al.

H. Loisel et al.

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Dear Editor,

You can find below our answers to all referee comments. Moreover, I would like to bring to your attention that a new co-author has been added (G. Dall’Olimo).

Reviewer 1

C3652

Full Screen / Esc

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Interactive Discussion

Discussion Paper



The primary objectives of this study were: 1) to re-examine the causes of the color anomaly found in ultra-oligotrophic waters of the Mediterranean Sea by adding measurements of the particulate backscattering coefficient, *bbp*, and 2) to test whether or not diurnal cycles in *bbp* could be observed. These are relevant questions within the scope of BG, and I believe that both of these objectives were well met. This is an excellent paper that carefully examines many details of the data that might escape notice if given only a casual examination. It is definitely a paper that will make a difference in studies of bio-optics and will be cited frequently.

We would like to thank W. Gardner for its comments and appreciation of our paper. All the different comments and suggestions were also much appreciated. All the few minor changes suggested by the reviewer in the text and in the figures have been taken into account. Below we present the reviewer's comments in bold and our answers in plain text.

Answer to the specific comments:

The specific particulate coefficient, cp^* ($=cp/TChl-a$), of the data was examined as done in Loisel and Morel (1998) as a means of determining changes with depth in the particle composition. This was addressed almost exclusively in vertical changes. It is worth noting that a global map of cp^* agrees with their estimates of 1.0 to 0.1 in surface waters of the Mediterranean, but also shows higher values in the open ocean oligotrophic gyres (Gardner et al., 2006, Fig. 10). Values in the gyres generally exceed 1.0 and during the Austral summer, estimated values are greater than 3 in the eastern South Pacific, the region of clearest surface waters found in the ocean (Morel et al., 2007: Morel, A., B. Gentili, H. Claustre, M. Babin, A. Bricaud, J. Ras, and F. Tieche (2007), Optical properties of the "clearest" natural waters, *Limnol. Oceanogr.*, 52(1), 217-229.)

These two references (Gardner et al., 2006; Morel et al., 2007) have been added when surface cp^* values are discussed in the new version of the paper.

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



The title and abstract are appropriate. Lots of excellent, appropriate references were cited. In my comments above I referenced a paper by Morel et al. (2007) and in the introduction of the annotated text file I noted another early paper that calculated net primary production from diel cycles in cp – Walsh et al. (1995).

The reference Walsh et al., 1995 has been added in the new version of the paper.

The only suggested change is in figure 12 where I suggested that it would be best to use different symbols for the two different measurements so that if the figure was copied/printed in black and white, the reader could still distinguish between the two measurements.

Figure 12 has been modified accordingly.

The paper is well written and the language is fluent and precise with impressively few grammatical/word corrections needed given that I don't think any of the authors are native English speakers. Thank you for your attention to detail. After hand writing corrections on my pdf printout, I downloaded the text version of the paper and made minor corrections in tracking mode.

All the grammatical/word corrections suggested by the reviewer in tracking mode have been considered.

Figure 4: It is not clear in the figures what the numerical depth represents – e.g. 170m in a, 250 m in b, etc.

The following sentence has been added in the Fig. 4 legend “The numerical depth values (e.g. 170, 250, and 200 m) indicate the depth, deeper than the DCM, from which the Log(cp(660)) vs. Log(TChl-a) relationship departs from linearity.”

Reviewer 2

We would like to greatly thank this anonymous reviewer for his thoughtful comments on our manuscript, which we believe have significantly improved the original manuscript.

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Below we present the reviewer's comments in bold and our answers in plain text.

General comments

The paper is well prepared and presented and the topic is definitely interesting to researchers in the field. In essence, the authors bring new measurements of backscattering to the question of the optical anomalies in the Mediterranean Sea. This data seems to indicate that higher than "normal" backscattering in the Mediterranean oligotrophic waters. Several points I feel should be addressed in this first part to make sure that the study is not biased and that the results can be trusted.

1) In oligotrophic waters the sensitivity of backscattering instruments are pushed near their limits and all correction and in particular the the dark measurements become crucial. Were dark measurement substracted from data? If so how?

Reply: We totally agree with this comment, and thank the reviewer for pointing out this issue, which was taken into account during the data processing, but not specify in the first version of the paper. Dark current measurements were performed in the dark few times during the cruises using a neoprene black cape to cover the instrument window. These measurements are very close to the values measured at the factory before the cruise, which indicates no electronic drift in the ECO-VSFs dark current, and are taken into account in the processing of the data.

We have added the following sentences in the data method section:

"Because of the very oligotrophic conditions encountered during the cruise, which push backscattering measurements near to their limit, dark current measurements were performed in the dark several times during the cruise using a neoprene black cape to cover the instrument window. The obtained values are very similar to those measured before the cruise during the calibration phase at the factory (WET Labs), emphasizing no electronic drift of this parameter".

2) Comparison with the data of Huot et al. (2008) is used to assess how "abnormal"

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



this data is. Although the spread in Huot et al. data is limited in the very low chlorophyll environment (probably due to a lack of measurements), the spread is clearly larger in more mesotrophic waters. The Mediterranean data in that sense may not be particularly high. I think the discussion has to go beyond just comparing to the trendline and need to include a discussion of the dispersion around this trendline (95% confidence interval on the fitted parameters are given in Huot et al. This might used as a guide in the discussion).

Reply: We agree with the reviewer comment, and the 95% confidence interval given in Huot et al. (2008) has been added in the new version of the Figure 7 (and the legend has been modified). This clearly shows that the dispersion of the Huot et al. data does not overlap part of our own data set.

The following sentence has been added: "The dispersion of the Huot et al. (2008) data points, as represented by their 95% confidence interval, does even not overlap part of the BOUM data set (Fig. 7a)."

3) The method used to derive the backscattering coefficient is different from that used in Huot et al. (2008) could this also cause a bias. Is it possible to derive the backscattering coefficient from a single angle (125 degrees) to make sure this is not underlying the observed differences?

Reply: The ECO-VSF instrument used in the present study allows to measure the scattering at 3 angles in the backward hemisphere (100° , 125° , and 150°). A third-order polynomial function is then fitted on the three resulting values once multiplied by $2\sin^2(\theta/2)$ and corrected from pure sea water scattering, pathlength amplification (θ is the scattering angle), and dark current. This fit also accounts for a fourth point for which the ordinate is 0 at $\theta = 0^\circ$. The availability of three measurements in the backward direction allows to get rid of the adoption of a conversion factor between the measurement performed at one given scattering angle and bbp . The three-angles ECO-VSF instrument was used by Sullivan et al (2005) as a reference, to fix the conversion fac-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tor between bbp and $\tilde{A}_s(\tilde{A}_s\tilde{A}_s\tilde{A}_s)$, when $\tilde{A}_s(\tilde{A}_s\tilde{A}_s\tilde{A}_s)$ is only measured at one scattering angle, $\tilde{A}_s\tilde{A}_s\tilde{A}_s$ using for example an ECO-BB3 as it is used in Huot et al., (2008). However, to be able to exactly compare our data with the formulation of Huot et al. (2008), and as thoughtfully proposed by the reviewer, we process the data using the same approach of Twardowski et al. (2007) also used in Huot et al. (2008). In their approach, bbp is derived from scattering measurements performed at 117° , $\tilde{A}_s(117)$, by assuming a conversion factor of 0.9 according to Sullivan et al. (2005). Based on the BOUM data set the conversion factor between bbp and $2\tilde{A}_s\tilde{A}_s\tilde{A}_s(125)$ is 1.0086, $r^2=0.84$. This small difference may be caused by the fact that the BOUM data set is for very clear water whereas to the data set used in Sullivan et al. (2005) encompasses measurements performed in coastal areas. By applying the conversion factor used by Twardowski et al. (2007) to our measurements collected at 125° we obtain higher bbp values (by about 30%) than the one derived using the information at three angles. Therefore, the derivation of the backscattering coefficient from a single angle, as it is done in Huot et al. (2008), would even increase the discrepancy observed with their bbp vs. TChl-a parameterization. Moreover, other bbp measurements were performed during the BOUM cruise using a quite different protocol (on water continuously pumped from about 9 m below the sea surface) and instrument (an ECO-BB3 WEL Lab measuring at 3 wavelengths and at one given angle, 117°). Particulate backscattering coefficients are calculated as in Dall'Olmo et al. (2009). Only the blue and green channels can be used because the red channel showed significant drifts in the calibration coefficients measurements. Comparison between the in situ bbp(650) values and the bbp values obtained from the measurements performed on pumped waters at 526 nm shows a relatively good agreement (Fig. 7b). So, even if these two sets of bbp measurements were acquired at different wavelengths and using different methodologies, the slight differences observed between these two data sets re-enforce our present conclusion about the backscattering anomaly, and clearly demonstrate that this is not an artifact of the measurements.

These different points have been added P20-21, as follows:” The fact that bbp follows

C3657

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

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Interactive Discussion

Discussion Paper



the same trend with TChl-a than those described in previous studies for oligotrophic waters gives us confidence in the present data set. However, to be able to faithfully compare the present bbp vs. TChl-a relationship with the formulation by Huot et al. (2008), we processed the data according to the procedure defined by Twardowski et al. (2007) also used in Huot et al. (2008). In their approach, bbp is derived from scattering measurements performed at one scattering angle (117°), $\bar{\mu}_s(117)$. Then, bbp is derived by assuming a conversion factor between bbp and $2\bar{\mu}_s(117)$. This conversion factor is fixed at 0.9, according to Sullivan et al. (2005). Based on the BOUM data set, the conversion factor between bbp and $2\bar{\mu}_s(125)$ is 1.0086 ($r^2=0.84$). This weak difference may be caused by the fact that the BOUM data set is focused on very clear waters whereas the data set used in Sullivan et al. (2005) encompasses measurements performed in coastal areas. By applying the conversion factor used by Twardowski et al. (2007) to our measurements collected at 125° we obtain higher bbp values (by about 30%) than those derived using the scattering measurements at three angles. Therefore, the derivation of the backscattering coefficient from a single angle, as it is done in Huot et al. (2008), would even increase the discrepancy observed with their bbp vs. TChl-a parameterization.

Moreover, other bbp measurements were performed during the BOUM cruise using a quite different protocol (on water continuously pumped from about 9 m below the sea surface) and instrument (an ECO-BB3 WEL Lab measuring at 3 wavelengths and at one given angle, 117°). Particulate backscattering coefficients are calculated as in Dall'Olmo et al. (2009). Only the blue and green channels can be used because the red channel showed significant drifts in the calibration coefficients measurements. Comparison between the in situ bbp(650) values and the bbp values obtained from the measurements performed on pumped waters at 526 nm shows a relatively good agreement (Fig. 7b). So, even if these two sets of bbp measurements were acquired at different wavelengths and using different methodologies, the slight differences observed between these two data sets re-enforce our present conclusion about the backscattering anomaly, and clearly demonstrate that this is not an artifact of the measurements."

4) How do the backscattering obtained from the AOP inversion compare with the one derived from the ECO-VSF ? Is there any information in the spectral shape of these inverted backscattering coefficient that could support the hypothesis made on page 7885 about the shape of the backscattering coefficient? Also why would the strongly absorptive particles required to have a higher bbp at 555 than 443 not be important in total absorption measurements (I think I know why but you need to convince the reader)?

Reply: The spectral variability of bbp, can now be calculated from the scattering measurements performed in the blue (470 nm) and in the green (526 nm) part of the spectrum on water continuously pumped from about 9 m below the sea surface, as described above. This information was not yet available for the first submission of the manuscript. For stations where the blue-to-green reflectance anomalies have been reported, the $\text{bbp}(470)/\text{bbp}(526)$ ratio is 1.04 ± 0.06 which confirmed our second scenario about the bbp spectral shape. In the first version of the paper, we indeed emphasized that this scenario ($\text{bbp}(555) = \text{bbp}(443)$) explains more than half of the BG anomaly. This information has been added in the text as follows:” The spectral variability of bbp calculated from the scattering measurements performed in the blue (470 nm) and in the green (526 nm) parts of the spectrum on pumped-water, as described in the section 3.2, emphasizes that the second scenario is the more reliable one. Indeed, the $\text{bbp}(470)/\text{bbp}(526)$ ratio is 1.04 ± 0.06 for stations where the blue-to-green reflectance anomalies have been reported. This ratio is significantly lower than the one measured in the most oligotrophic part of the Atlantic ocean during the AMT19 cruise ($\text{bbp}(470)/\text{bbp}(526) \approx 1.2$) using the same measurement protocol (Dall’Omo, personal communication). This feature again stress the peculiar bio-optical character of these Mediterranean waters sampled.”

5) Backscattering at station BOUSSOLE (Antoine et al. 2011, their figure 5) tend to be lower than Huot et al. (2008) relationship during oligotrophic periods. This needs to be addressed as it is in the opposite direction from the present observations.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Reply: Comparison between the Huot et al. (2008) and BOUSSOLE parameterizations is only provided at 443 nm in their Figure 5 panel A. In panel B, the Huot et al.(2008)'s formulation is not plotted. Based on the comparison shown in panel A, for which the wavelength is quite different from the one used in our study (650 nm), the bbp measurements performed at BOUSSOLE are only slightly higher than the Huot (2008)'s relationship (but not lower). Moreover, the comparison between our present data set and the BOUM data set is biased as the very clear waters sampled at the BOUSOLE station, and shown in their Figure 5, come from an exceptional winter mixing event occurring in January-February 2006, for which the impact of dust, if present in the surface water, can not be noticed due to the extreme hydrological condition encountered (mixed layer depth at 2440 m, inducing a extreme dilution of the suspended particulate matter in presence). At last but not least, the surface TChl-a range is different for the both data set, as the minimal chlorophyll concentration measured at BOUSSOLE ($\sim 0.05 \text{ mg.m}^{-3}$) almost match our maximal TChl-a values.

6) The effect of CDOM absorption is assessed using the inversion of remote sensing reflectance. The unpublished inversion algorithm used is said to have an RMSE of 0.02 m^{-1} for total absorption, yet the retrieved absorption of aCDOM+asp retrieved is 0.0054 m^{-1} . Of course, I understand that the stated 0.02 m^{-1} is not necessarily representative of the ability of the model in these waters, nevertheless, a better statistics of its performance in oligotrophic waters need to be given to convince the reader that the value provided is not off by a factor of 4 or more (especially since the error given on the 0.0054 m^{-1} is 0.0011 m^{-1}).

Reply: We thank the reviewer for pointing out this incoherence. A new validation exercise has then been performed only for oligotrophic waters ($\text{Chl} < 0.3 \text{ mg.m}^{-3}$), showing that the RMSE is 0.0022 and 0.024 for a-aw(443) and bbp(443), respectively. The sentence has then been modified as follows: "Based on a synthetic data set (IOCCG, 2006) bbp(443) and a-aw(443) are retrieved with a Root Mean Square error of 0.024 and 0.0022 for oligotrophic waters ($\text{Chl-a} < 0.3 \text{ mg.m}^{-3}$)."

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



7) How do the profiles of lithogenic silicates presented in figure 10, compare with other open ocean area. Are they really much higher than those in other oligotrophic waters?

Reply: The following paragraph has been added P27: "Lithogenic silica data in the open ocean are very scarce, as LSi is often measured only in coastal environments as a way to correct BSi measurements from lithogenic interference (Raguenuau and Tréguer,1994; Ragueneau et al, 2005). However, LSi concentrations for open oligotrophic at the surface level are areas usually close to $\sim 0.01 \mu\text{M}$ (Leblanc, pers. comm. from unpublished data). Concentrations $>0.01 \mu\text{mol L}^{-1}$ are usually clearly associated with either : samples close to the sea floor and containing suspended sediment, samples collected at coastal sites or near river mouth, or dust deposition events. Unfortunately, to our knowledge, there are no data comparing dust collected during a dust storm and in situ lithogenic silica concentrations. However there is no doubt that LSi increases in the water column trace either sediment or aerosol presence in the form of aluminosilicates eroded from the earth crust. Hence in open waters far from the coast and with deep bathymetry, LSi increases can only trace either lateral advection of sediment particle with a strong current, or aerosol deposition from the atmosphere which is the most likely explanation in our present study"

8) If the lithogenic silicate is an important cause of backscattering, why don't we see profiles of bbp similar to those measured for lithogenic silicate?

Reply: The presence of lithogenic silicate is here used as a proxy of the presence of Saharan dust. Two main reasons can explain the fact that the bbp and LSi profiles are not necessarily similar. First, the concentration of LSi in Saharan dust is not necessarily proportional to the concentration of the optically significant material which compose these dust particles. For example, particles may have the same LSi concentration, but different size, refractive index and structure (internal composition and shape), and then different bbp values. Note that the two last parameters have a great effect on bbp. Second, bbp can be divided into the sum of two components bbp-organic (phytoplankton, bacteria, detritus, etc) and bbp-dust, this last term being only significant in the surface

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



layer due to its very low sedimentation rate (as indicated by the LSi profile). While surface value of bbp is certainly driven by bbp-dust, the vertical profile of bbp is mainly driven by the vertical profile of bbp-organic.

9) I find it surprising that given the suggested large influence of the submicron lithogenic silicate on bbp, that the changes during the day of bbp (second aspect discussed in the paper, p. 7889, line 5 to 10) are only slightly smaller than those of cp which would be much less affected by this non-living part of the particle pool. In other words, while the authors tend to follow one line of evidence, there are several observations that must be addressed to verify that their hypothesis is really supported by their observations.

Reply: This is mainly due to the fact that the reported changes are not driven by processes occurring in the surface layer, but correspond to a vertically integrated quantity. Moreover, the presence of dust only affects the absolute value of bbp at surface (and also cp, to a lesser extent, as written in the text) and can be seen as a background signal, while the diel cycles of both bbp and cp are only driven by biological processes (superimposed on a background signal of cp and bbp).

General comment on the second part of the paper: My main comment here is that I feel the presentation of the results of diurnal variations in bbp is fine, novel and interesting, but the discussion surrounding is it too long and mostly unsupported. As such the discussion about the sources of potential sources of variability could be shortened. As well the derivation of production rates appears to me a bit far fetched, while it can be done mathematically and compared with other values it really doesn't bring anything to the paper as it cannot be validated nor do we have any way to know what it means in reality (since we do not know the sources of variability in diurnal changes of bbp). These variations, once we know their amplitude (say 14% per day) can be very simply transformed into production rates using some POC values: it doesn't mean that it means anything to do it. In my opinion this section should be shortened considerably, results can be put in a table for future uses and a minimum discussion of the

C3662

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



diurnal variation should be kept. To me the most important finding related to these diel changes is that a significant fraction of the bbp is most likely caused by living (growing and respiring) organisms (or their diurnally variable wastes). This is what should be highlighted (though, as noted above, it is somewhat at odds with the first part of the paper.

Reply: According to the remarks of the reviewer, the discussion related to the potential sources of variability in bbp and biogeochemical application has been shortened by 1 page (over 6 initially). We do believe that the paragraphs presenting biogeochemical applications of such optical measurements (i.e. cp and bbp) should be kept (even though they have been shortened). Indeed, this part of the paper mainly deals with 3 important topics, which for 2 of them are not related to bbp only, and for which it was necessary to remind the work performed previously in the same area. These topics provide relevant elements supporting the use, with an increased accuracy, of cp and bbp as proxies for estimating biogeochemical rates such as GCP.

First, we underlined that bbp and cp diel variations more likely correspond to the diel changes in living organisms that temporally moderate a constant background of particulate matter (including in particularly detrital particulate material for which no diel cycle has been noticed). This clearly emphasizes that estimates of GCP from cp and bbp as a meaning since they are based on the relative changes in these optical descriptors being therefore independent from the absolute background signal.

Second, we emphasize that the discrepancies usually observed between GCP rates estimated by classical and optical approaches are actually originating from issues related to the production rates estimated by the classical ^{14}C based technique, which neither provide a gross production rate nor a net production rate measurement. As a matter of fact, the application of a correction factor on ^{14}C GCP estimates (Moutin et al., 1999) induces clearly a better agreement between the two approaches.

We finally demonstrate the crucial need to use vertically integrated relationships be-

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tween optical (bbp or cp) and biogeochemical parameters (such as POC concentration) for deriving biogeochemical rates from cp or bbp. Indeed, single depth relationships, which have been commonly used in previous studies, does not provide representative description of the whole water column and induce a major overestimation of the GCP rates estimated from optical parameters.

Technical points

1) p. 7862, line 7. No need to define and use the abbreviation BP, it is more confusing than anything else as it is often used for “bacterial production”.

Reply: we agree with this remark, this abbreviation has been removed from the text.

2) P. 7863, line 10. “Marginal” seems an inadequate adjective as used for seas since marginal seas already have a specific meaning. Perhaps another adjective can be found.

Reply: according to the first reviewer recommendation we have chosen the adjective “unusual”.

3) P. 7871, lines 13-15. I think it is an oversimplification to state that the DCM is caused by an increase in the intracellular chl content. You might skim the results of Grob et al. (2007) which clearly suggests that cell numbers also play an important role in this feature. Papers cited here though excellent are a bit dated (before the flow cytometry era).

Reply: We thank the reviewer for pointing out this oversimplification. This part has been modified as follows: “As already discussed in several papers, the DCM is partly explained by an intracellular increase in Chl-a (Kiefer et al., 1976; Cullen, 1982). Indeed, the phytoplankton community physiologically adapts to the low irradiance level, and to the vicinity of the top of the nitricline. The recent development of appropriate in situ instrumentation to characterize the vertical profile of marine particles also highlights that phytoplankton cells can play an important role in this vertical feature (Oubelkier and

Full Screen / Esc

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Interactive Discussion

Discussion Paper



Sciandra, 2008; Grob et al., 2007). For instance, cytometry measurements performed in the Ionian Sea show a maximum of picophytoeukaryotes in the 50-90 m layer, with a deep chlorophyll maximum located at 90 m (Oubelkier and Sciandra, 2008). In the same way, a deep picophytoeukaryotes maximum was recorded in the deep chlorophyll maximum at the center of the South Pacific gyre (Grob et al., 2008).”

4) P. 7871, lines 17 to 20. The section explaining why there is an increase in the fluorescence/ chl a ratio is confusing and perhaps even wrong. Shouldn't the ratio discussed be fluorescence / Tchl a for this discussion to makes sense? Are the authors assuming divinyl chlorophyll a is not fluorescing (it is in very similar ways to monovinyl chlorophyll a)? In any case I do not follow the logic here.

Reply: We agree that the way it was presented was awkward and confusing. This part of the paper has been removed as the message was also stress at the end of the next paragraph “This diversity in the phytoplankton assemblages at the two DCM of station B which are characterized by the same Chl-a (as measured by HPLC) could explain the difference observed in the fluorescence peak intensity.”

5) P. 7872, line 2 to 5. I don't understand how these two sentences follow each other. Prochlorococcus and Synechococcus are both part of the picoplankton.

Reply: This was an error, and the sentence which has been modified now directly refers to the paper of Mauriac et al.: “This is in agreement with cytometry counting and microscopic identification (Mauriac et al., this issue).”

6) p. 7873, line 17. I think “photoacclimation” should be replaced by “photoadaptation” since we are most likely dealing with different genotypes here (see for example Raven & Geider, 2003).

Reply: As stressed by Falkowski and Laroche (1991) the term photoadaptation has sometimes been used in the literature for photoacclimation. We use the term photoacclimation in this paper to refer to physiological processes, in contrast to photoadaptation

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

which refers more to evolutionary processes.

7) Figure 3 Backscattering panel. I think the important information to show here is the mean profile; therefore the axis could be scaled so that extreme peaks are outside the graph (say 0.0001 to 0.002 m⁻¹). Similarly for cp, the x-axis could be limited to 0.12 m⁻¹.

Reply: The figure has been modified according to the reviewer comment.

Interactive comment on Biogeosciences Discuss., 8, 7859, 2011.

BGD

8, C3652–C3668, 2011

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

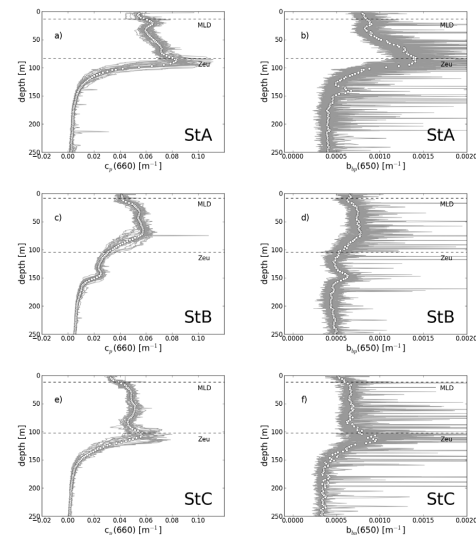


Figure 3

Fig. 1.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



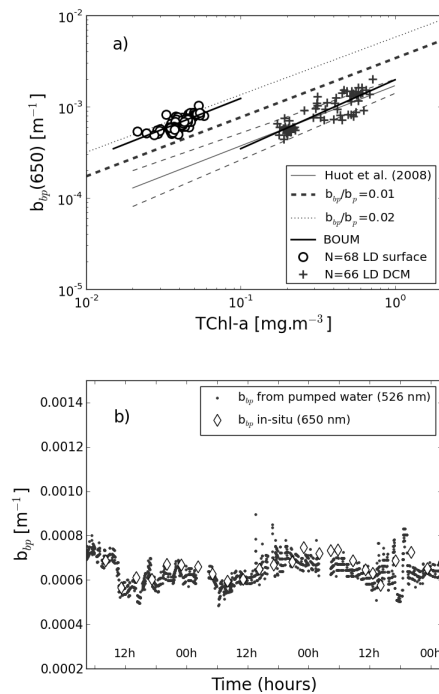


Figure 7

Fig. 2.