Horizontal and vertical distributions of colored dissolved organic matter during the Southern Ocean Gas Exchange Experiment

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Field and remote sensing measurements of colored dissolved organic matter (CDOM) were acquired in the Southern Ocean during the 2008 Gas Exchange experiment. Values of CDOM absorption coefficient at 440 nm ($a_{440}$) ranged from $\sim 0.02$ to $\sim 0.06$ m$^{-1}$. In general, CDOM was higher in the region sampled during this study than in other regions of the Southern Ocean. CDOM showed an inverse correlation with salinity, and the spectral slope parameter $S$ varied directly with salinity. These relationships, water circulation patterns, and characteristics of South Georgia Island suggested that runoff was a source of CDOM in the study site. Analysis of seasonal variability of $a_{440}$ using ocean color imagery of areas away from the effect of South Georgia Island showed seasonal fluctuations between $\sim 0.02$ to $\sim 0.03$ m$^{-1}$. CDOM production models showed that in situ production could also account for seasonal changes in CDOM.


1. Introduction

The Southern Ocean (SO) is one of the least studied bodies of water. Distance from port and bad weather challenge traditional field research expeditions and new remote sensing techniques. Yet, the importance of the Southern Ocean to the global carbon budget is well recognized. The SO is an important sink of CO$_2$ due to cooling of warm sub-tropical waters and enhanced primary productivity from high concentrations of nutrients [Clementson et al., 1998; Takahashi et al., 1999; Schlitzer, 2002]. The Antarctic Circumpolar Current plays a major role in global ocean circulation and the Antarctic Convergence creates a distinct body of water with unique biogeochemical conditions.

The region selected for this study has high primary productivity attributed to an island mass effect from South Georgia Island [e.g., Atkinson et al., 2001] and high values of colored dissolved organic matter (CDOM) as revealed in historical satellite imagery [Siegel et al., 2002]. Documented CDOM absorption spectra from the SO are limited. Most spectra are for Antarctic coastal waters and the Australasian and Pacific sector of the SO. Although additional data are now available from the CLIVAR and Carbon Hydrographic Data Office (http://whpo.ucsd.edu/), we could not identify any data from our study site. Despite limited data, several general characteristics of CDOM dynamics can be presented. Clementson et al. [2001] reported that CDOM dominated light absorption by dissolved and suspended substances in the SO; CDOM light absorption coefficients at $\sim 440$ nm, $a_{440}$, were three times higher than absorption by chlorophyll (chl). Siegel et al. [2002] estimated that CDOM (CDM in their nomenclature) contributes more than 55% to light absorption south of latitude 50$^\circ$S. Clementson et al. [2001] and Zafiriou et al. [2003] reported values of $a_{440}$ of $\sim 0.1$ m$^{-1}$. A more detailed study by Fierani et al. [2006] reported $a_{440}$ in the Ross Sea ranging from $\sim 0.025$ to 0.125 m$^{-1}$. CDOM is an important light absorber in the marine environment that can control light penetration in both coastal and blue waters. As a result, CDOM is important for the heat budget as well as a contaminant to remote sensing estimates of chlorophyll concentrations.

The primary objective of this study was to examine the distribution of CDOM in the waters sampled during the Southern Ocean Gas Exchange (SOGasEX) Experiment that took place between March and April 2008 on board the NOAA research vessel Ronald Brown [Ho et al., 2011]. Here, we present data on the vertical and horizontal distribution of CDOM and comment on potential sources of CDOM in the region.

2. Methods

The Southern Ocean Gas Exchange expedition departed from Punta Arenas, Chile on 29 February 2008, and returned to Montevideo, Uruguay on 12 April 2008. The main objective of the SOGasEx experiment was to determine piston velocities in oceanic regions with high wind speeds, hence the Southern Ocean [Ho et al., 2011]. The cruise track and location of CTD stations (Figure 1) were determined based on the needs of projects dealing with gas exchange experiments. These included the injection and tracking of passive tracers, and the deployment of instrumented buoys. Weather and mechanical conditions were extraordinary and limited the deployment of instruments.
problems also modified the cruise track. Therefore, the cruise activities were not driven by our study.

2.1. Field Samples

Water samples for CDOM analysis were collected at 51 CTD stations. Samples were drawn from Niskin bottles at selected depths within the mixed layer, the base of the thermocline, and several depths below the thermocline. When possible, samples were collected close to local noon (to attempt satellite comparison), but some samples were collected during night casts (Table 1). Water was drawn into acid-washed amber-colored glass bottles and filtered through a 47 mm 0.2 μm nylon filter (Whatman Nuclepore) under low vacuum pressure (<5 in Hg) using an amber-color polycarbonate filtration rig. Filters were cleaned using consecutive volumes of methanol (25 ml), nanopure water (~150 ml), and sample (~50 ml). Filtration blanks were collected at each station to evaluate the performance of our filtration methods. Absorption scans showed that the filtration method did not add color to the samples.

CDOM absorption spectra were obtained for all samples using an Ultrapath (WPI, Inc) absorption system. The Ultrapath consists of a single beam optical path that contains a high intensity deuterium and halogen light source, a multiple path length (2, 10, 50, 200 cm) liquid waveguide, and a fiber optic spectrometer (Tidas-1, WPI Inc). Optical density spectra (250–721 nm) were acquired using the 2 m path length cell following Miller et al. [2002]. Reference optical density spectra were made using nanopure water. Corrections for the difference in refractive index between seawater and the blank were done according to Nelson et al. [2007]. The spectral slope parameter S was calculated between 400 and 500 nm (i.e., wavelength range relevant to remote sensing of CDOM) using least squares regression of the log-transformed data (a$_g$440 values). Values of CDOM absorption coefficient were reported as a$_g$440 for comparison with remote sensing data. Sensitivity of the Ultrapath was sufficient to measure a$_g$440 for all samples during the study. CDOM absorption spectra were submitted to NASA’s SEABASS.

2.2. Remote Sensing

Remote sensing imagery from the Sea-viewing Wide Field of View Sensor (SeaWiFS), and the Moderate Resolution Imaging Spectrometer (MODIS – AQUA, last re-processing) were downloaded from NASA’s Ocean Color web-site (http://oceancolor.gsfc.nasa.gov/). L1 data were processed to L2 and L3 using SEADAS software (version 6.2). Remote sensing reflectance values were extracted and the quasi-analytical algorithm of Lee et al. [2002] used to calculate a$_g$443. We focused our analysis of historical imagery on the area covered by the GasEx site and the South Georgia Island Shelf. We also used the imagery to locate a region near South Georgia Island (SGI) that is not impacted by the island mass effect. The area selected is Northwest of SGI and is bound by latitudes −47.6477°:−52.9200°, and longitudes −50.5500°:−41.0668°. It was selected by inspection of SeaWiFS imagery collected between 1997 and 2007. Remote sensing data from this region were used to contrast with the high productivity waters influenced by the island mass effect.

3. Results and Discussion

Profiles of salinity, temperature, and a$_g$440 showed a well-mixed surface layer throughout the cruise. The depth of the mixed layer varied between 50 and 60 m depending on weather conditions. Figure 2 shows a vertical profile of averaged a$_g$440 values for all samples and a vertical profile of data collected as part of the Global CDOM project [Nelson et al., 2010]. The average a$_g$440 value in the mixed layer during SOGasEx was 0.047 m$^{-1}$ - more than twice the values observed below the thermocline (0.023 m$^{-1}$) during our study and those reported by Nelson et al. [2010] for all depths (~0.021 m$^{-1}$). Our values below the thermocline
were similar to values measured by Nelson et al. [2010] during 2005. Possible sources of CDOM in the mixed layer are discussed in this section.

Average mixed layer values of \( a_{\text{440}} \), \( S \), temperature and salinity for all CTD stations are shown in Table 1. Data are averages of samples collected in the mixed layer (<50 m), typically 5, 15, and 35 m (other depths were sampled sporadically). There were significant changes in mixed layer \( a_{\text{440}} \), salinity, and temperature during the cruise (Figures 3a and 3b). After 20 March 2008 (Station 14) \( a_{\text{440}} \) doubled, temperature decreased from 6 to 4 °C, and salinity from 33.745 to 33.731 suggesting the crossing of a front. There was a significant inverse correlation between \( a_{\text{440}} \) and salinity, \( S \) showed a weaker but statistically significant relationship with salinity, and \( S \) was inversely correlated with \( a_{\text{440}} \) (Figure 4). These data failed the normality test (Shapiro-Wilk), but natural log transformation [Zar, 1996] did not cause qualitative changes in the regression statistics. These results suggest that we transited through a region in the Southern Ocean where CDOM behaved conservatively. This hypothesis was tested using two end-member mixing models that simulate the behavior of CDOM under conservative mixing [De Souza-Sierra et al., 1994; Del Castillo et al., 2000]. We modeled 20 absorption spectra for salinities corresponding to stations 28 through 50. A two end-member mixing model mathematically combines the absorption spectra of two salinity end-members. For example, let seawater end-members A and B have salinities of 10 and 35, respectively. An intermediate salinity of 22.5 PSU is obtained by combining equal volumes of A and B. To obtain modeled CDOM absorption spectrum of the mixture (e.g., sal = 22.5), the absorption spectra of each end-member is multiplied by 0.5 and then added (corresponding to a 50% mixture of A and B).

![Figure 2.](https://example.com/fig2.png)  
**Figure 2.** Depth profiles of \( a_{\text{440}} \) obtained during CLIVAR cruise A16S in 2005 [Nelson et al., 2010] and SOGasEx cruises. We are only showing CLIVAR cruise data collected between latitudes ~48.0026° and ~56.60° and between longitudes ~35.8421° and ~32.7517°. These spanned the latitudinal range of GasEx but transit east of our sampling area. All values are averages of several samples at each depth. Error bars are the standard deviation of the average. Note that values below the mixed layer matched within the standard deviation of the measurements.
In our model, end-members were combined to produce modeled spectra corresponding to each field salinity sample. Laboratory dilution mixtures and modeled mixtures match well [e.g., Del Castillo et al., 2000]. The end-members used were mixed layer averages of absorption spectra and salinity data from stations 16 and 51 representing values at the beginning and end of the transit through the CDOM gradient (Figure 3). Comparisons between field data and mixing models (Figure 4) indicated that CDOM behavior approached conservative mixing. The changes in CDOM properties observed along the cruise track are consistent with conditions found in coastal areas affected by runoff [Blough and Del Vecchio, 2002]. These observations were made over a small salinity range in the mixed layer and are only possible due to the high precision of the salinity and ag measurements. Based on bottle samples analyzed in a temperature controlled lab on board the R/V Brown, the accuracy of the CTD salinity measurements was ~0.005 (pss78), and the precision in the mixed layer was typically better that 0.002. The accuracy of the ultrapath system is discussed by Miller et al. [2002]. Samples collected at 200 m were used to establish the precision of the ag440 measurements. CDOM should not be highly variable at this depth because there are no major sinks or sources and because we sampled a small volume of the Southern Ocean during a short period of time. Average ag440 values were 0.0244 m$^{-1}$ and the standard deviation of the mean was 0.0020 m$^{-1}$. This compares well with the values reported by Nelson et al. [2010], who sampled over a much larger area. [11] High values of CDOM have been observed in satellite images in the region of the SO GasEx study [e.g., Siegel et al., 2002]. However, the source of this CDOM was not clear. Vertical profiles of CDOM showed that deep-water entrainment cannot be a source of high CDOM for surface waters because CDOM is lower under the thermocline. Therefore, there are two possible sources of CDOM: runoff from SGI and in situ production.

**Figure 3.** Changes in $a_g440$ versus (a) salinity and (b) temperature during the SOGasEx cruise. Drastic changes in CDOM occurred after crossing a frontal region south of −51° latitude. All values are the average in the mixed layer (<50 m). Error bars were omitted here for clarity. See Table 1 for information on standard deviation.
Figure 4
Figure 5. Concentrations of chlorophyll derived from SeaWiFS data for the South Georgia shelf and for a quadrant northwest of the island delimited by latitudes −47.6477: −52.9200, and longitudes −50.5500: −41.0668. All data are monthly averages at 9 km resolution using the standard chlorophyll product. Data for 2008 are from MODIS-Aqua because SeaWiFS was disabled.

[12] Historical satellite imagery from the region (SeaWiFS and MODIS-AQUA) shows a persistent region of high chlorophyll around SGI during the summer [Atkinson et al., 2001; Meskhidze et al., 2007]. Figure 5 shows a chlorophyll climatology from SeaWiFS imagery for two regions near the study site: the SGI shelf, and the region northwest of SGI where our climatology shows no island mass effect from SGI. Figure 5 shows the island mass effect on seasonal variability in chlorophyll concentrations [Atkinson et al., 2001; Korb and Whitehouse, 2004; Meskhidze et al., 2007]. Our analysis of SeaWiFS and MODIS images showed high abundances of CDOM typically extending toward the west from coastal SGI and curving northward toward the Antarctic Convergence Zone (ACC), often extending over the region sampled during SOGasEx (Figure 6). Figure 7 shows CDOM climatology for the same areas presented in Figure 6. The amplitude in seasonal variability of ag443 was higher near SGI than in regions away from the island mass effect. This again suggested that SGI influenced the abundance of CDOM in the region.

[13] Runoff due to ice melting during the summer is responsible for low salinity in shelf waters of SGI [Atkinson et al., 2001; Brandon et al., 1999, 2000; Meredith et al., 2003, 2005] and for intense productivity in shelf waters, inshore, and fjords [Atkinson et al., 2001; Whitehouse et al., 1999]. The vegetation and soils of SGI are typical subantarctic tundra with little or no permafrost [Bockheim and Ugolini, 1990]. The flora consists of grasses, mosses, ferns, lichens and some small flowering plants. Soils arepeat and subantarctic Brown [Bockheim and Ugolini, 1990] with 7–17% carbon content—the highest carbon content in the subantarctic region [Bockheim and Ugolini, 1990; Smith and Walton, 1975]. Therefore, runoff from the Island is likely to contain high concentrations of terrestrial CDOM. Field data, including drifters [Meredith et al., 2003], and models [Trathan et al., 1997] have shown that water flow around the Island is to the west, turning north between longitudes −40 and −42, producing a cyclonic circulation south of the boundary with the Antarctic Circumpolar Current. This cyclonic circulation causes retention of SGI shelf waters (area shown in Figure 6 north of SGI). This is considered a factor in the high primary productivity observed over the shelf [Atkinson et al., 2001] and may explain the high concentrations of CDOM observed during this study. This circulation pattern also explains why the station closest to South Georgia (lat −53.23; lon −36.39) and data from cruise AIS6S showed low CDOM values typical of Southern Ocean blue waters (Figure 8). Although it is likely that runoff contributed CDOM to the region, runoff cannot entirely explain the relationship between ag440 and salinity. The regression for the line shown in Figure 4a has the form

\[ \text{ag440} = -1.07\times\text{salinity} + 36.168. \]

The slope of equation (1) is an order of magnitude higher than other CDOM to salinity relationships elsewhere, and implies that the runoff from SGI has ag440 values of > 30 m⁻¹, an unrealistic number. This strongly suggests that some of the changes in CDOM were independent of salinity and likely produced in situ.

[14] CDOM could be produced in situ by bacteria (see Nelson et al. [1998, 2004, and references therein] for a thorough discussion). The area northwest of SGI (Figures 4, 5, and 7) did not seem to be influenced by the island mass effect. Nevertheless, this area shows a small, but consistent seasonal variation in both chlorophyll and CDOM. Values of ag443 typically change from ~0.016 m⁻¹ in the winter, to ~0.024 m⁻¹ in the summer. This range of values was similar to field measurements made away from the influence of SGI (Figures 2 and 8). If this region does not receive significant terrigenous input of CDOM then the seasonal changes in CDOM must be the result of in situ production. We used the work of Nelson et al. [1998] to evaluate the feasibility of bacterial production of CDOM in our study site. According to Nelson et al. [1998], the accumulation of CDOM is a balance between bacterial production and photodegradation. Accordingly, the rate of change of CDOM can be expressed as

\[ \frac{d\text{CDOM}}{dt} = \varepsilon[\mu_b][\text{CDOM}] + a[\text{CDOM}]e^{-bz}, \]

where \( \mu_b \) is the specific bacterial production (d⁻¹), \( \varepsilon \) is the fraction of production resulting in CDOM, [CDOM] is the background CDOM abundance, \( a \) (d⁻¹) is the photodegradation rate of CDOM (see Nelson et al. [1998] for further detail), \( b \) is an extinction coefficient (m⁻¹), and \( z \) in the water column depths (average mixed layer depth of 50 m in our case). Absent bacterial production values for our study site, we experimented with values reported by Nelson.
et al. [1998] for the Sargasso Sea. Recognizing that the Sargasso Sea and the Southern Ocean are different, this exercise was conducted to better understand CDOM production rates and the time required to produce the seasonal changes in CDOM observed. Two scenarios were explored. The first scenario considered the region NW of SGI away from island mass effect where seasonal changes in CDOM should be caused by biological activity. In this area, historical SeaWiFS data show a seasonal change in $a_{	ext{g}443}$ from $\sim0.016$ to $\sim0.024\text{m}^{-1}$. The second scenario examined the SOGasEx and SGI shelf area where historical SeaWiFS data show seasonal $a_{	ext{g}443}$ fluctuations between $\sim0.022$ to $\sim0.050\text{m}^{-1}$. For both cases we used the highest values of $\mu_b$ (0.1 d$^{-1}$), and half of the photodegradation rates used by Nelson et al. [1998]. The photodegradation rates were halved because NASA’s Surface Meteorology and Solar Energy Database data from 1983 to 2005 show that annual solar irradiance in the SGI region is about half of that in the Sargasso Sea region. For the SOGasEx site it was estimated that it would take $\sim250$ days (~8 months) for productivity to increase CDOM from the background levels to the maximum average level measured ($a_{	ext{g}443}$ from 0.0223 to 0.0457 m$^{-1}$). Based on SeaWiFS data (Figure 7) the observed changes in CDOM only took between two and three months. In contrast, for the region northwest of SGI

![Figure 6](image-url)  
**Figure 6.** SeaWiFS image showing typical distribution of CDOM ($a_{	ext{g}443}$) near the study site and around South Georgia Island. This is a monthly composite from December 1999. Crosses within the circle mark the stations sampled during the GasEx cruise in 2008. White crosses around SGI mark shelf areas from where we extracted remote sensing estimates of chlorophyll and $a_{	ext{g}443}$ from 1997 to 2008. The areas NW of SGI (away from island mass effect) are not visible in the image.

![Figure 7](image-url)  
**Figure 7.** CDOM ($a_{	ext{g}443}$) derived from SeaWiFS data for the South Georgia Shelf and for a quadrant northwest of the island delimited by latitudes $-47.6477$: $-52.9200$, and longitudes $-50.5500$: $-41.0668$. All data are monthly averages at 9 km resolution using the quasi-analytical algorithm of Lee et al. [2002]. Data for 2008 are from MODIS-Aqua because SeaWiFS was inactive.
data. Therefore, we could not evaluate the remote sensing retrievals based on direct match-ups with field data. All we could attempt was a qualitative evaluation. Historical SeaWiFS and MODIS AQUA \( a_{440} \) retrievals in areas with high CDOM near SGI vary between \( \sim 0.04 \) and \( \sim 0.06 \) \( \text{m}^{-1} \), and values of \( a_{440} \) in low CDOM areas away from SGI vary between \( \sim 0.010 \sim 0.035 \) \( \text{m}^{-1} \) (Figure 7). These historical remote sensing values were within the range observed here and by Nelson et al. [2010] (Figures 2 and 3). This suggests that the spatial variability (Figure 6) and seasonal trends (Figure 7) inferred from the satellite imagery were reasonable and real.

4. Conclusions

[17] The SOGasEx cruise transited areas of the SO under the influence of the island mass effect from South Georgia Island. CDOM was well mixed in the surface mixed layer and average values were double of those in deep water. Values of \( a_{440} \) were on average twice those observed away from the influence of South Georgia Island. SeaWiFS and MODIS satellite imagery show seasonal fluctuations in CDOM throughout the SO and near SGI in particular. The relationships between \( a_{440} \) and salinity, \( S \) and salinity, prevailing currents and the characteristics of SGI suggested that land runoff from the island could be a source of CDOM. However, the relationship between \( a_{440} \) and salinity also showed that runoff alone cannot account for seasonal changes in CDOM. In situ CDOM production modeled based on the work of Nelson et al. [1998, 2004] suggested that in situ production can account for seasonal fluctuations in CDOM observed away from SGI. Under CDOM production rates observed in laboratory experiments, in situ production may account for all the changes in CDOM observed. However, our analysis and location of sampling stations were not adequate to discriminate between sources of CDOM in the area. Future work should include more detailed spectroscopic analyzes (e.g., excitation emission matrix fluorescence spectroscopy), samples from water run-off, and inshore offshore transects.

[18] Both concentrations of CDOM and chlorophyll were high in the SOGasEx cruise area. These conditions are not typical of the Southern Ocean. Therefore one should be cautious in extrapolating results from this region to the greater Southern Ocean.

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References


Blough, N. V., and R. Del Vecchio (2002), Chromophoric DOM in the Coastal Environment, in *Biogeochemistry of Marine Dissolved Organic*
DEL CASTILLO AND MILLER: CDOM SOUTHERN OCEAN GAS EXCHANGE EXPERIMENT


