Biogeosciences Discuss., 9, C4331–C4344, 2012
www.biogeosciences-discuss.net/9/C4331/2012/

Biogeosciences
Discussions

Interactive comment on "Variability of carbon monoxide and carbon dioxide apparent quantum yield spectra in three coastal estuaries of the South Atlantic Bight" *by* H. E. Reader and W. L. Miller

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Received and published: 27 September 2012

Comments on the research article in BG, "Variability of Carbon Monoxide and Carbon Dioxide Apparent Quantum Yield Spectra in Three Coastal Estuaries of the South Atlantic Bight" by H. E. Reader and W. L. Miller (MS No.: bg-2012-200) General comments The manuscript presents seasonal measurements of apparent quantum yield spectra for the photoproduction of DIC and CO at three estuaries of South Atlantic Bight. Such seasonal studies are rare and the present study is a welcome addition to the scientific community assessing the rates of DOM-photochemistry in surface waters.

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The photochemical reactivity of DOM varied less than ca. 20

The photochemical reactivity was poorly explained by the optical characteristics of DOM, and the most likely explanation (although not proved) for the variability of AQY was the magnitude of DOMs pre-exposure to solar radiation. The large parts of results were presented in a way, which was not explained in the methods detailed enough. The presentation of results was also such that the comparison of the results of the present study to those of other studies is difficult. I encourage the authors to recalculate their results or at least explain the calculation methods clearly enough. The discussion would get stronger by comparing the results of present study to those of similar earlier studies highlighting apparent quantum yields and the role of photochemical reactions in the carbon cycling in the coastal waters.

Detailed comments P 6950, L 2: The PhD-thesis of Johannessen may not be available for everyone, please,add an additional reference e.g., Wang et al. 2009.

Relevant reference added.

P 6952 L 23: The AQYs were determined sometimes with fresh samples and sometimes with samples stored 6 months. There is a possibility for abiotic transformation (e.g., the aging of iron associated to DOM) and biotic transformations of DOM under long storage. Did the authors observe any changes in DOM during the storage? How such changes could have influenced AQYs?

We did not observe any changes in the CDOM during storage. Previous work suggests that changes during storage are minimal and were thus not considered.

Added to text: “Previous evaluations in our lab (unpublished) and work such as Stedmon and Markager (2001) and Swan et al (2012) has shown that storage had little effect on CDOM absorption and thus storage was determined not to be an issue.”

P 6956 L 11: How did you get E0(ôĂĄŔ) referred as the scalar irradiance entering the top of cell? If you measured it with a spectroradiometer with a cosine corrected en-

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Discussion Paper

trance for the incoming irradiance, you likely measured irradiance incident on a plane. This is referred as vector irradiance or just irradiance (not scalar). If you irradiated your samples in air, you should account for the reflection of irradiance at the interface between air and quartz cell. The refractive index of air is 1 and that of quartz ca. 1.4-1.5. The difference in the refractive indices reflects some of irradiation from the interface between air and quartz reducing the amount irradiance entering the cells (compared to values measured in air). If you irradiated the samples in water (RI = 1.34), such a reflection is small, because the refractive index of water and quartz is similar. Please, report your E0(ôĂĄŔ) in more detail.

Irradiance was measured, as stated in the methods (section 2.3) using an Optronic 756 spectroradiometer, with a two-inch integrating sphere. The cells were placed in a tightly fitted, chilled aluminum block, holding them at exactly 90 degrees to the incident light. Details were added to the method text to explain further our irradiation system as follows:

"Photochemical irradiations were performed following the multispectral methods of Johannessen and Miller (2001). A tightly-fitted 2.4 cm thick black plastic lid with 1.6 cm diameter holes drilled directly above each spectrophotometric cell served as effective Gershun tubes for each cell to minimize off-axis light, thus minimizing reflection at the air-glass surface of the cells. To create distinct irradiation conditions for the samples in each of 14 spectrophotometric cells, duplicate Schott-glass long-pass cutoff filters (WG280, WG295, WG305, WG320, GG385, GG420, GG475) were placed directly over the lid, between the quartz cells and the light source. An opaque disk was used above the 15th cell in the chilled Al block to provide a dark control."

As the reviewer is certainly aware, Snell's law ($\sin\Theta 1 = n1/n2 * \sin\Theta 2$) indicates that incident light arriving at 90 degrees to a surface (i.e. 0 degrees from normal) will not reflect off of that surface regardless of refractive index differences ($\sin 0 = 0$, thus $\Theta 1 = \Theta 2 = 0$). Since we measured the incident irradiance under the "Gershun tube" lid, we can assume that this incident light is almost entirely incident on the cells at 90 degrees. This means that the total photon flux that we measure is also the total photon flux that enters the cell. While it is true that the geometry of this flux likely qualifies it as radiance, for purposes of AQY calculations, it also represents the entire integrated photon flux from every direction (in the case of a particle-free sample with no reflection, scalar irradiance = downwelling radiance). Consequently, for use of these equations in real ocean applications, we choose to refer to this total photon flux as scalar irradiance. Quantitatively, this is the identical photon flux to what we measure in our experimental system.

P 6957 Eq. 5: I believe you used spectral values in Eq. 5. Please, use AQY(ôĂĄŔ) and Qa(ôĂĄŔ) (instead of AQY and Qa) in Eq. 5 following their earlier use in Eq. 2-4.

This has been revised.

P 6958 L 1-17: The purpose here is to examine variability in AQY (or the photoreactivity of DOM). It is possible to carry out these examinations as indicated here. However, the results of these calculations in units e.g., mol CO s-1 reported in Figs 3, 4, 5, 6, and 7 are not environmentally relevant. I believe that most readers of this paper are not interested in the rates taking place in a 30 mL irradiation cell under artificial irradiation. At least it is very hard to compare the results of this study in mol CO s-1 30 mL-1 under artificial irradiation to other studies. I encourage the authors to report their results differently so that the results are comparable to other studies. There are many ways to assess the variability of AQY. Here, I suggest a simple modification of Eq. 7 as an alternative. Eq. 7 actually estimates the photochemical rate per volume and time (mol vol-1 time-1) at the given E0(ôĂĄŔ),ag(ôĂĄŔ)and AQY(ôĂĄŔ). The units for these parameters are [mol m-2 s-1 nm-1] for E0(ôĂĄŔ),[m-1 nm-1] for ag(ôĂĄŔ) and [mol CO mol photons-1 nm-1] for AQY(ôĂĄŔ). In this case, the unit is [CO mol m-3 s-1 nm-1] for d[product]dt-1. When Eq. 7 is normalized with arbitrarily selected ag,Nov08(ôĂĄŔ), it will be modified to: E0(ôĂĄŔ) *ag(ôĂĄŔ) * ag,Nov08(ôĂĄŔ)-1 * AQY(ôĂĄŔ). Now ag(ôĂĄŔ)ag,Nov08(ôĂĄŔ)-1 will have an arbitrarily unitless spectrum for each time. The unit for d[product]dt-1 will be modified to [mol m-2 s-1 nn-1].

In order to get the units[nmol product s-1 cell-1; given at the page 6958 line 5) authors must have accounted for the area, the dimensions, and volume of their irradiation cells. Additionally, the Eq. 7 must have been integrated over the some spectrum of wavelengths. These details are not given in the methods, so it is hard to understand how the normalized rates were actually calculated. I suggest that the authors simplify their Eq.7 to d[product]dt-1 = ôĂŮňôĂňűôĂňÿôĂň¡ôĂňźôĂňťôĂňť E0(ôĂĄŘ) AQY(ôĂĄŘ) dôĂĄŘ modified Eq. 7 where d[product]dt-1 has units [mol product m-2 d-1], E0(ôĂĄŔ) is the Ed0-(ôĂĄŔ) is the daily annual mean downwelling solar irradiance at their study site used later in Eq.10 with a unit [mol photons m-2 d-1 nm-1] and AQY(ôĂĄŔ) is the spectrum of AQY determined for each sample [mol product mol photons-1 nm-1]. In this case, the modified Eq. 7 would estimate the mean daily photoproduction of CO or CO2 over the entire water column at their study site assuming that CDOM is responsible for the absorption of photolytic solar radiation. The modified Eq. 7 is the same used earlier by the present research group – see Eq. 8 of Miller et al. 2002 LO-paper. The values of modified Eq. 7 would be environmentally relevant and comparable to estimated made by Eq. 10 of this study and many other earlier and future studies.

We would like to thank the reviewer for this thorough comment. We did use Qa here in this calculation and the text has been amended to reflect this. We used Qa (calculated with a standard absorption spectrum and a standard irradiance spectrum) specifically so that we would get a rate that the reader did NOT think signified that this comparison of AQY spectra was an environmental rate. This was done so as not to mislead the reader since, to be truly rigorous with environmental photochemical rates, we would need to change both the absorption spectrum and the irradiance spectrum with each month and location, and therefore would defeat the purpose of exclusively evaluating only the changes in the AQY spectra which was the goal of this paper. If we had used a true environmental irradiance spectrum, we felt that it would mislead the reader into thinking that these rates were truly the rates that would be encountered at some point in time in the estuary and coastal ocean, and since this is strictly not true, we used a calculation that was clearly artificial to perform our assessment of the variability in the

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Discussion Paper

apparent quantum yields. It is a relatively simple calculation for the reader to use the reported AQY spectra and their reported variability with appropriate solar irradiance and CDOM spectra to estimate in situ rates. While the reviewer's point is well taken, we strongly argue that adjusting the equation as suggested would mislead the reader as to the point of the calculation.

As further clarification of this approach, a sentence has been appended to the end of section 2.5 to indicate that these rates are not in situ environmental rates, and the reason why we specifically took this calculation approach.

"It should be noted that these rates are not true environmental rates, but were solely calculated for the purpose of eliminating the variation due to CDOM and irradiance in the photochemical reactions that would naturally occur in an environmentally rigorous calculation of photoproduction. The purpose of this calculation was to specifically isolate only the effect of changing AQY spectra on photoproduction, and we do not want to mislead the reader by suggesting that these rates are estimates of those found in the coastal waters sampled. For a discussion of the environmentally relevant rates, please refer to section 2.7."

In response to another point in the above comment, the wavelengths over which the integration was performed (260nm-450nm) are already explicitly stated in the text of section 2.5.

P 6959 Eq. 8: If you followed Helms et al. your Eq. 8 for the calculation of spectral slope coefficient should be: ag(ôĂĄŔ) = ag(275)e-S(ôĂĄŔ-275) where ag(275) is the absorption coefficient of CDOM at the reference wavelength selected to 275 nm by the authors of present study. Please, modify your equation and recalculate your results so that they are comparable to the other studies following the method of Helms et al.

Helms et al (2008) did not specifically state the reference wavelength used in their paper. The choice of reference wavelength, however, does change the value calculated for S. Helms (2008) and we both used equations from Twardowski (2004). Because

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Helms et al. did not specifically mention the reference wavelength used in their paper, we decided that for ease of calculation and for future comparisons, we would use the general form of the exponential equation from Twardowski (2004) (Equation 2), thus removing the need for a reference wavelength and future confusion about this matter.

P 6960 Eq. 10: Please, re-place the integral sign between '=' and 'Ed0-(ôĂĄŔ)'.

Equation 10 has been rewritten to better represent the total areal production.

P 6960 L 5: [mol photons yr-1 m-2 nm-1]

The units have been corrected to say mol photons yr-1 m-2. Since this has been previously stated to be a spectral quantity, adding nm-1 is redundant and adds confusion to the calculation and is not required.

P 6960 Eq. 11: This is a nice and infrequently done approach to account for the absorption of photolytic photons by CDOM in the water column. However, in strict sense one should address the ratio of CDOM absorption to the total absorption in the water column (rather than the attenuation of solar radiation). In addition to the absorption of photons, the attenuation of solar radiation is influenced also by scattering (mainly from particles). In terms of photochemistry, the scattered photons will be eventually absorbed by water column and they contribute to photochemistry if absorbed by CDOM (unless they exit the water column to the atmosphere or sediment). In the present approach (Eq. 11), scattered photons are lost and not involved in the photochemistry in the water column. The use of Eq. 11 will underestimate the rate of photochemical reactions in the water column. On the other hand, the modified Eq. 7 assumes that CDOM absorbs all photolytic solar radiation and lead to overestimation of photochemical rates (by not accounting the absorption of photons by other optically active components – mainly particles in the coastal waters studied here). Therefore, the comparison of photoreaction rates by two methods would be interesting in the results of this study (compare the modified Eq. 7 to Eq. 10 with embedded Eq. 11).

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Interactive Discussion

Discussion Paper

The reviewer is correct that the ratio of a(g) to a(t) is the critical ratio when scattering is not a part of the system. To integrate over depth, however, the spectral distribution of solar radiation with depth is critical to drive photochemistry. Kd describes the total change of downwelling irradiance over depth. While it is reasonable to think that photons scattered away from the vertical path will simply be absorbed somewhere else. However, this is not the way it works. Kd incorporates vertical changes in irradiance due to absorbance together with photons scattered BOTH out of AND into the spot of measurement from which the Kd is calculated. Scattered photons in the ocean are mostly scattered at forward angles and change their angular geometry without being simply "lost" from the vertical flux as suggested. Since Kd is a cosine measurement and has been shown to be roughly equal to the attenuation of scalar irradiance in the ocean, comparing a(g) to Kd is the appropriate ratio for calculating photochemical reaction rates at any given depth since it accounts for changing geometry and the small loss from backscatter. Using the ratio of a(g) to a(t) would leave out the small scattering loss at depth and underestimate the production rate. Equation 7 is appropriate for looking at our filtered samples but not for application in the ocean. Comparing the two is apples and oranges.

P 6960 L 15: Please, explain how you calculated means. Notice that typical arithmetic averages at linear scale do not work with your non-linear parameters. For example, the arithmetic mean of 1 and 2 is 1.5. But if 1 and 2 are exponents like in AQY-spectrume1 and e2, their mean is 5.05 (not e1.5 = 4.48).

The reviewer is correct that using a mathematical mean is incorrect. We have recalculated using a pooled data set of all experiments to create a "mean" AQY spectrum that is not an arithmetic average. The text and numbers have been updated to correct this, and quotation marks have been put around mean, in order to avoid confusion.

P 6960 L 21 and Fig. 2: Please, add the data from Aarnos et al. 2012 JGR to Fig. 2 A.

This has been added.

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Interactive Discussion

Discussion Paper

Table 1. There is a mismatch between Salinity, DOC and ag320, and their respective units. Additionally DOC is obviously given as ôĂĄŘmol L-1 (not as mg L-1).

This has been corrected.

P 6961 L 6-14 and Fig. 3: Consider presenting your data differently. It is impossible to compare your results reported in mol CO2 or CO s-1 to other studies. Please, explain also how you calculated SE. Calculating SE helps to identify the source of variability in the spectral AQY. For example, it seems that that the CDOM-normalized photoproduction of CO2 varied typically <20more than four-orders of magnitude i.e., > 1000000

The calculation of errors is stated in section 2.5. Briefly, we calculated the error from the root mean square error of the modeled AQY fit. Because we were using an iterative non-linear fitting routine to fit multiple data points, the MATLAB program (nlinfit) is able to calculate the error of the modeled fit based on the least-squares minimization process. This value is calculated for each AQY fit, and then is propagated through the multiplicative calculation of production using normal error propagation methods.

This error does not represent an error at a specific wavelength (i.e. 480), but rather the error of the whole equation for AQY. Because the influence of AQY at 480 is far smaller than the influence of AQY at 280, for example, variation and errors here are minimized with respect to the entire spectrum, which is what we are assessing in figures 3-7.

No changes have been made to the text.

Figures 4, 5, 6 and 7: Try to express your data in a way, which makes it environmentally relevant and comparable to other studies. It is very hard to tell anything about the measured photoreaction rates given in units given nmol CO or CO2 s-1. Please, give your measured rates e.g., in units mol L-1 s-1. Please, try to relateyour results e.g, to values representative of daily rates at the surface conditions of your study sites. The CDOM normalized production is given in units mol CO2 or CO/s/L although the methods explain other units (nmol products s-1 cell-1; P 6958 L 15). I do not understand how you obtained the CDOM normalized production. Please, revise your manuscript so that a reader can understand the way how you got your results. I do not understand all symbols used in Figures 4-7. The symbol key gives nice explanation for the samples at your study sites at high or low tide – this is OK. I do not understand the additional black circles and grey squares. What are they?

The “black circles” and “grey squares” was a typo from a previous version of the manuscript and this has been fixed in all relevant figure captions. For the discussion of why we used the number we used, and the additions to the methods, please see above.

R2 values in Fig. 4 and 7: How is possible to have negative R2 value (-0.08) in Fig. 4? In Fig. 7, the R2 value for the normalized data looks much lower than 0.46 given. Mistake?

The method that MATLAB uses to calculate R2 in the curve fitting toolbox allows for negative R2 values when the model that it is attempting to fit is fundamentally inappropriate for the data presented. This R2 just means that the data in Fig 4 is in no way linear.

In figure 7, a robust fit was used to guide the reader’s eye, and so the R2 reflects the fact that the outliers were strongly downweighted in the linear regression. This fact has been added to the figure legend for figure 7.

The section 3.3: It is possible to follow the relative differences in the data presented. However, I did not fully understand how the data presented in Figures 3-7 was obtained. Please, revise the methods, the results and the figure legends for clarify the results obtained.

Please refer to the above discussion of this.

Fig. 6: Please, calculate the S275-295 correctly. You values for S275-295 should be

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Interactive Discussion

Discussion Paper

between 0.010 nm-1 and 0.035 nm-1, not unitless and between 0.0065 and 0.0085 as shown in Figure 6.

This has been addressed above. Units have been added to figure.

P 6962 L 4-5: Please revise the expression “carbon fuel”, since CDOM is a simple optical parameter and does not measure carbon directly. Please revise “CDOM concentration” to “the absorption by CDOM” and refer to Eq. 7, which shows that the photochemical rate per volume depends linearly on CDOM

This sentence has been modified. Please see response to reviewer 1.

P 6962 L 26 and P 6963 L 3: SAB instead of SABi. 3.4 and Table 3. Please, give error estimates for the annual photoproduction rates. For example, the range of CO2 production spans from 0.25 °âĂŤ 1011 g C yr-1 SAB-1 to 4.33 °âĂŤ 1011 g C yr-1 SAB-1 when estimated over the observed range of CO2:CO ratio (Table 2).Because the maximum estimate is nearly 20-fold larger than the minimum estimate, CO2:CO ratio is not a good way to estimate CO2-production. There must be an error associated to your estimate based on AQY – please, report the magnitude of error and explain where it comes from. Please, report also the rates per square meter basis. These values are most frequently reported in the literature. For example, Miller et al. 2002 estimated that photoreactions produce ca. 2000-3000 umol biologically available photoproducts m-2 d-1 in your study region. If I calculated correctly the photoproduction of CO and CO2 were 36 and 636 ôĂĄŘmolm-2 d-1, respectively, in your present study. The photoproduction of CO and CO2 in this study is low compared to the production of BAPs. More data for similar comparisons in found e.g., in the review by Vähätalo 2009 Encyclopedia of Inland Waters (Light, Photolytic reactivity and chemical products).

4.1: Please, compare your data to that reported by Aarnos et al. 2012 (JGR), which also addressed seasonality of photoreactions. It seems that the previous exposure of CDOM to solar radiation can explain the photoreactivity of CDOM (Andrews et al. 2000 LO, Vähätalo Wetzel 2004 Mar Chem). Therefore, the marsh CDOM with little expo-

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Interactive Discussion

Discussion Paper

sure to solar radiation can be expected tobe more photoreactive that CDOM exposed to intense solar radiation during spring and summer.

Discussion of the other aspects of seasonality has been added to the text, please see response to Reviewer 1. Reference to Aarnos (2012) and their seasonality of DIC has been added to section 4.1 as well.

4.2: For example, Belager et al. 2006 and Aarnos et al. 2012 have made estimates about CO2 photoreactions at the coastal seas based on AQYs. Accounting for the large variability in CO2:CO ratio, it is better to measure CO2 production directly than through CO-production.

We agree that it is better to use directly measured parameters in modeling situations. However, it is quite common in the literature to use the CO2:CO ratio, and there are situations that CO AQY data are available and/or much more reliable than the same required data for CO2, which is why we actually calculated CO2 photoproduction using both methods and presented the results in the text. This comment does not require the text to be amended since we did what was suggested.

P 6966 L 25: The absorption coefficient of CDOM and spectral slope coefficient are frequently linked. High CDOM absorption correlates with low slopes. This may explain the results in Fig. 6 A.

While this is true (i.e. high CDOM correlating with low S), it is not clear to us how this explains figure 6A.

4.4: Please, include a section to discussion, where you compare your AQYs to those obtained earlier. Please, extend your discussions also to cover the estimated photoreaction rates. SAB in perhaps the most intensively studied coastal sea in terms of environmental photochemistry. The discussion of present study ignores the numerous earlier photochemical studies done in SAB and rivers draining into it. For example, please, compare your results to those published by Vodacek et al. 1997 LO and Moran

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Interactive Discussion

Discussion Paper

Zepp 1997 LO followed by many other studies where e.g., Bill Miller, Moran and Zepp have been involved. These studies have been done at the same coastal region, where the present study was carried out.

We feel that an extended discussion beyond what we have already done, becomes redundant and would unnecessarily extend the length of the paper. Figure 2 attempts to present AQY comparisons with other studies in a concise visual manner instead of adding to the text. There are no AQY spectral data for CO2 in the SAB that we are aware of. Vodacek, Blough, and company worked in the Mid Atlantic Bight (not the SAB). There are a couple of CO AQY for the SAB from the Zepp et al crowd. We have not extended the discussion.

You concluded that ca. 2any other explanations? Scattering of photons (Eq. 11)?

Earlier studies by Miller and Zepp, and Miller et al. did not measure AQY spectra for CO2, but rather in Miller and Zepp (1995) they compared direct photoproduction from full spectrum irradiation in quartz cells in the lab, finding a large range of CO2 to CO ratios, where the ratio of 15-20 was found to be the most common. Miller et al. (and other studies afterwards) used this ratio to extrapolate to whole ocean photochemical production estimates for CO2, based on the more easily measured CO AQYs. In the present study we measured AQYs for both CO and CO2, eliminating the need to use ratios determined nearly 20 years ago. Aarnos et al (2012) used a few AQYs for CO2 photoproduction in the Baltic Sea and calculated that photochemical mineralisation of DOC could potentially balance the yearly input of DOC to the Baltic Sea. There are numerous differences between Aarnos et al. (2012), and the present study. First, both of these numbers were calculated for a specific total area. The area of the Baltic Sea is 10X the area of the South Atlantic Bight (inner shelf area) used for the calculation of the present study, The residence time of water in these two systems is also quite different. Accounting for area alone, this brings the per meter photochemical production rate of Aarnos et al (2012) down to only twice that of the present study. It is also important to note that Aarnos et al (2012) used a different equation than in the present study to calculate photoproduction, making the assumption that all light is absorbed by CDOM. As we have discussed above, and which the authors of that study note themselves, this assumption will necessarily overestimate the amount of photochemical production. Because of these confounding factors, the discussion of these results is necessarily lengthy and only comparitive to a single other study. The aim of the present study was to investigate the variability within a large set of apparent quantum yield spectra for both CO and CO2 , and to determine to what extent we can use optical and seasonal parameters to estimate AQY spectra in the future, rather than to determine how photochemical production varies from study to study. In addition, the complexity of the biological response to photochemical transformations in this system is not included in the present study and we do not feel that introducing an entirely speculative point about this in the conclusions is warranted just for comparative purposes. We believe that an extended discussion of these factors will needlessly lengthen the paper and detract from the main aim of the study, which is to investigate the variability and optical indicators of apparent quantum yield values for CO and CO2. Consequently, we feel that no expanded discussion along these lines need be made to the text.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/9/C4331/2012/bgd-9-C4331-2012-supplement.pdf

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Interactive comment on Biogeosciences Discuss., 9, 6947, 2012.