Decadal time-series of SeaWiFS retrieved CDOM absorption and estimated CO_2 photoproduction on the continental shelf of the eastern United States

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[1] Published algorithms were employed to convert SeaWiFS images of normalized water-leaving-radiance to absorption images of CDOM (chromophoric dissolved organic matter). The best performing algorithm was employed to produce decadal time-series of CDOM monthly composites from 1998 through 2007. Deficits in CDOM absorption coefficient for surface waters across the shelf over the summer were then acquired relative to the uniformly mixed waters prior to and following stratification (spring and fall, respectively). Estimates were attained of the photochemical oxidation of carbon to CO_2 on and beyond the shelf of the Middle Atlantic Bight. Approximately $3-7 \times 10^{10}$ g C as CO_2 were estimated to be produced via photooxidation of CDOM over the summertime, highlighting the significance of CDOM photochemistry and pointing out the importance of CO_2 photoproduction at a global scale. In principle, this approach could be applied to global ocean color data. **Citation:** Del Vecchio, R., A. Subramaniam, S. Schollaert Uz, J. Ballabrera-Poy, C. W. Brown, and N. V. Blough (2009), Decadal time-series of SeaWiFS retrieved CDOM absorption and estimated CO_2 photoproduction on the continental shelf of the eastern United States, *Geophys. Res. Lett.*, *36*, L02602, doi:10.1029/2008GL036169.

1. Introduction

[2] CDOM plays an important role in determining the aquatic light field, as well as being the primary photo-reactive organic species in natural waters [*Blough*, 1997; *Blough and Del Vecchio*, 2002; *Blough and Zepp*, 1995; *Mopper and Kieber*, 2002; *Moran and Zepp*, 1997]. Based on the results of a long-term seasonal study that examined the spatial and temporal variability of CDOM in the Middle Atlantic Bight (MAB) and Delaware and Chesapeake Bays from 1997 to 2003 [*Del Vecchio and Blough*, 2004], we showed that CDOM is primarily of terrestrial origin and that a significant photochemical loss of CDOM absorption (photobleaching) occurs in surface waters of the MAB shelf during summertime stratification, consistent with earlier work [*Vodacek et al.*, 1997].

[3] Atmospherically-important trace gases (e.g., CO_2, CO and COS) are produced upon CDOM photobleaching [*Bélanger et al.*, 2006; *Johannessen and Miller*, 2001; *Jones and Amador*, 1993; *Miller and Zepp*, 1995; *Mopper et al.*, 1991; *Stubbins et al.*, 2006; *Valentine and Zepp*, 1993; *Weiss et al.*, 1995; *Xie et al.*, 1998; *Zafiriou et al.*, 2003]. Several authors have reported significant photochemical loss of dissolved organic carbon (DOC) (from 15 to 60%) when normalized to the complete loss of CDOM absorption (or fluorescence) [*Moran and Zepp*, 1997; *Opsahl and Zepp*, 2001; *Skoog et al.*, 1996; see also *Mopper and Kieber*, 2002, and references therein]. However, fewer studies have examined the relation between CO_2 photoproduction and absorption loss. *Miller and Zepp* [1995] provided evidence that about 15% of total carbon was photooxidized to CO_2 with an $\sim$100% loss of CDOM absorption for various fresh and coastal waters from the South Atlantic Bight, while *Xie et al.* [2004] reported approximately 44% for other waters.

[4] Several algorithms have been developed to distinguish among phytoplankton and other absorbing constituents such as CDOM [*Carder et al.*, 1989; *Fichot et al.*, 2008; *Hoge et al.*, 1995; *Johannessen et al.*, 2003; *Kahru and Mitchell*, 2001; *Lee et al.*, 1994; *Mannino et al.*, 2008; *Maritorena et al.*, 2002; *Siegel et al.*, 2002], thus allowing remote retrievals of CDOM on both local and global scales. Among these models, the *Johannessen et al.* [2003] and the *Mannino et al.* [2008] algorithms were specifically developed from in situ data acquired in part from the MAB, while the GSM01 algorithm [*Siegel et al.*, 2002] has been widely applied on global scales.

[5] Here, a novel approach is introduced for estimating the photochemical loss of CDOM absorption and CO_2 photoproduction on continental shelves based on Sea-Viewing Wide Field-of-view Sensor (SeaWiFS) retrievals of summertime CDOM absorption deficit. Several algorithms [*Johannessen et al.*, 2003; *Mannino et al.*, 2008; *Siegel et al.*, 2002] are used to convert SeaWiFS images of normalized water-leaving radiance to CDOM absorption images from 1998 through 2007, producing monthly composites of CDOM. The best performing algorithm, validated with in situ measurements, is then chosen to approximate CDOM absorption deficits for surface waters across the continental shelf of the MAB over the summer relative to the spring and fall months, providing estimates of the spatial CDOM absorption deficits caused by photobleaching. Using published relationships between absorption loss and CO_2 photoproduction, these absorption

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deficits are then converted to estimates of photochemical oxidation of carbon to CO_2.

2. Methods

2.1. Testing the CDOM Algorithms

[6] Three simple and easily applicable algorithms [*Johannessen et al.*, 2003; *Mannino et al.*, 2008; *Siegel et al.*, 2002] were employed to convert SeaWiFS level 3 images of monthly averaged normalized water leaving radiance [nLw(λ)] to CDOM absorption [$a_{CDOM}(\lambda)$] at various wavelengths (323, 355 and 443 nm), depending on the algorithm employed thus producing monthly composites of CDOM absorption from 1998 to 2007. The recently reported Fichot et al. algorithm [*Fichot et al.*, 2008] was not employed, owing to its complexity and difficulty in application. CDOM retrievals were then compared to in situ CDOM measurements from nine different cruises from the MAB to identify the best performing algorithm (Figure 1). The *Johannessen et al.* [2003] algorithm systematically underestimated CDOM absorption during the summer and overestimated it in spring and fall, exaggerating the difference between these two seasons, and thus overestimates the naturally-induced photobleaching (Figure 1a, red versus black symbols) and the CO_2 photoproduction (see below). The CO_a355S algorithm [*Mannino et al.*, 2008] retrieved in situ measurements to ~20%, with no systematic seasonal differences (Figure 1b, red versus black symbols). A statistical analysis indicated that the slope obtained for the summertime data (0.726) was undistinguishable from that obtained in other seasons (0.603) (Figure 1b, red and black equations, respectively). The March 2003 retrieval was however offset with respect to the rest of the data, and thus a separate linear regression was obtained excluding this cruise (Figure 1b, blue equations). The slope of this latter regression (0.693) was closer to that of the summer retrievals (0.726) as compared to that of all other off-summer data (0.603), providing additional evidence of no systematic seasonal differences among retrievals. The GSM01 algorithm [*Siegel et al.*, 2002] retrievals did not show systematic seasonal differences at high CDOM values, but did exhibit seasonality at low CDOM magnitudes (Figure 1c). The GSM01 retrievals were obtained employing a single value of the spectral slope, which certainly influenced algorithm performance, as the in situ data show a significant range in spectral slopes for the area under study [*Del Vecchio and Blough*, 2004]. Although in situ spectral slopes could have been incorporated in the algorithm to test its performance in more detail, our goal was to employ the simplest algorithm that provided the best retrievals of CDOM absorption coefficients. As the CO_a355S algorithm best fulfilled this requirement, it was thus employed in this study.

2.2. Estimates of CO_2 Photoproduction

[7] From the CDOM monthly composites, changes of CDOM absorption coefficients were estimated for surface waters across the shelf over the summer relative to the springtime (uniformly mixed water column prior to photobleaching) and to the fall (uniformly mixed water column following summertime photobleaching) thus providing estimates of the spatial CDOM absorption deficits caused by photobleaching.

[8] To calculate CO_2 photoproduction rates, the following was assumed: (a) a constant summertime mixed layer depth (15 m) across the MAB shelf, averaged from our in situ measurements [*Del Vecchio and Blough*, 2004]; (b) a linear relationship between absorption loss and CO_2 photoproduction reported by *Miller and Zepp* [1995]; (c) an approximately constant CDOM specific absorption coefficient (i.e., a_{CDOM} normalized by the organic carbon content, a_{CDOM}/DOC) at 355 nm [$a^*_{CDOM}(355)$] of 0.01 μM org. C^{-1} m^{-1} [*Del Vecchio and Blough*, 2004]. The absorption deficits were converted to areal estimates of photochemical oxidation of carbon to CO_2 as follows:

$$CO_2 \text{ photoproduction} = \left[\left(a^{ref}_{CDOM} - a^{month}_{CDOM}\right)/a^*_{CDOM}\right) \times (mld \times 0.15) \quad (1)$$

where the superscript '*month*' refers to the *month of observation* and the '*ref*' refers to the month chosen as the *reference month* (April); a^*_{CDOM} is the CDOM specific absorption coefficient from in situ data below the mixed layer (0.01 μM org. C^{-1} m^{-1}) [*Del Vecchio and Blough*, 2004]; *mld* is the mixed layer depth; and 0.15 represents the 15% photooxidation of carbon to CO_2 relative to ~100% loss of color [*Miller and Zepp*, 1995]. Note that the values reported hereafter for CO_2 photoproduction represent a lower bound since *Miller and Zepp* [1995] and not the *Xie et al.* [2004] data were employed. Equation (1) provides the CO_2 photoproduction in units of μmol C/m^2 (or g C/m^2 when multiplied by the appropriate constant) integrated across the months of study (i.e., starting at the reference month and ending at the observing month). The monthly C flux was obtained by subtracting each integrated CO_2 photoproduction image from its preceding one. The total C fluxes were obtained for the summertime only, from May to August, the time of greatest CDOM photobleaching.

3. Results and Discussion

3.1. Seasonal Change in CDOM Absorption As Evident From Ocean Color Measurements

[9] Previous work provided evidence that CDOM within this region was primarily of terrestrial origin [*Del Vecchio and Blough*, 2004]. Previous work also showed a strong seasonal loss of CDOM absorption in surface waters of the MAB shelf [*Blough and Del Vecchio*, 2002; *Del Vecchio and Blough*, 2002, 2004; *Vodacek et al.*, 1997]. During the summertime, a_{CDOM} in shelf surface waters decreased in a non-conservative manner over a very small salinity range; a_{CDOM} values for waters below the thermocline were much higher and fell closer to a conservative mixing line [see *Del Vecchio and Blough*, 2004, Figure 7; *Vodacek et al.*, 1997, Figure 10]. This behavior was not observed in the spring when the water column was well mixed and the solar irradiance was lower, nor was it observed in October when stratification was lost. These data provided strong evidence of a substantial photochemical sink of CDOM in the surface waters of the MAB shelf over the summer [*Del Vecchio and Blough*, 2004]. Although this same seasonal pattern was observed in over a decade of shipboard observations [*DeGrandpre et al.*, 1996; *Del Vecchio and Blough*, 2004; *Vodacek et al.*, 1997], these measurements lack the continuous

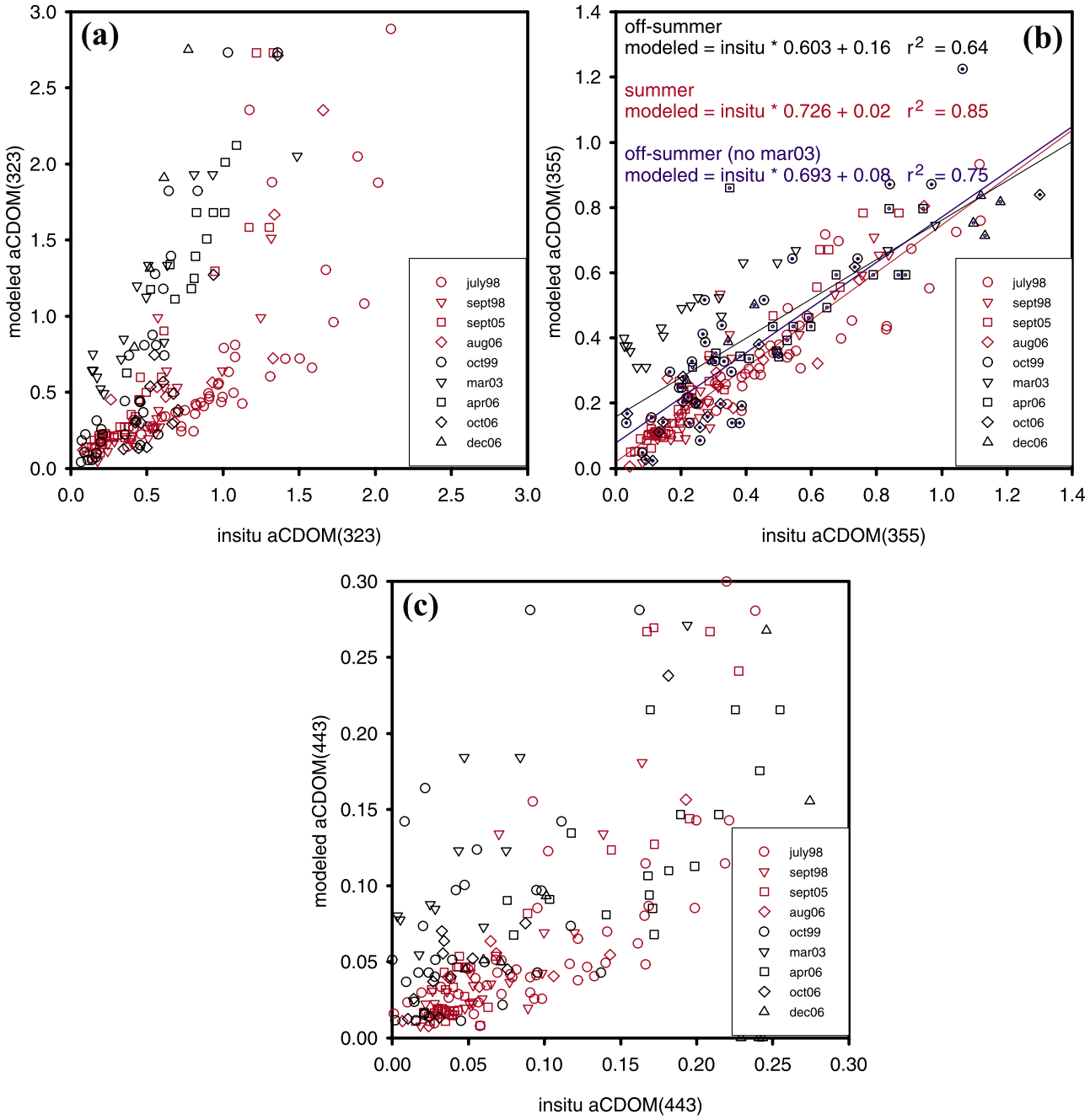

Figure 1. Algorithm products ((a) [*Johannessen et al.* [2003], (b) *Mannino et al.* [2008], and (c) *Siegel et al.* [2002]) versus in situ $a_{CDOM}(\lambda)$ for waters across the MAB during summertime (July 1998, September 1998, September 2005, August 2006) (red symbols) and off-summertime (March 2003, April 2006, October 1999, October 2006 and December 2006) (black symbols).

temporal and spatial coverage that is potentially achievable with satellite data.

[10] The satellite-retrieved data over the decadal time-series 1998–2007 exhibit the same seasonal patterns as obtained in prior field work and provide additional strong evidence for a summertime decrease of CDOM in surface waters from photobleaching. Annually, the highest CDOM absorption values were always observed during spring months and extended across the entire shelf to the shelf break (200 m isobath, ~100 km offshore, −74W−38N) (Figure 2a and Animation S1).[1] a_{CDOM} decreased during summertime reaching the lowest values in July/August and then increased again in the fall when unbleached CDOM from below the thermocline was mixed into surface waters during the seasonal overturn. However, the overall increase during fall never reached the spring a_{CDOM} values due to the extent of CDOM photobleaching in surface waters over the summer

[1]Auxiliary materials are available in the HTML. doi:10.1029/2008GL036169.

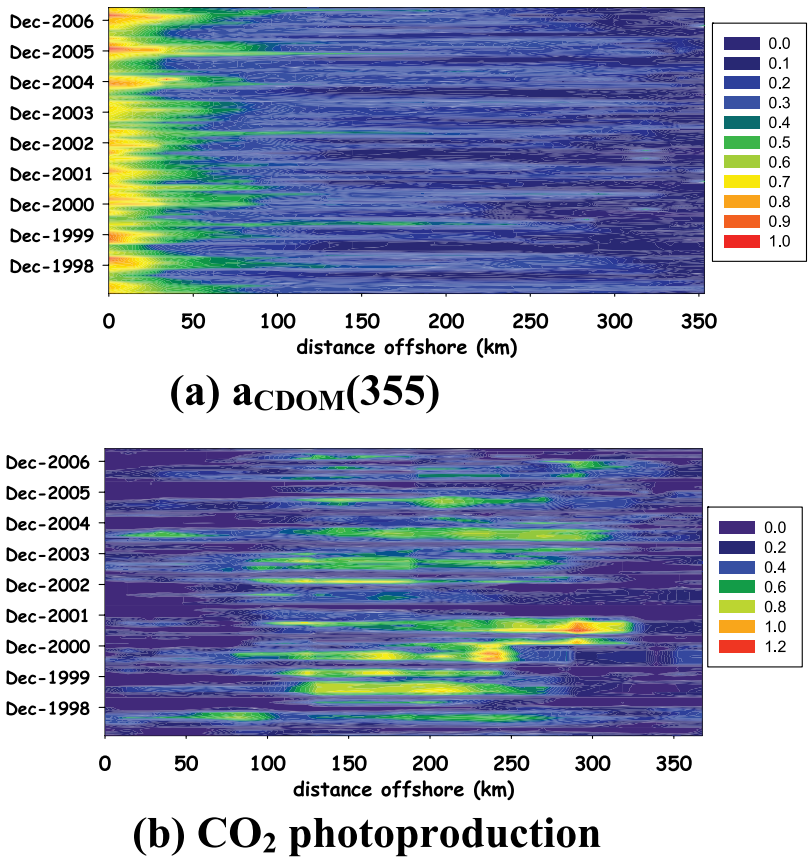

Figure 2. Time-series from January 1998 to September 2007 of (a) the algorithm product [$a_{CDOM}(355)$ (m^{-1})], (b) the CO_2 photoproduction (g of C/m^2 integrated across the months of study) for the diagonal transect crossing the MAB continental shelf from the Delaware Bay mouth to the Gulf Stream (38.8N, −75W to 36.41N, −72W).

(Figure 2a and Animation S1), consistent with prior work [*Del Vecchio and Blough*, 2004]. CDOM absorption decreased offshore reaching extremely low values at >100 km offshore (Figure 2a and Animation S1). Occasionally, locales of higher CDOM absorption were observed offshore during the summer months due to advection from the south of water masses with different CDOM signature moving in a northeastward direction (see below) [*Hoge et al.*, 1995]. In addition, a tongue of water that was extremely low in CDOM absorption (most likely the Gulf Stream) was also observed beyond the continental slope. This feature appeared sporadically during spring months and separated highly colored waters on continental shelf from less colored waters of the Sargasso Gyre (Animation S1).

[11] The largest CDOM absorption deficits (not shown) were observed over the summer months and increased offshore reaching highest values between 150–250 kilometers offshore, while values similar to the reference month were detected over late spring and fall for the entire time-series. Occasionally, the presence of water with CDOM absorption that was significantly different from the surrounding waters was observed. This could be due to upwelling of unfaded water from below the mixed layer, to benthic sources of CDOM that becomes entrained in surface water, or to a pulse of riverine CDOM following large storm related rain events. These waters were observed as 'filaments' that seemed to be moving in a northeastward direction (Animation S1). Because these filaments carried water with CDOM absorption higher than the reference month, they did not show evidence of photobleaching.

3.2. Translating the CDOM Absorption Deficit to CO_2 Photoproduction

[12] Calculated CO_2 photoproduction exhibited significant interannual variability due to changing hydrology. However, annually it was always minimal during the spring, increased over the summertime, becoming quite significant in June through September, and then decreased in the fall (Figure 2b and Animation S2).

[13] Estimates of CO_2 photoproduction increased weakly with distance offshore peaking at about 200 km and decreased somewhat thereafter. On the basis of this weak variation we estimated that approximately 0.4, 0.6, 0.3 gC/m^2/summertime of CO_2 was produced at 100, 200, and 300 km offshore respectively, based on a summertime average (May through August) across the 1998–2007 period.

[14] Employing an MAB shelf area of 120×10^3 km^2 [*Wright and Parker*, 1976] and the values for the variation of the CO_2 photoproduction with distance offshore reported above, areal CO_2 photoproduction values ranging from $3–7 \times 10^{10}$ g C were estimated for the MAB. These values are about three fold lower than those obtained using the Johannessen et al. algorithm [*Johannessen et al.*, 2003], which retrieved between 1.2 and 3.3×10^{11} g C on the

MAB shelf within 100 kilometers offshore and much smaller values beyond the shelf. Although these fluxes are small with respect to primary production on the MAB shelf (~100 fold lower) [*Mouw and Yoder*, 2005; *O'Reilly and Busch*, 1984], they likely represent a significant fraction of the terrestrial carbon introduced to the shelf and highlight the importance of CDOM photochemistry to the removal of this material. This analysis was based on a series of assumptions (a constant summertime mixed layer depth; a linear and appropriate relationship between absorption loss and CO_2 photoproduction; unbleached filaments), thus this net result represents a lower bound to the CO_2 photoproduction.

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