

Validation of Chlorophyll-*a* concentrations in the Estuarine Waters of Bay of Bengal using OCM-2 Data: A case study in the Godavari basin

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Abstract

Chlorophyll measurements were made on a coastal cruise during March 2012 in the estuarine waters of Bay of Bengal in Godavari basin along Off Kakinada and Yanam coast. *In-situ* optical data were collected at 21 stations (surface to 150m) using Underwater radiometer (Hyperpro-II). *In-vivo* chlorophyll data were collected using wet labs fluorometer integrated with underwater Hyperspectral radiometer. Apart from this chlorophyll-*a* concentrations were measured using HPLC by collecting the water samples at each sampling location. And also chlorophyll-*a* concentrations were estimated from the OCM-2 satellite data, processed using global SeaWiFS Data Analysis System (SeaDAS) software v.6.2 with the existing global ocean colour algorithms namely, OC2 and OC4V4. At all the 21 stations 33 samples collected for chlorophyll-*a* estimation, however, surface water samples of all the stations only being used for direct comparison among chlorophyll concentrations of HPLC, *in-situ* (fluorometrically measured with Hyperpro-II) chlorophyll-*a* with satellite derived chlorophyll from OCM-2. A good correlation between the fluorometer derived and HPLC measured chlorophyll-*a* concentration with an R^2 value of 0.78 was observed. The relation between Chlorophyll-*a* concentration measured from HPLC and retrieved from OCM-2 (OC2 and OC4V4 algorithms) using SeaDASv.6.2 for 10 samples has been compared for validation and obtained an R^2 value of 0.6. Also comparisons done with the *in-situ* measured (fluorometer) Chlorophyll-*a* concentration with OCM-2 chlorophyll data (OC4 -V4 and OC2 algorithms) and validation with 10 concurrent *in-situ* surface measurements showed a significant overestimation by OCM-2 at low chlorophyll-*a* concentrations and underestimation at high chlorophyll-*a* concentrations.

Keywords: Chlorophyll, validation, *in-situ*, HPLC

1.Introduction

Ocean Color satellite measurements provide an important tool to monitor climate relevant changes in the oceans on a global scale. Nevertheless, it is necessary to validate remote sensing measurements with ground-truth data. Especially in the coastal ocean waters where the measurements are scarce. Chlorophyll is considered as the most reliable index of phytoplankton biomass. The relationship between phytoplankton assemblages and the associated optical properties of the water body is important for the further development of algorithms for large-scale remote sensing of phytoplankton biomass and the identification of phytoplankton functional types (PFTs), which are often representative for different biogeochemical export scenarios. Optical *in-situ* measurements aid in the identification of phytoplankton groups with differing pigment compositions and are widely used to validate remote sensing data. Ground-truth data is essential for the retrieval of remote sensing data and the use of various methods to analyze phytoplankton composition that will facilitate interpretation of results in future. The southern Bay of Bengal region along the east coast of India exhibits strongly varying oceanographic signatures within a small geographic province namely, the Godavari basin in terms of chlorophyll and other oceanographic parameters. This allows a comprehensive fine scale survey to characterize the biological and bio-optical variability in the Godavari basin. The mean chlorophyll ratios in this estuarine region show the possibility of healthy phytoplankton populations in lower light intensity and low turbulent areas. Earlier studies (Tripathy et. al., 2005; Sarma et. al., 2009) reported that Godavari estuary is net met heterotrophic water column respiration far exceeds over the mean photic zone productivity. River discharge was identifies as the main source of nutrients in the Godavari estuary by Sarma et. al., (2011). In this study we present results from an exclusive coastal cruise conducted in the Godavari basin in March 2012.

2. Study Area

Godavari is the largest of Indian peninsular rivers; the river divides into two main distributaries Gautami and Vasishta which gives rise to a sprawling estuarine deltaic system fringed with tidal creeks and dense mangrove forests before reaching the Bay of Bengal. The Godavari estuary is well mixed up with the tidal effect dominating in the lean season. The area between the Gautami and Godavari and Kakinada bay has dense vegetation of mangrove forests and mudflats. The shallow Kakinada bay opens into the sea on its northern side and is bordered along by a narrow sand bar.

The study area encompasses the estuarine waters of the Godavari basin along Off Kakinada and Yanam during March 1-10, 2012 covering 21 stations from $16^{\circ} 41.125'N$ to $16^{\circ} 58.099'N$ latitudes and $82^{\circ} 32.141'E$ to $82^{\circ} 23.425'E$ longitudes. The figure (1) shows the geographical distribution of the locations of *in-situ* data collected. Among all the 21 stations, 19 stations covers the Coastal waters (Case-2) at varying depths from surface to 75m whereas 2 stations covers the intermediate waters varying from 100m to 150m of depth covering the Kakinada Bay and Gautami Godavari estuarine region of the Bay of Bengal. The first four stations as shown in figure(1) were covered in all the days from 02 to 05 of March 2012 and the other 17 stations are covered during 06 to 09 of arch 2012.

3. Materials and Methods

***In-situ* data**

Hyperpro-II

Hyperspectral Underwater radiometer (Hyperpro-II) from Satlantic Inc. measures the colour of the ocean and its spectral variability throughout the euphotic zone. It provides observations of the optical properties of the ocean to investigate the fundamental biological and physical processes that involve light in the ocean. Currently, the modular design of the Profiler II allows the system can be configured by Satlantic to be either a free-falling profiler with detachable float for near-surface measurements. The profiler system is easily mounted for the real time and near surface measurements. Irradiance and Radiance measurements can be collected as close as 5cm from the sea surface. The operational integration of the Fluorometer (Wet Labs ECO series) within Hyperpro-II is used for determination of chlorophyll fluorescence in profiling mode. The Chlorophyll-fluorescence serves as a valuable indicator of active phytoplankton biomass and chlorophyll concentration in waters. These measurements are used for tracking biological variability and abundance in the water column. The accuracy of the measurements of chlorophyll concentrations are followed by the ACT protocols.

The *in-situ* data was collected from the cruise in the Bay of Bengal from March 01 -10 2012 in coincidence with the OCM-2 satellite pass. The in-vivo chlorophyll-a fluorescence profiles data using Fluorometer in these coastal waters was collected from surface to 150m of depth. Sampling was carried out daily by collecting seawater from 7 depths (0, 5, 15, 25,30, 50 and 75m) using Niskin water samplers. Filtrations were done immediately, using Whatman GF/F filters and stored $-20^{\circ}C$ to extract the Chlorophyll pigments by HPLC analysis.

Satellite Data

OCEANSAT-2 spacecraft of Indian Space Research Organization (ISRO) is the second satellite in ocean series, which was successfully launched on September 23, 2009 from Shriharikota by Polar Satellite Launch Vehicle (PSLV)-C14 rocket. The OCEANSAT-2 satellite carried three main instruments namely i) Ku band pencil beam Scatterometer, ii) Ocean Colour Monitor (OCM) and iii) Radio Occultation Sounder of Atmosphere (ROSA) instrument of Italian Space Agency (ASI). The OCEANSAT-2 OCM is mainly designed to provide continuity to the OCEANSAT-1 OCM instrument and OCM will collect data in 8 spectral bands 400 nm and 885 nm with a spatial resolution of 360 m and temporal resolution of two days, 1420 km swath, higher signal to noise ratio and a payload tilt mechanism to avoid sun glitter and the imaging principle of OCM is based on push-broom technique. Ocean Color Monitor (OCM-2) instrument one of the payloads is designed to obtain quantitative information of ocean-colour variables e.g. chlorophyll-*a* concentration, vertical diffuse attenuation of the light, (K_d) and total suspended matter (TSM) concentration in coastal waters. OCEANSAT-2 OCM is almost identical to OCEANSAT-1 OCM, however central wavelength of two spectral bands i.e. band 6 and 7 have been shifted from 670 nm to 620 nm for improved quantification of suspended sediments and 765 nm to 740 nm to avoid oxygen (O_2) absorption.

Relatively cloud free data of OCM-2 data during the study period covering Godavari basin of row: 10 and path: 14 has been selected. The global processing software namely SeaWiFS Data Analysis System (SeaDAS v.6.2) was used for processing the OCM-2 data. chlorophyll-*a* concentration was estimated using the available global ocean colour chlorophyll algorithms namely Ocean Colour 2 (OC2), Ocean Colour 4 (OC4-V4)(O'Reilly et. al., 1998) in SeaDAS software and compared with the *in-situ* measured chlorophyll-*a* concentration data for validation in the coastal waters Off Kakinada and Yanam regions as shown in the study area. As the sampling dates of the cruise are from 02-10 March 2012, the OCM-2 satellite pass covering the Godavari basin due to the 2-day repetivity were available as shown in the Table. 1.

4. Data processing methods

There are various techniques to measure chlorophyll, including Spectrophotometry, high performance liquid chromatography (HPLC), Fluorometry and Satellite retrieval. The methodological variability is

caused by merging measurements from different instruments, both below surface and above surface, processed with variable procedures.

4.1 *In-situ* data processing

The chlorophyll-*a* concentration from the radiometer profiles were estimated using (Prosoft 7.7.16) the existing SeaBAM and Gordon models for the surface waters. In order to validate the *in-situ* measurements with the satellite data the radiometric measurements of chlorophyll-*a* concentrations were averaged to a subsurface depth of 5m.

4.2 Satellite retrieval of *Chlorophyll-a*

The simultaneous raw OCM-2 Local Area Coverage (LAC) coverage data with 360m resolution for the corresponding cruise dates were acquired. The processing of OCM2 imageries were implemented with SeaDAS version6.2 software (running on LINUX and IDL). As is well known, SeaDAS is globally accepted ocean colour data analysis software equipped with advanced processing features. OCM-2 has been incorporated in SeaDAS v.6.2 software. The present processing sequence of OCM-2 in SeaDAS v.6.2 involves the conversion of level1b (L1B) data to level2 (L2) format. In the process of generating the L2 products which involve different processing methods along with atmospheric correction, flagging and masking with appropriate thresholds for cloud, land and glint affected areas / pixels a correction of suitable algorithm is being applied for the study locations for that scene/area.

In oceanic remote sensing, the total signal received at the satellite altitude is dominated by radiance contribution through atmospheric scattering processes and only 8–10% of the signal corresponds to oceanic reflectance (Chauhan et al.,2003). Before any interpretation and detection of the ocean colour data in the retrieval of ocean colour parameters from space such as chlorophyll concentration in near shore waters involves two major steps, the first is atmospheric correction of visible channels to obtain normalized water leaving radiance, $\rho_w(\lambda)$ and the second is the application of bio-optical algorithms for water parameters retrieval. Therefore, it becomes mandatory to correct for atmospheric effect, to retrieve any quantitative parameter from space. Gordon and Wang (1994) developed the basic atmospheric correction algorithm based on single-scattering algorithm for non-absorbing aerosols was adopted for the atmospheric correction of OCM-2 data. The basic algorithm also includes the multiple scattering interactions between air molecules and aerosols. It has been shown that for near infrared (NIR) channels,

the water leaving radiance, coming out of ocean was assumed negligible (Gordon,1997; Siegel et al.,2000) and approximately considered equal to zero, can be used to estimate the aerosol properties in the NIR bands , and aerosol modelling can be used to extrapolate it from NIR to the visible bands by using appropriate aerosol models and finally used to compute the water leaving radiances in the visible wavelengths. This approach uses data from band 7 and band 8 of OCM-2 and specific F_o values, wavelengths, Rayleigh optical depth data are substituted. The data on solar zenith and azimuth angles and sensor zenith and azimuth angles are obtained from the corresponding L1B data of OCM-2. However, accurate atmospheric correction in coastal environments is tricky because land, urban coastal areas, and oceanic environments co-exist. The derived water leaving radiances data are then used as input for the different bio-optical algorithms. In this regard, the existing chlorophyll algorithms like OC2 and OC4-V4 (O'Rielly et al., 1998) were used for estimating the chlorophyll concentrations.

The OC2 and OC4-v4 algorithm has the following functional form as shown.

$$(a) \quad \text{Chl_OC2} = 10.0^{(a[0]+a[1]*R+ a[2]+R^2+a[3]*R^3) + a[4]}$$

$$R = 490/555$$

$$a = \{0.2974, -2.2429, 0.8358, -0.0077, -0.0929\}$$

$$(b) \quad \text{Chl_OC4} = 10.0^{(a(0) + a(1)*R + a(2)*R^2 + a(3)*R^3 + a(4)*R^4)}$$

$$R = \text{alog}_{10} ((R_{rs443} > R_{rs490} > R_{rs510}) / R_{rs555}) \text{ [maximum band ratio]}$$

$$a = [0.366, -3.067, 1.930, 0.649, -1.532]$$

Maximum-band-ratio (MBR) refers to the variable R, which varies with spectral shape. The figure (2) shows the chlorophyll images generated after processing in SeaDAS 6.2 for the cruise dates.

4.3 High Performance Liquid Chromatography Analysis

Samples were collected in plastic bottles and for the pigment analysis samples were immediately filtered on a GF/F filter (pore size $0.7\mu\text{M}$) avoiding exposure of the filter paper to direct light and high temperature. The filter paper was stored in liquid nitrogen until for analysis in the laboratory. The frozen filters were immersed in 3 ml 95% acetone (v/v in de ionized water) for extraction using a sonicator probe (5s, $25\mu\text{M}$) under low light and temperature (4°C) followed by storage at -20°C for 4h. Pigments Analysis was done by High Performance Liquid Chromatography (or high pressure liquid chromatography) as per the JGOFS protocols 1994. From this the chlorophyll-*a* pigment concentration

has been extracted from the samples collected at different locations at different depths. For validation with the *in-situ* measurements the extracted concentrations were averaged to a subsurface depth of 5m and surface measurements were considered for validation with satellite data.

5. Results and Analysis

The spatial distribution of chlorophyll-a along the transects for the corresponding cruise dates are shown in figure(2) which shows a decrease in the chlorophyll-a concentration while moving away from the coast towards the offshore waters of Kakinada and Yanam regions on the corresponding satellites passes. Validation of the chlorophyll algorithms was carried out by comparing chlorophyll-a derived from OCM-2 images with *in situ* data collected concurrently (± 2 hours) and HPLC chlorophyll-a data. A total of 33 matching chlorophyll-a measurements were considered for comparison of *in-situ* and HPLC data and 10 matching data points were found between 02 and 09 March 2012 for comparison of Satellite measurements with HPLC, *In-situ* data. All the two chlorophyll algorithms produced approximately similar results (figures4&6). In general, they overestimated chlorophyll-a at higher concentrations and underestimated it at lower concentrations. When comparing satellite-derived chlorophyll with *in-situ* measured and HPLC chlorophyll data, on 5th and 7th March 2012 data in some parts of the sampling locations were masked out in the processing scheme (i.e., atmospheric correction) become dominant over the bio-optical algorithm.

5.1 Comparison of *in-situ* chlorophyll-a with OCM-2

As a part of validation the *in-situ* measured chlorophyll-a concentration has been compared with satellite derived chlorophyll-a during the study period using various chlorophyll-a algorithms like OC2 and OC4-V4 (O'Reilley et al., 1998). As mentioned in Table1 of the acquired satellite passes with corresponding cruise dates were used as input to the SeaDAS processing software for generation of the chlorophyll images. A scatter plot was made between the *in-situ* measured chlorophyll-a concentration and the satellite derived (a) OC2 and (b) OC4) chlorophyll concentration as shown in figure (3). From the scatter plot it is observed that for all the sampling points there is not very significant correlation noticed for concentrations greater than 2.0 mg m^{-3} in case of OC2 and $>3.0 \text{ mg m}^{-3}$ in case of OC4 derived chlorophyll. From this it is clear that there is an under estimation of chlorophyll-a concentration in the coastal waters of the OCM-2 data.

5.2 Comparison of *in-situ* (radiometer) chlorophyll-*a* with HPLC

As mentioned in section 4.3 chlorophyll-*a* concentration was measured using HPLC technique for all the stations and for all the depths. The highest concentration of chlorophyll-*a* concentration found was 18 mg m^{-3} in 2007 that increased to 22 and 28 mg m^{-3} in 2008 and 2009 (Acharrya et al., 2012) whereas in this case the high concentrations of chlorophyll-*a* about 7 mg m^{-3} was observed in Kakinada Bay compared to the Godavari estuarine region. However, an attempt is made to compare the chlorophyll-*a* concentration measured from HPLC and *in-situ* measurements. As the radiometric and HPLC measurements of chlorophyll-*a* concentration were averaged to subsurface depth of 5m and showing an increment in the chlorophyll-*a* concentration. A very good correlation between these measurements were observed with an R^2 value of 0.78 as shown in figure (5) and statistics were also derived for the data points as mentioned in Table-2.

5.3 Comparison of HPLC chlorophyll-*a* with OCM2

Apart from the inter comparison of the *in-situ* measured chlorophyll-*a* concentration with OCM-2 derived as well as with the HPLC measured chlorophyll-*a* concentrations an attempt is made to compare the HPLC measured chlorophyll concentrations with the OCM-2 derived chlorophyll-*a* concentrations as shown in figure(6). From the analysis it is observed that a good correlation with an R^2 value of 0.6 and 0.59 was observed with OC2 and OC4 respectively.

6. Conclusions

From this analysis it is observed that the existing global ocean colour algorithms over estimates in the near shore coastal waters as well as estuarine regions of Godavari. In this optically complex waters near the estuarine waters if the chlorophyll-*a* concentration is greater than $\sim 2.5 \text{ mg m}^{-3}$ the current global ocean colour algorithms fail. If we consider a small local / regional geographical province and then apply these algorithms for a particular province these algorithms works better rather than taking the total basin as a whole for validating the algorithms. This could be attributed to chlorophyll concentration plays a major role like the sediment re-suspension, pigment and the shell structure which is being formed by calcification. The costal system is more optically complex because of short-term coastal upwelling, enhancement of nutrients because of river run-off and anthropogenic activity and biological process like nitrification, de-nitrification, carbonate system etc which has direct bearing with phytoplankton growth and their pigment characterization. Besides the area is dominated by unicellular

diatoms basically contains silica. Hence the coastal process becomes more complex in terms of bio-geo chemical behavior. Hence retrieval of chlorophyll becomes erroneous in its quantification. Further refinement of the atmospheric correction is needed for OCM-2 to attain its goal of accuracy for chlorophyll retrieval in the coastal waters. This requires specific, suitable regional bio-optical algorithms such as fluorescence based and inherent optical properties (IOPs) based algorithms to overcome this problem.

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Table 1: The co-incident Oceansat-2 Ocean Colour Monitor passes covered (used) for validation

Date	Path	Row
03 March 2012	10	14
05 March 2012	10	14
07 March 2012	10	14
09 March 2012	10	14

Table-2: HPLC data values (\pm 2 hours) selected for validation with OCM-2 data

Cruise Date	Location	Depth (m)	Time (hr)	Chl-a HPLC	Chl-a OC4	Chl-a OC2
7-Mar-12 (Transect)	Station3	0	11:00 AM	4.11	3.4084	1.9637
	Station4	0	12:30 PM	1.45	2.9431	1.7765
	Station5	0	13:45 PM	1.27	1.444	1.0864
5-Mar-12 (Transect)	Station2	0	12:00 PM	3.30	1.936	1.3336
	Station3	5	13:00 PM	1.08	1.8488	1.2918
3-Mar-12 (Time series)	Station1-50m	0	11:00 AM	0.79	0.71616	0.63725
		0	12:00 PM	0.54	0.71616	0.63725
		0	13:00 PM	0.75	0.71616	0.63725
9-Mar-12 (Time Series)	Station1-75m	0	11:00 AM	1.26	3.3789	1.9521
		0	13:00 PM	2.07	3.3789	1.9521

Figure 1: Geographical Spatial distribution and *in-situ* sampling site locations for Chl-a concentrations in the Godavari basin during 02nd to 09th March 2012.

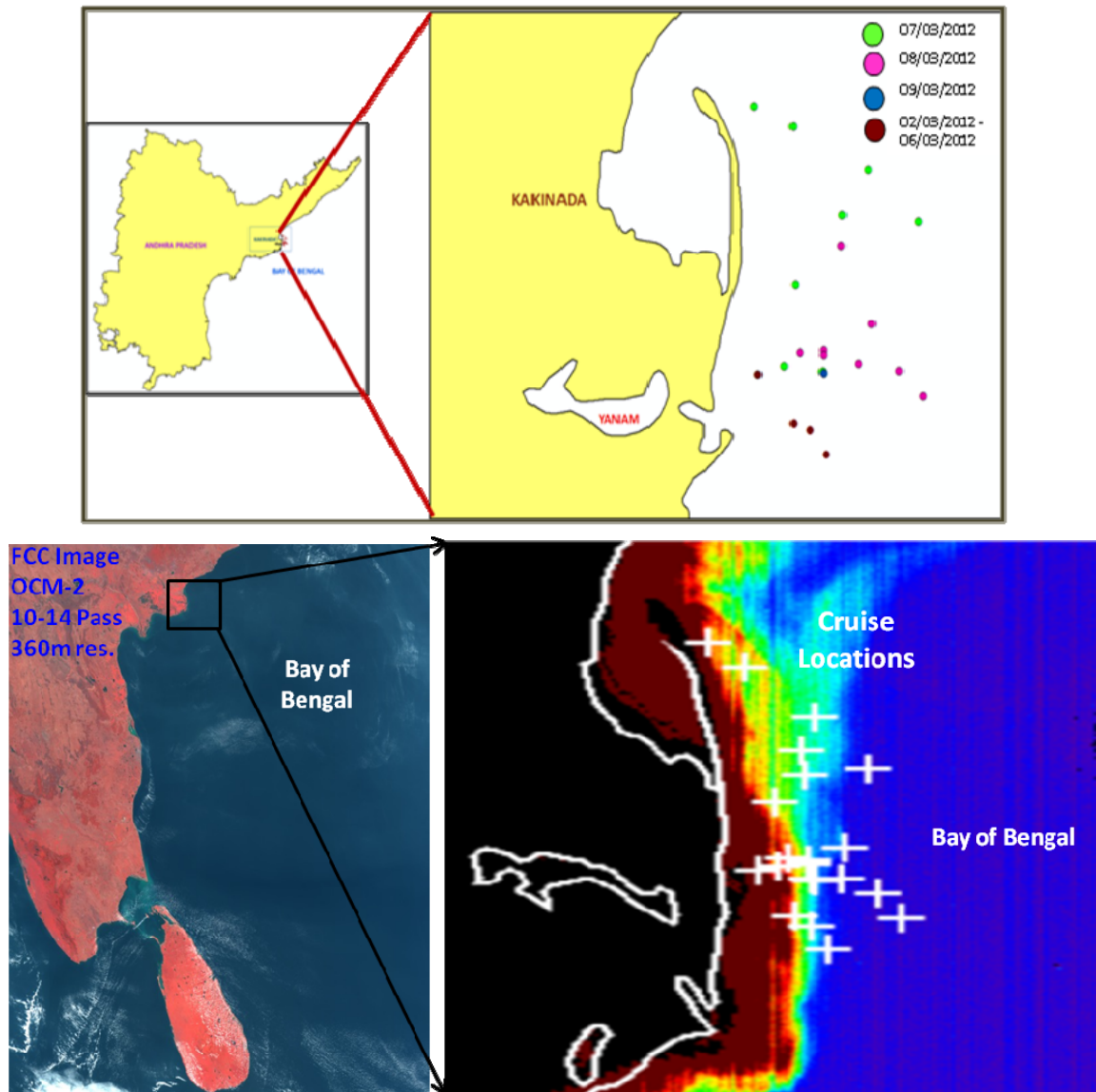


Figure 2: Spatial distribution of Chlorophyll-a derived from OCM-2 on corresponding cruise dates

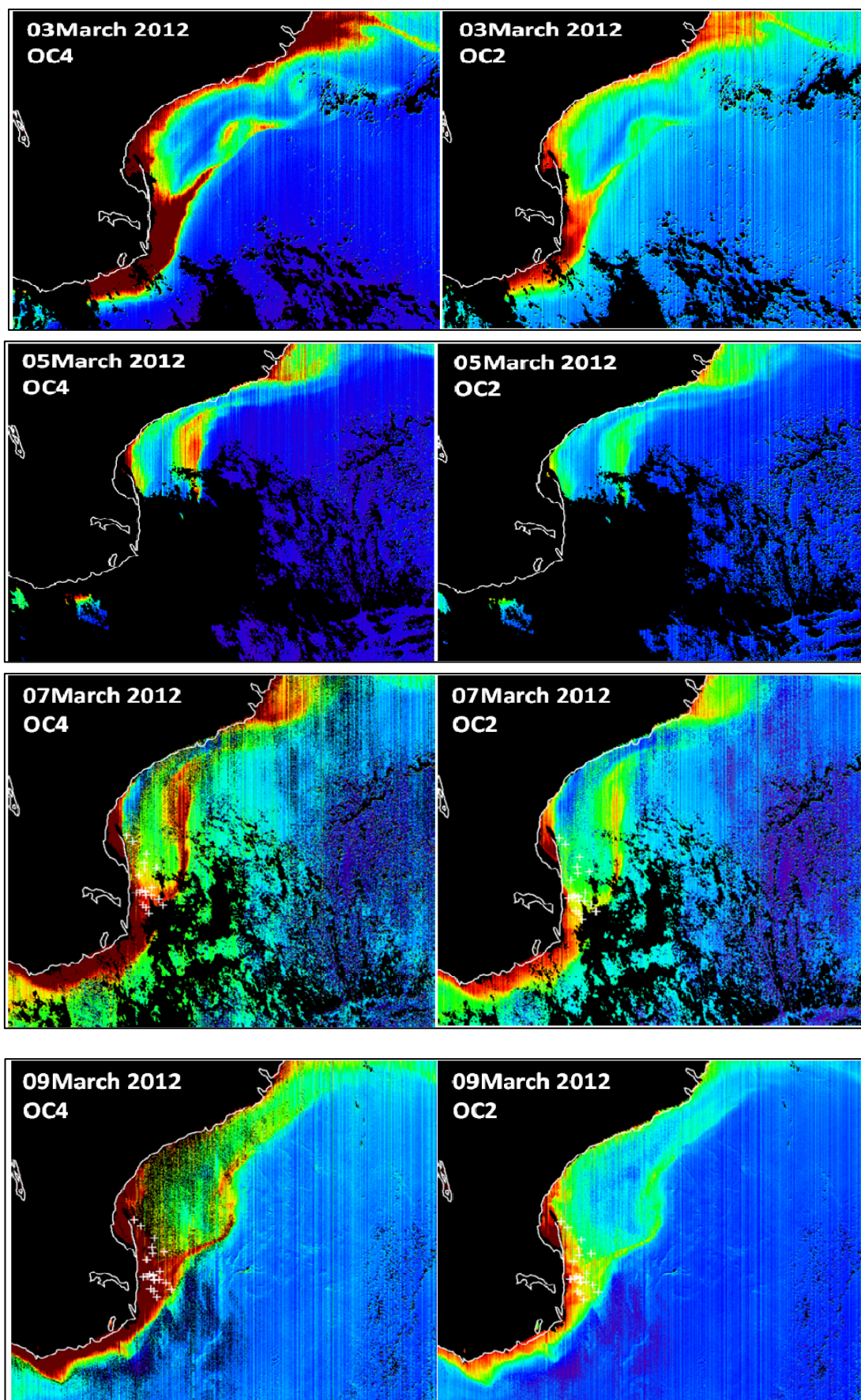


Figure 3: Comparison of *in-situ* (radiometer) Chlorophyll-a with OCM-2 derived Chlorophyll-a

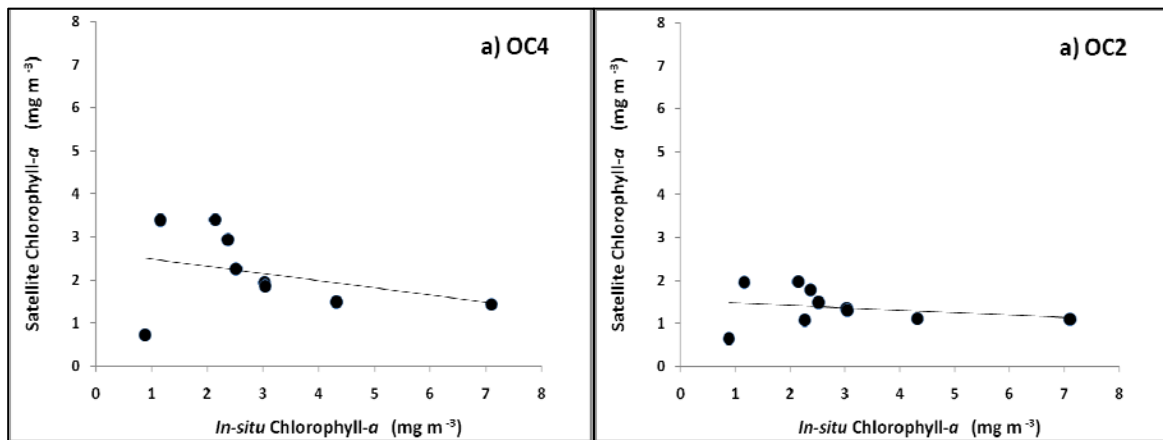


Figure 4: *In-situ* (radiometer) Chlorophyll-a compared with OCM-2 derived Chlorophyll-a on 5th and 7th March 2012.

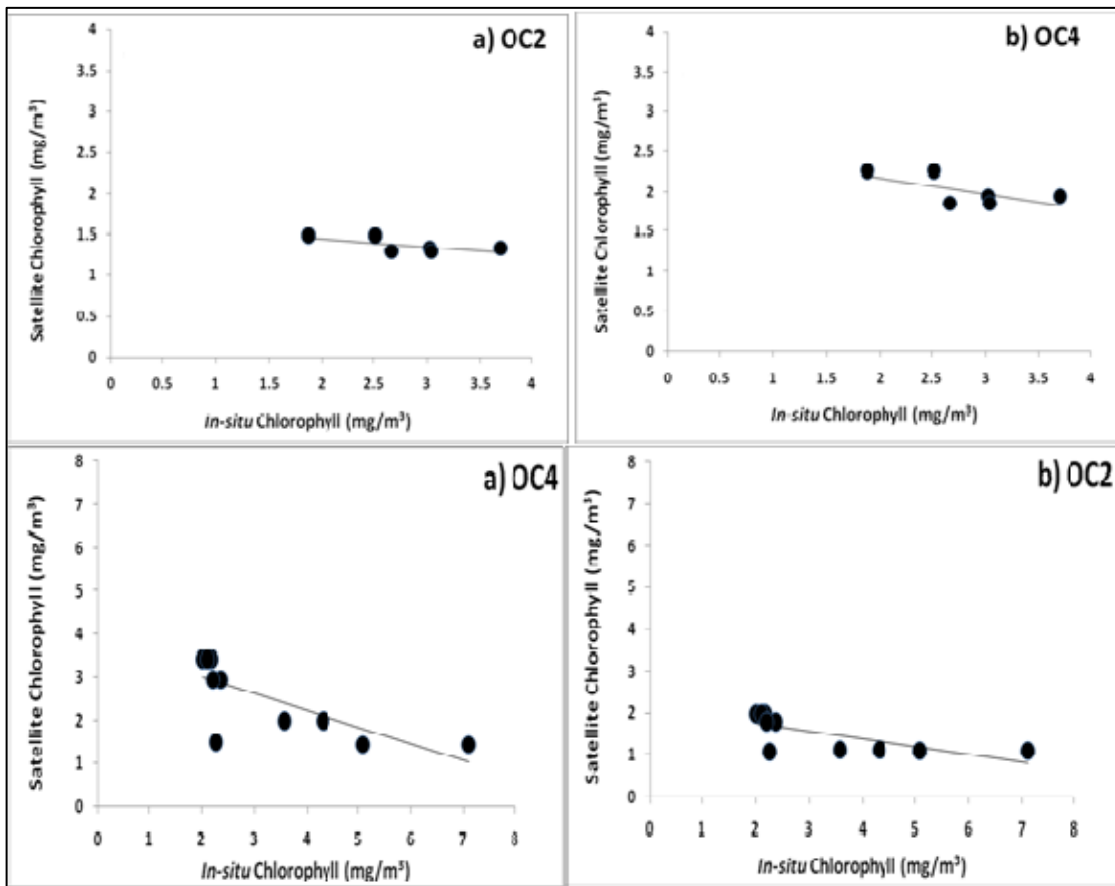


Figure 5: HPLC measured Chlorophyll-a concentrations compared with *In-situ* (radiometer) Chlorophyll-a

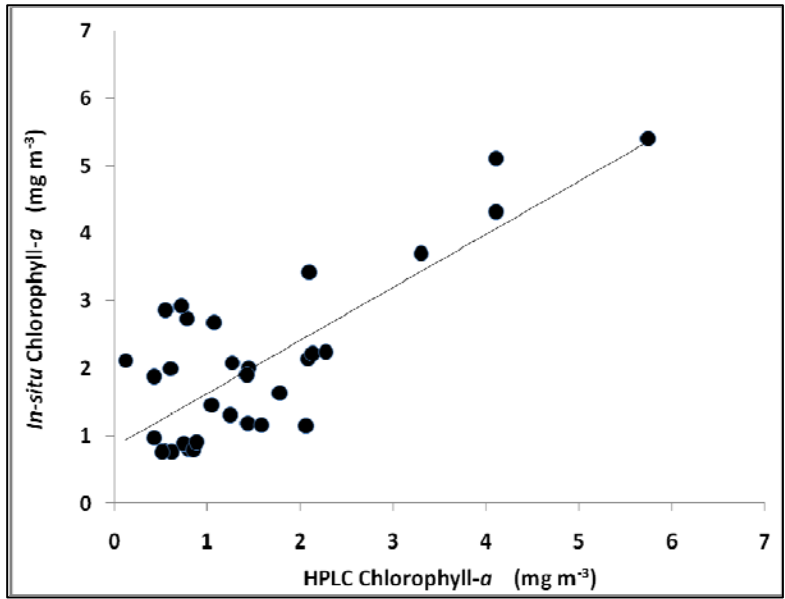


Figure 6: HPLC measured Chlorophyll-a concentrations compared with OCM-2 derived Chlorophyll-a concentrations.

