COMPARISON OF CHLOROPHYLL CONCENTRATION ESTIMATION USING TWO DIFFERENT ALGORITHMS AND THE EFFECT OF COLORED DISSOLVED ORGANIC MATTER

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Abstract. The effect of colored dissolved organic matter (CDOM) on the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) OC4v4 and the MODIS algorithms used to estimate chlorophyll-a was studied using satellite and in situ data collected during seasonal cruises in the Northeastern Gulf of Mexico between 1997 and 2000. For chlorophyll-a concentrations <50 mg m''^{3}, OC4v4 generally overestimated chlorophyll-a concentrations up to -300%. The MODIS algorithm provided better estimates of chlorophyll-a concentration by up to a factor of three compared to OC4v4 in regions of high CDOM concentration, found typically nearshore in northern summer and spring. For oceanic waters where chlorophyll-a concentrations <1.0 mg m", both OC4v4 and MODIS algorithms had errors within the SeaWiFS mission specification (±35%) during fall. The OC4v4 algorithm is more susceptible to artifacts due to CDOM absorption of light at 443 nm.

Keywords: chlorophyll-a, Mississippi River plume, SeaWiFS, upwelling, OC4v4

1. Introduction

The original at-launch SeaWiFS algorithm used to compute chlorophyll-a concentration was called OC2, for ocean-color estimates using two bands (O'Reilly *el el,* 1998; O'Reilly *et al,* 2000). This empirical algorithm related remote sensing reflectances, R_{IS}, in the 490 and 550 nm bands to chlorophyll-a concentration. The OC2 algorithm performed well in Case-1 waters in chlorophyll-a concentrations (CJ between 0.03-1 mg m", but overestimated C_n at higher concentrations (Maritorena and O'Reilly, 2000). A refined algorithm, termed OC2v2, still generated unacceptably high biases and errors and this led to the formulation of a four-band algorithm, i.e. OC4v4 (O'Reilly *el a/.,* 2000; Maritorena and O'Reilly, 2000). This algorithm provided more accurate C, estimates because, in general, in more eutrophic waters strong absorption of blue light results in lower water-leaving radiances at 412 nm and 443 nm relative to 490 nm and 510 nm, leading to noise in the OC2 algorithms.

Carder *et al.* (1999) developed algorithms for the Moderate-Resolution Imaging Spectroradiomcter (MODIS) based on a semianalytical bio-optical mod This algorithm uses the 412 nm band to d. inguish CDOM from chlorophyll-a pigment 'ecause of the strong absorption of CDOM at 412 nm If the Carder *el al.* (1999) algorithm doesn't return a viable value for absorption coefficient of phytoplankton pigment at 675 nm (a(675)) owing to, f. r example, low values of $R_{,s}$(412) in eutrophic waters, the algorithm reverted to the OC3 algorithm (O'Reilly *el al.*, 2000; Maritorena and O'Reilly, 2000) to calculate chlorophyll-a concentration.

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Here, we used the OC4V4 and the Carder *et al.* (1999) algorithm to assess the effects of colored dissolved organic matter (CDOM) factor on "standard" NASA bio-optical algorithms using extensive field data collected in a continental margin environment, the Northeastern Gulf of Mexico (NEGOM). This region receives the discharge of three large rivers (Mississippi, Mobile, and Apalachicola) and several smaller ones. Of specific interest was estimating the difference in chlorophyll-a concentration estimate using the different algorithms in areas that contain higher levels ofCDOM.

2. Methods

2.1. Study Area, *In situ* Data Collection, Processing and Analysis

The NEGOM area is defined as the region that extends from the Mississippi River Delta to the West Florida Shelf off Tampa Bay, bounded inshore by the 10-m isobath and offshore by the 1000-m isobath (Figure 1). Nine two-week cruises were conducted in three different seasons between 1997 and 2000 onboard the Texas A&M University (TAMU) R/V *Gyre* (Table 1). Each cruise surveyed eleven cross-margin transects from the 10-m to the 1000-m isobath (Figure 1).

Using a flow-through system for *in vivo* chlorophyll-a and CDOM fluorescence estimates, along-track surface data were collected every two minutes. Flow-through data were collected from a hull depth of 3 m. The water fed into the laboratory was treated in a debubbler and mixing chamber of 10-liter volume with a residence time of about one minute. Two Turner Designs™ model-10 Fluorometers were used, one configured for chlorophyll-a fluorescence and one for CDOM fluorescence observations.

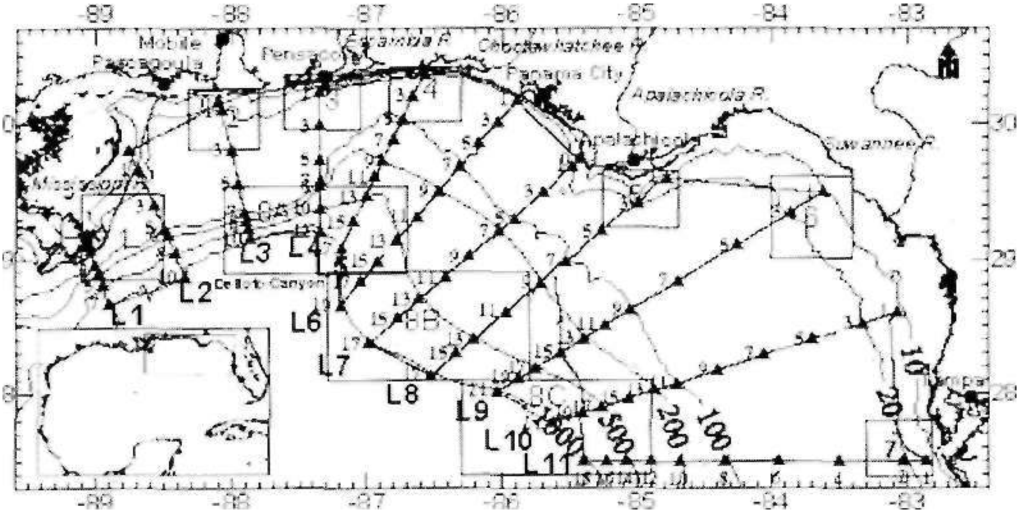

Figure I. The NEGOM cruise track and discrete sampling stations (triangles), with cross-shelf transect lines numbered Ll-Ll I. Along the cruise track, satellite estimate chlorophyll-a concentrations were extracted and compared with CDOM and *in situ* chlorophyll-a concentration. Inset: the Gulf of Mexico.

Table 1 Cruise number dates and seasons

Cruise no.	Start date	End date	Cruise ID	Cruise season
Nl	16 Nov. 1997	26 Nov. 1997	Fa-97	Fall-1997
L_ N 2	4 May 1998	15 May 1998	Sp-98	Spring-1998
N3	25 July 1998	6 August 1998	Su-98	Summer-1998
N4	13 Nov. 1998	24 Nov. 1998	Fa-98	Fall-1998
N5	15 May 1999	28 May 1999	Sp-99	Spring-1999
N6	15 August 1999	28 August 1999	Su-99	Summer-1999
N7	13 Nov. 1999	23 Nov. 1999	Fa-99	Fall-1999
N8	15 April 2000	26 April 2000	Sp-00	Spring-2000
N9	28 July 2000	8 August 2000	Su-00	Summer-200

Discrete water samples from the fluorometer outflow hose were collected for chlorophyll measurements at about 100 CTD stations to calibrate the *in vivo* fluorescence data. Glass fiber filters (GF/F) were used to filter the water samples. Pigments were extracted in 90% acetone and analyzed at sea using an additional, calibrated Turner Designs™ model-10 Fluorometer.

At about 30 of these stations, water samples from the flow-through outflow used for CDOM absorption measurement were filtered using 0.2 urn Millipore filters. The filtrate was collected in amber-colored glass bottles precombusted at 500°C for 24 h. Samples were stored in a freezer for later analysis of the CDOM (Gelbstoff) absorption coefficient (a_g). The absorption spectra were derived using a Hitachi U-3000 Double Beam Spectrophoto-meter (10-cm pathlength). Absorption coefficients were determined using the equation: a_g(A.)=(A(A,)*2.303)/L where, *A(X)* is the absorbance spectra and L is the cuvette length (m). The a_g spectra were smoothed to eliminate instrument noise, and corrected for residual scattering by subtracting absorption at 700 nm from the entire spectrum. The flow-through CDOM fluorescence data were converted to a_{g4}43 (a_g at 443 nm). The 30 stations were selected for coverage of various water types and a broad dynamic range. Linear regression coefficients (r~) between these variables for each cruise ranged from 0.80 to 0.96; only a_{g44}3 is reported in this study.

2.2. Satellite Data Collection, Processing and Analysis

SeaWiFS satellite ocean color measurements were collected using a high, resolution picture transmitter (HRPT) antenna located at University of South Florida (USF), St. Petersburg, Florida, USA. SeaWiFS data were processed using the atmospheric correction algorithms described by Gordon and Wang (1994), and chlorophyll-fl concentration fields were derived using the OC4v4 bio-optical algorithm described by O'Reilly *et al.* (2000). The Carder *et al.* (1999) algorithm was used for MODIS chlorophyll-a concentration and CDOM absorption estimates based on the remote sensing reflectance spectra.

We estimated the mean relative error (MRE) error in the difference between *in situ* and satellite observations as follows:

N

MRE = r£((sate11itei - *in situ-^lin situfiW* (')

where i is the index for all valid data points and N is the total number of valid points.

To avoid biases, data were grouped into two categories, namely satellite, < *in situ,* (MRE1), and satellite, >*in situ,* (MRE2). This helped assess large positive errors separate from large negative errors and avoid small and inaccurate mean errors.

3. **Results and Discussion**

To improve spatial coverage and reduce noise, SeaWiFS products were averaged as image composites of valid pixels over the time period covered by each of the nine cruises (Table 1). These chlorophyll-a images were compared with *in situ* chlorophyll-a concentration by extracting pixels co-located along cruise tracks from the images. Figure 2 shows the *in situ* chlorophyll-a concentration and CDOM estimates as a_{g443} along with the SeaWiFS (0C4v4) retrievals. The correlation coefficient between *in situ* and satellite chlorophyll-a estimates and the MRE are also shown.

The positive MREs range from 84.24% (cruise Fa-99) to 283.40% (Su-98). Most SeaWiFS matchups (-75%) overestimated the *in situ* chlorophyll-a concentration. This is consistent with the finding of Hu *et al.* (2003). The higher positive MRE values occurred where both *in situ* chlorophyll-a and CDOM concentrations were high. During summer seasons, relatively high CDOM values were observed offshore along with high SeaWiFS chlorophyll data. Negative MRE values ranged -8.46% (Sp-00) to -38.60% (Sp-99).

To assess the performance of the SeaWiFS OC4v4 algorithm in low chlorophyll-a concentrations, and to understand errors due to suspended materials, CDOM and/or bottom reflectance, we segmented SeaWiFS chlorophyll-a concentration data between 0.01 mg m'^{3} and 1.0 mg m'^{3} and compared these with *in situ* data (Figure 3). The satellite-derived estimates generally agreed well with the *in situ* data (Figure 3). The correlation between *in situ* and satellite measurements, and the mean relative errors for fall (Fa-97, Fa-98, Fa-99) were quite good outside of the area of influence of the Mississippi plume. The MREs for these three cruises were generally within ±35%. However, in spring and summer, SeaWiFS tended to overestimate *in situ* chlorophyll-a concentration even at the lower-chlorophyll-a concentrations. The positive MRE for spring and summer cruises ranged from 60.07% (Sp-00) to 146.80% (Sp-98) (Figure 3).

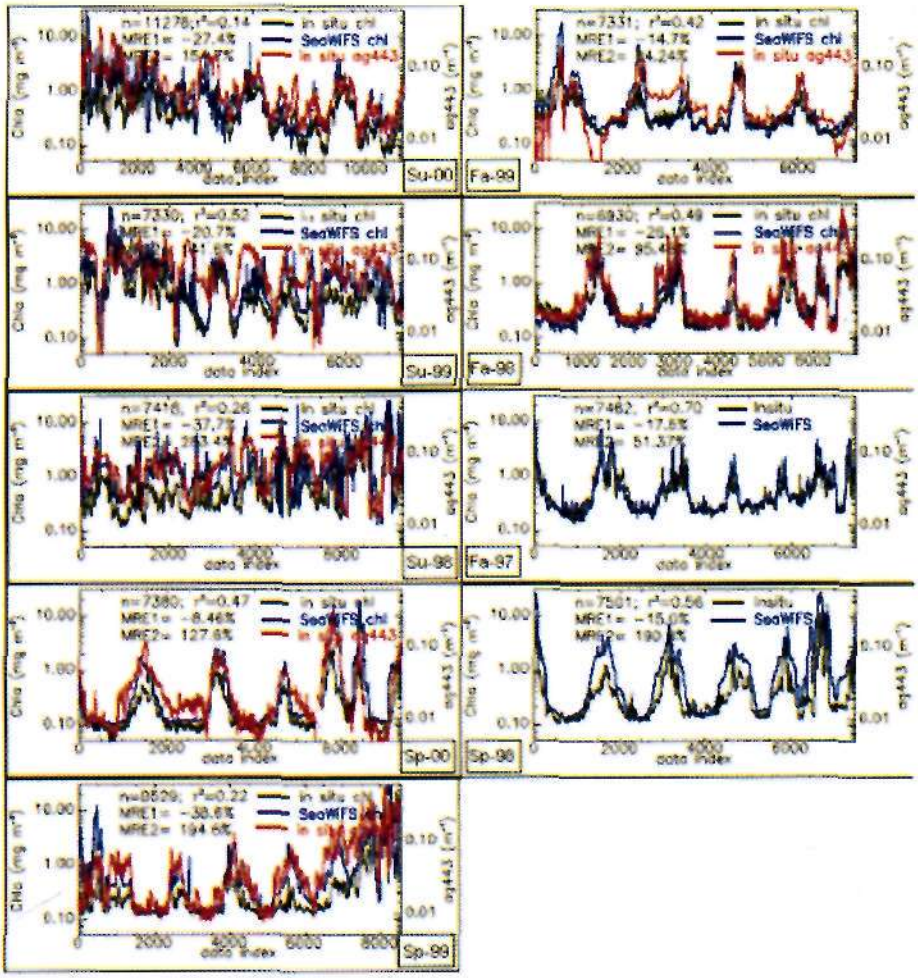

Figure 2. Comparison between *in situ* a^, and chlorophyll-a and SeaWiFS chlorophyll-a (OC4v4) concentration estimates (<50 mg m^J) and along ship track lines for nine NEGOM cruises. MRE1 includes only negative errors for chlorophyll-a comparisons and MRE2 includes positive errors.

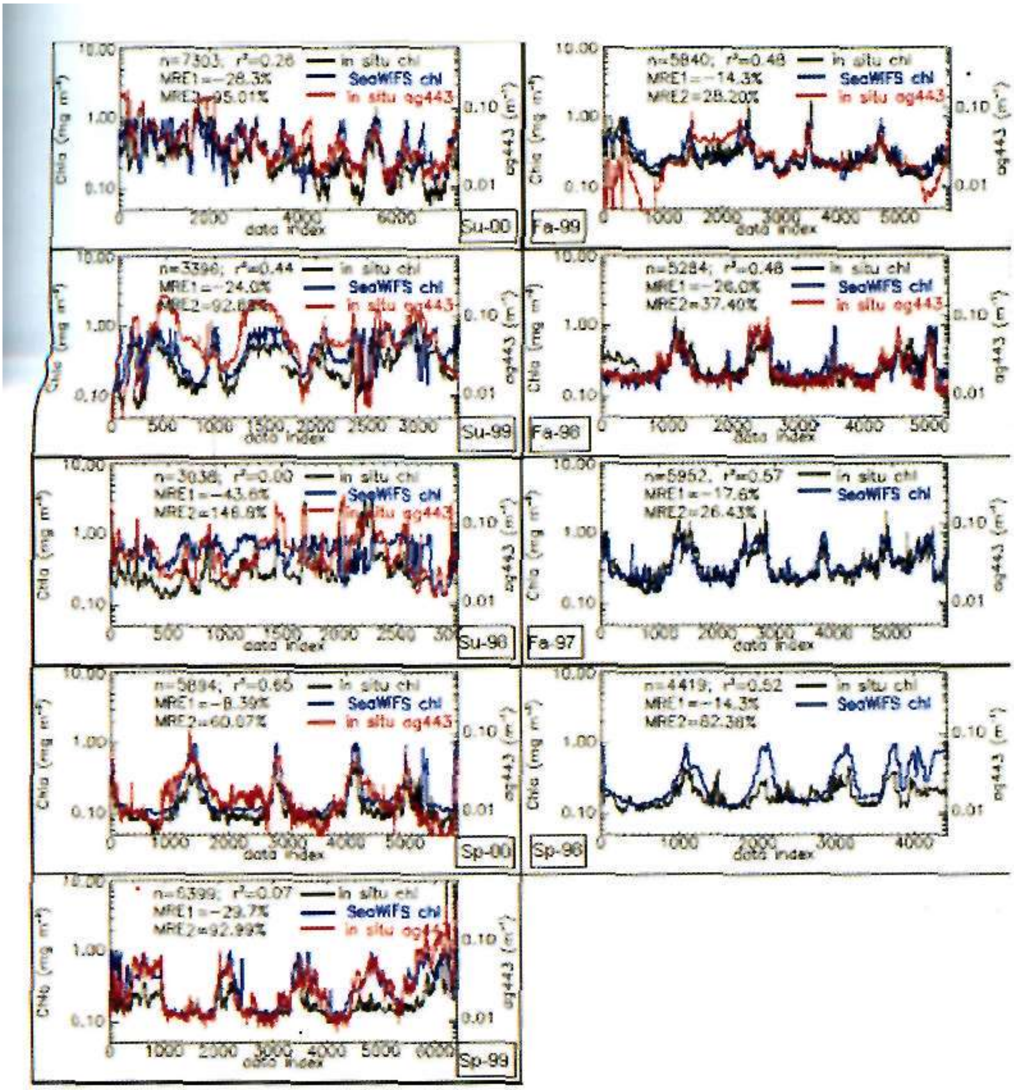

Figure 3. Same as for Figure 2 but only using SeaWiFS-derived chlorophyll-a concentrations <1.0 mg m

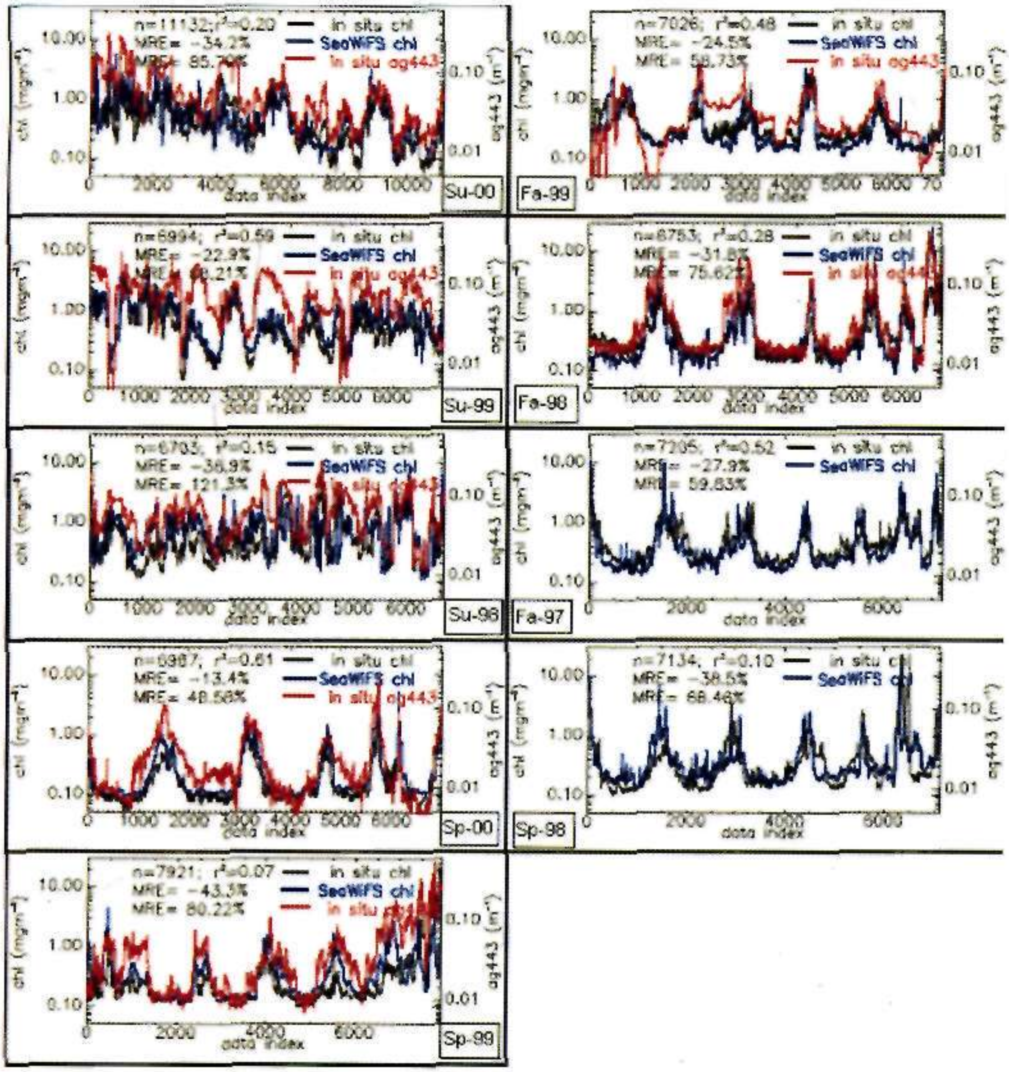

Figure 4. Comparison between *in situ* a^, and chlorophyll-a and SeaWiFS chlorophyll-a derived using the Carder *el al.* (1999) MODIS algorithm along ship track lines for nine NEGOM cruises. MRE1 includes only negative errors for chlorophyll-a comparisons and MRE2 includes positive errors.

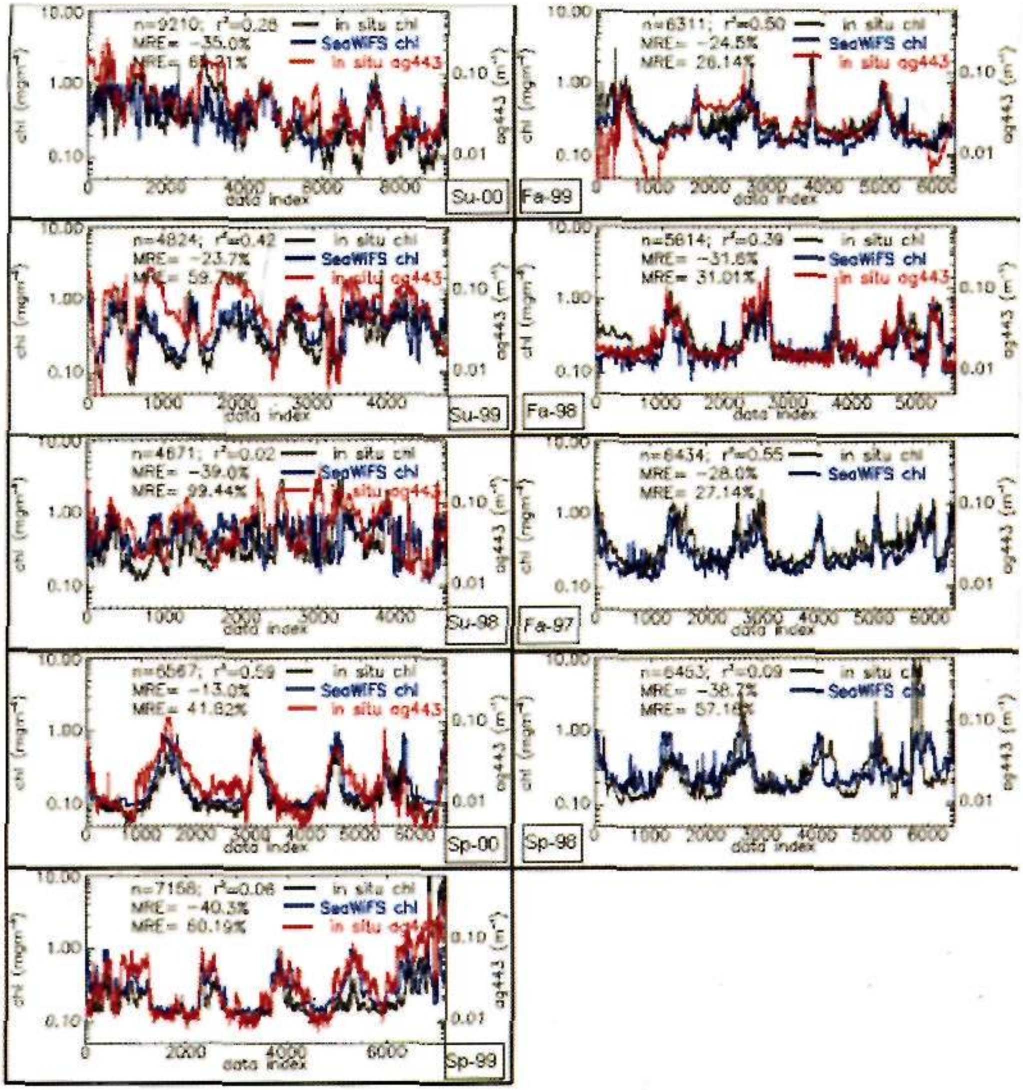

Figure 5. Similar to Figure 4 but for SeaWiFS estimates using MODIS algorithm of chlorophyll-o concentration <1.0 mg m$^{'3}$.

Some factors that may lead to a divergence between satellite and *in situ* measurements are the temporal differences between the 2-week satellite data average and the instantaneous *in situ* estimates. It is also possible that the atmospheric correction used was flawed because of effects of the turbid coastal water (Hu *et al.*, 2000).

It is clear that the SeaWiFS chlorophyll algorithm was affected by CDOM absorption of light. Where higher CDOM concentrations were observed, there was a larger departure between *in situ* and satellite derived chlorophyll-a concentrations during summer 1998,1999,2000 and spring 1999 and 2000.

Results obtained using the MODIS algorithm proposed by Carder *et al.* (1999) to estimate chlorophyll-a concentration and CDOM absorption from satellite data were

5). MRE values ranged from 48.58% (Sp-00) to 121.30% (Su-98) (Figure 4). These errors were almost three times smaller than the errors produced by the OC4v4 algorithm. For the lower range of chlorophyll-a concentrations (<1.0 mg m) improvements were even more significant, with MRE values from 41.82% (Sp-00) to 99.44% (Su-98) (Figure 5). The Carder MODIS algorithm is not immune to contamination by CDOM. Clearly, more research is needed to properly separate effects such of those from CDOM in the algorithms.

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4. Conclusions

For chlorophyll-w concentrations <50 mg m'\ comparison between *in situ* and SeaWiFS retrieved chlorophyll-a concentration employing OC4v4 in areas where CDOM occurs show thai satellite estimates generally overestimate HI *situ* data up to about 300%. For the same range of chlorophyll-^ concentration, the Carder *el at.* (1999) MODIS algorithm showed almost up to 3 times improvements in estimates of chlorophyll-*? concentration, specifically within the regions of relatively high CDOM concentration. For chlorophyll-^ concentration <I .0 mg m", both OC4v4 and MODIS algorithms produced errors falling within the SeaWiFS mission specification (±35%) during fall seasons. However, during spring and summer seasons, when high CDOM concentrations were observed, the Carder MODIS algorithm led to improved results.

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