Author version: *ISPRS J. Photogramm. Remote Sens., vol.66(4); 2011; 545-552*

Dynamics of chromophoric dissolved organic matter in Mandovi and Zuari estuaries – A study through *in situ* and satellite data

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Abstract

The spatial and temporal distribution of absorption of chromophoric dissolved organic matter at 440 nm (a_{CDOM} (440)) in Mandovi and Zuari estuaries situated along the west coast of India, has been analyzed. The study was carried out using remotely sensed data, obtained from the Ocean Colour Monitor (OCM) on board the Indian Remote Sensing satellite – P4, together with *in situ* data during the period January to December 2005. Satellite retrieval of CDOM absorption was carried out by applying an algorithm developed for the site. A good correlation (R = 0.98) was obtained between satellite derived CDOM and *in situ* data. Time series analysis revealed that spatial distribution of CDOM has a direct link with the seasonal hydrodynamics of the estuaries. The effect of remnant fresh water on CDOM distribution could be analyzed by delineating a plume in the offshore region of Zuari estuary. Though fresh water flux from terrestrial input plays a major role in the distribution of CDOM through out Mandovi estuary, its role in Zuari estuary is significant up to the middle zone. Other processes responsible for feeding CDOM in both the estuaries are coastal advection, *in situ* production and resuspension of bottom settled sediments. The highest value of a_{CDOM} (440) was observed in the middle zone of Mandovi estuary during post-monsoon season. The relation between a_{CDOM} (440) and S (spectral slope coefficient of CDOM) could differentiate CDOM introduced in to estuaries through multiple sources. The algorithm developed for Mandovi estuary is $S = 0.003 [a_{CDOM} (440)^{-0.7091}]$ while for Zuari estuary, $S = 0.0031[a_{CDOM} (440)^{-0.777}]$, respectively.

Keywords. Chromophoric dissolved organic matter (CDOM), Mandovi and Zuari estuaries, Monsoons, salinity, optical remote sensing.

1. Introduction

Chromophoric dissolved organic matter (CDOM), commonly referred to as yellow substance, is one of the optically active substances responsible for the absorption of light and thus affecting the bio-optical properties of the coastal and estuarine waters (Bricaud, 1981; Hojerslev and Åas, 2001; Menon *et al.*, 2005., Foden *et al.*, 2008). Having been introduced into the coastal environment through *in situ* production (decomposition of aquatic plants) and land drainage, CDOM significantly attenuates Photosynthetically Available Radiation (PAR) and thus affects the productivity of the area (Carder *et al.*, 1989; Arenz *et al.*, 1996; Vodacek *et al.*, 1997; Magnuson *et al.*, 2004; Odriozolaa *et al.*, 2007). The effect of CDOM concentration can prevail up to 650 nm of the optical spectrum of electromagnetic radiation, if it exists in high concentration (Menon *et al.*, 2005). Interest in the study of CDOM in coastal and estuarine waters has increased substantially in the recent past due to the role of CDOM as an indicator of the area which is a perennial source of CO_2 (Muller-Karger *et al.*, 2005; Menon *et al.*, 2006 b**).** In the present context, this point is valid as the waters of western Indian coast are identified as a region of hypoxia (Naqvi *et al.*, 2000). Since the estuaries discharge to the western margin of the Indian subcontinent, it is pertinent to understand the spatial and temporal variation of CDOM in these estuaries. Data generated onboard trawlers in these estuaries were used for decades to characterize the phytoplankton and inorganic suspended matter dynamics (Singbal, 1973; Devassy and Goes, 1989; Padmavati and Goswami, 1996; Krishnakumari *et al.*, 2002). But these studies were often limited to specific season with limited spatial coverage. A solution to this under-sampling is optical remote sensing of the estuarine waters. Menon *et al.* (2006a) were successful in developing algorithms to retrieve estuarine colour components, such as chlorophyll_a, sediment, and CDOM, from Ocean Colour Monitor (OCM) data**.** Though it is known that seasonal rainfall is the major contributor of CDOM to Mandovi and Zuari estuaries, as the dynamics of the estuarine waters differs from season to season, it is imperative to know the augmented effect of these dynamics on the CDOM distribution. Nevertheless, no rigorous efforts were made in this direction until now. The present study is carried out with the following objectives:

1) to analyze the temporal and spatial variability of CDOM in Mandovi and Zuari estuaries based on satellite and *in situ* data over a year.

2) to characterize CDOM optical properties in water end-members in the study area through relations between CDOM absorption at 440 nm (a_{CDOM} (440)) and slope coefficient (*S).*

2. Data and methods

2. 1. Study area.

Mandovi and Zuari estuaries in the state of Goa are complex ecosystems joining the Arabian Sea at the central west coast of India (Fig. 1). Estuarine hydrodynamics along the Indian coast is controlled by both river runoff and tides during monsoon (June – September) season. After the withdrawal of monsoon, runoff decreases rapidly and by November it reaches negligible levels. Subsequently, the flow propagated by the tide (semi-diurnal with a range 0.2 – 2 m), at the mouth, becomes the sole driving force of transport into the estuarine network. This initiates different hydrodynamic processes between dry (non-monsoon) and wet (monsoon) seasons, resulting in the formation of homogenous, salt-wedge and partially mixed estuaries during pre-monsoon (February – May), monsoon (June – September) and post-monsoon (October – January) seasons, respectively (Qasim, 2003)**.** The cross-sectional area of both the estuaries decreases up-stream, classifying them under converging category. This results in the influence of tides up to a distance of 50 km upstream **(**Shetye *et al.*, 1995**)**. As the catchment area of Mandovi estuary is 1150 km^2, twice the area of Zuari estuary (550 km^2), the annual average fresh water discharge in Mandovi is almost double that in Zuari. Though the estuaries are interconnected by Cumbarjua canal, its cross sectional area is too small to have any impact on the estuarine characteristics (Shetye *et al.*, 1995).

2.2. *In situ* observations

Observations were carried out on 22 hydrographic stations on 12th February, 18th March, 13th April and 11th May (pre-monsoon), 15th August and 17th September (monsoon), on 11th November and 9th December (post-monsoon) seasons during the year 2005 (Fig 1). Two water samples of 5 liters each were collected from the subsurface of each station along the axis of the estuaries. Among these samples, one was used for the analysis of suspended matters such as chlorophyll_a and sediment and the other for CDOM. Along with the collection of water samples, observations were also carried out using a secchi disk, Conductivity, Temperature and Depth (CTD) instrument, Microtops II sunphotometer, temperature and humidity meter at each station. The sampling details, selection of stations and the precautions taken in the field are discussed in Menon *et al.* (2005, 2006a).

2.3. Water sample analysis

Coefficient of CDOM absorption was determined by analyzing the water samples as per the method used by Kowalczuk and Kaczmarek (1996). The samples were filtered through 0.2 µm Whatman cellulose membrane filters and the sample transparency was measured using Perkin Elmer

Lambda 35 UV/VIS spectrophotometer over the spectral range 400 to 700 nm with an interval of 1 nm against distilled water as blank. Absorption coefficients were corrected for backscattering of small particles and colloids which pass through filters, as per Green and Blough (1994):

$$a_{corr}(\lambda) = a(\lambda) - a_{700}\ (\lambda/700) \qquad \text{(Eq. 1)}$$

where a_{corr} (λ) is the corrected absorption at a given wavelength λ and a_{700} is the measured absorption at 700 nm. The reference wavelength used to calculate a_{CDOM} (λ) was 440 nm:

$$a_{CDOM}(\lambda) = a_{CDOM}(440)\ \exp(-S\ (\lambda - 440))\ (m^{-1}) \qquad \text{(Eq. 2)}$$

where S is the slope coefficient, calculated as the slope of the curve resulting by plotting logarithm of a_{CDOM} (λ) against wavelengths in the range 400 – 550 nm. The magnitude of a_{CDOM} (440) was used as a proxy to the concentration of CDOM.

For estimating chlorophyll_a concentration, one sample from each station was filtered through glass fiber filter of 0.45µm pore size. The pigment was extracted using 90% acetone in dark at low temperature. The Optical Density (OD) was then measured through spectrophotometer, using a 1 cm cell, in the spectral range of 400 to 700 nm, with an interval of 1 nm, against the cell containing 90% acetone as blank. The chlorophyll_a concentration was then calculated using trichometric equations as per Strickland and Parsons (1972).

Suspended sediment concentration was calculated using the method suggested by Strickland and Parsons (1972). Samples for estimating suspended sediments were filtered in the laboratory through pre-weighed 0.45µm Whatman membrane filter. The filters were dried in hot air oven at 70^0 C for 6 hours and weighed again. Subsequently the concentrations were estimated.

2.4. Zonation of the estuaries

Spatial variability of salinity in the estuaries is the rationale behind the zonation. A haline front formed due to the convergence of sea water and river water is a permanent feature in the estuarine hydrodynamics. Hence, the characteristics and source of CDOM on the seaward side and riverward side of the front are different. Since the fronts migrate forward and backward directions during monsoon and non-monsoon seasons, an average position of the frontal zone is considered as the middle zone. In short, the seaward side of the front is the lower zone and riverward side of the front is upper zone while the frontal zone itself is the middle zone (Fig.1).

2.5. Satellite data processing

Synoptic analysis of CDOM was carried out using the data obtained from the Ocean Colour Monitor (OCM) on board Indian Remote Sensing satellite–P4 (IRS – P4). OCM has six visible and two NIR bands in the range 402 nm – 885 nm centered at 412 nm, 443 nm, 490 nm, 510 nm, 555 nm, 670 nm, 765 nm and 865 nm. The spatial resolution and band-width of the visible bands of OCM are 360 m and 20 nm respectively. The images were geo-referenced using ground control points and the study area was extracted from the full scene through ERDAS Imagine 8.4. Atmospheric correction of remotely sensed data involves elimination of Rayleigh and aerosol components. Rayleigh component was computed and removed from each pixel using Doerffer's method (1992). As water in the study area was turbid, pixels of NIR bands of OCM could not be used to remove aerosol path radiance. Hence, aerosol radiance was computed by deriving aerosol optical depth (AOD) using a sunphotometer (Chylek *et al.*, 2003) having filters at 380, 440, 500, 675 and 870 nm. Subsequently, aerosol correction was carried out on each pixel of OCM and water leaving radiance was derived for selected bands. Then the algorithm developed by Menon *et al.* (2006a) was applied to retrieve a_{CDOM} (440) from OCM. This was carried out through a calibrated radiative transfer model (Menon, 2004 and Menon *et al.*, 2005) . The algorithm developed to extract CDOM from the area of study was:

$$a_{CDOM}(440) = 2.9393\,(L_w412/L_w670)^{-2.2486} \qquad \text{(Eq. 3)}$$

where, L_w412 and L_w670 are the water leaving radiances at 412 nm and 670 nm, respectively. Pixels from the upper zones of both the estuaries were contaminated by land radiance (widths of the estuaries are less than three times the spatial resolution of OCM sensor). To analyze CDOM from this zone, *in situ* data supplemented satellite data. Similarly, *in situ* data were used to derive CDOM variability during monsoon season. Cloud free scenes of OCM on 8th January, 12th February, 18th March, 13th April, 11th May, 23rd September , 6th October, 11th November and 9th December of the year 2005 were used to study the spatial and temporal variability of CDOM absorption.

3. Results

3.1 Seasonal distribution of salinity in Mandovi and Zuari estuaries.

3.1.1 Pre-monsoon season

Orientation of isohalines revealed that both Mandovi and Zuari estuaries are vertically homogeneous. Salinity encountered at the lower zone of Mandovi estuary was 34.5 while that at the corresponding zone of Zuari estuary is 35.5 PSU **(**Fig. 2a and Fig. 2b), indicating the dominance of sea water flux due to tide. Notable difference between the two estuaries is the gradient in salinity between middle and lower zones of the estuaries. The magnitudes of these gradients are 8 PSU and 4 PSU in Mandovi and Zuari estuaries respectively.

3.1.2 Monsoon season.

Fig. 2c clearly indicates the dominance of fresh water in Mandovi estuary during this season. Fresh water is present between lower and upper zones of Mandovi estuary and the salinity prevailing at the lower zone is 5 PSU. A wedge of sea water is seen intruding in to the lower zone and exchange of water is restricted to the wedge. Salinity distribution at the bottom of the middle zone (4 km upstream from mouth) shows stratification with a vertical gradient 10 PSU.

Salinity profiles in Zuari estuary are distinctly different from those in Mandovi estuary. At the lower zone, the surface salinity is around 25 PSU (Fig. 2d). Saline water intrusion is up to the middle zone of the Zuari estuary. A vertical gradient of salinity with magnitude 8 is observed below 1 m from the surface and 10 km upstream from the lower zone.

Thus the changes in seasonal hydrodynamics of the estuaries are clear from their transformation from homogeneous into salt-wedge estuaries. Also, circulation in Mandovi estuary is more fresh water dominant than that in Zuari estuary.

3.2. OCM – *in situ* comparison.

In order to validate satellite retrieved CDOM, *in situ* data were chosen in such a way that widths of the stations were more than three times 360 m, the spatial resolution of OCM. This precaution was taken to avoid overlapping of water pixels with land pixels. Along with the correlation analysis, root mean square (RMS) and bias of the data were also calculated. The data sets were logarithmically transformed (base 10) to calculate RMS and bias. The RMS log error is 14.25 % and log difference bias is 3.89 %. A good correlation, R equals 0.98 (Fig.3), less error and bias further explained the ability of the algorithm in retrieving the sequential variation of CDOM concentration in association with the seasonally varying hydrodynamics of the estuaries.

3.3. CDOM optical properties.

Mean values of a_{CDOM} (440) in the upper, middle and lower zones of both the estuaries along with the corresponding standard deviations are given in table 1. From the table, it is apparent that middle zones of both the estuaries encountered maximum CDOM absorption with highest standard deviations during post – monsoon season. But during pre-monsoon season, maximum absorption **was** seen at lower zones of both the estuaries and the standard deviation encountered at the lower zone of

Mandovi was three times more than that in the respective zone of Zuari estuary. In short, Mandovi estuary encounters more CDOM absorption than Zuari estuary during all the seasons.

3.4. Spatial and temporal variability of CDOM through OCM data.

An Algorithm (equation.3) to analyze CDOM from OCM, was developed for typical CDOM absorption variability range in the study area (0.1 to 2.2 m^{-1}). It worked well in this study except in December 2005, when exceptionally high values of a_{CDOM} (440) were recorded in the middle zone of both the estuaries (5.5 m^{-1} and 3.37 m^{-1} at stations M07 and Z05).

3.4.1. Pre-monsoon

The pre-monsoon distribution of CDOM is explained through OCM data of February, March, April and May (Fig. 4). By the end of the season (May), the lower zones of both the estuaries and coastal inshore region, north of Mandovi and south of Zuari estuaries, encountered high CDOM. At the middle zone of Mandovi estuary, CDOM decreased between March and May and absorption was around 0.6 m^{-1} in May. But the same was not observed in Zuari estuary. Moreover CDOM retrieved during May was found to be an overestimation in the Zuari estuary.

An important feature of the geometry of fairway channels of the estuaries is that their cross-sectional area and depth decreases rapidly in the upstream direction (Unnikrishnan *et al.*, 1997). Hence, in a tidally controlled estuary during pre-monsoon, shoaling across the fairway channel (navigation channel) generates more turbulence and mixing, resulting in a homogenous estuary, as seen in Fig. 2a and Fig. 2b. An overlapping of radiance from shoaling and those from the bottom of fairway channel might have resulted in an overestimation.

3.4.2 Post- Monsoon

To study the effect of remnant fresh water on CDOM distribution, OCM data, during the period of receding phase of monsoon (September), were analyzed. Fig. 4 depicts a uniform CDOM distribution between upper and middle zone of Mandovi estuary and thereafter decreases towards the lower zone. Though a similar pattern was exhibited between upper and middle zones of Zuari estuary, the distribution was different beyond middle zone. Depiction of a sharp gradient in a_{CDOM}(440) at the middle zone and a secluded plume in the offshore region were the two distinct features.

During October, lower zone of Zuari estuary encountered high CDOM absorption but in the respective zone of Mandovi estuary it is low. It is also worth mentioning the CDOM build up at the coastal inshore waters south of Zuari estuary during this month.

In November, there was a clear depiction of increase in CDOM at the middle zones of both the estuaries. It also increased at the southern bank of Mandovi estuary. But in the lower zone of Zuari estuary, CDOM concentration is reduced considerably compared to earlier months. The plume observed at the offshore region of the Zuari estuary during September had diffused in November. In December, CDOM distribution showed highs and lows along Mandovi estuary with clear depiction of CDOM rich waters at the middle zone. Though CDOM concentration in the lower zones of both the estuaries increased compared to the previous month, the rate of increase was more in Mandovi than in Zuari estuary. During January, CDOM concentration in the lower zones decreased and showed uniform distribution at middle and upper zones.

Overall, a distinct well defined variation in CDOM was not observed in Zuari estuary and it was not possible to distinguish CDOM between upper and middle zones of Zuari estuary in December and January.

4. DISCUSSION

The analysis revealed an intra-seasonal and inter-seasonal variability in the spatial distribution of CDOM between the two estuaries. Though situated adjacently in the same latitudinal belt, a discrepancy was seen in the absorption of CDOM between the two estuaries. To investigate this further, it is necessary to identify different processes (river input, advection and *in situ* production) acting as mechanisms to feed CDOM in to each estuary. This was carried out by examining the relation between S, a proxy to the composition of CDOM, and $a_{CDOM}(440)$, an index of concentration of CDOM. The relation is found to be different and the respective algorithm in each estuary is as follows:

In Mandovi estuary, $S = 0.003(a_{CDOM}(440))^{-0.7091}$ (Eq. 4)

While in Zuari estuary, $S = 0.0031\,(a_{CDOM}(440))^{-0.777}$ (Eq. 5)

The relation between S and CDOM absorption at 440 nm is inverse and exponential in both the estuaries (R = -0.78 in Zuari and R = -0.78 in Mandovi), (Fig. 5a, 5b).

Maximum S observed in Mandovi estuary is 0.022 nm^{-1} while in Zuari estuary it is 0.044 nm^{-1}. An increase in S is due to transformation of terrestrially derived CDOM and/or its replacement by *in situ* production of CDOM (Carder *et al.*, 1989; Vodacek *et al.*, 1997). Further they pointed out that a change in the stratification of the area, during the period of field survey, could also change S. Vodacek *et al.* (1997) explained that when terrestrially derived CDOM is present in surface waters under conservative mixing condition, S is less than or equal to 0.02 nm^{-1}.

4.1 Pre-monsoon

Analysis of $a_{CDOM}(440)$ through satellite and *in situ* observations indicates an increase in its concentration in the lower zone of both the estuaries by the end of pre-monsoon season (May). Also, during this season, CDOM encountered at different zones of both the estuaries was less than that depicted during post-monsoon season. Table 2 gives the mean concentrations of chlorophyll_a and sediment encountered at lower, middle and upper zones during different seasons.

An examination of the contribution of chlorophyll_a and sediment to CDOM revealed that though a_{CDOM} (440) has a positive relation with chlorophyll_a and sediment in Mandovi estuary, the respective coefficients are poor (Table 3). This is clear from the weak negative relation of S with chlorophyll_a (R=-0.37) and sediment (-0.29). But the scenario prevailing in Zuari estuary is different. Here $a_{CDOM}(440)$ has a negative relation with chlorophyll_a (R = -0.42) and a weak positive relation with sediment (R = +0.38). The effect of sediment on CDOM could be ascertained from its strong negative linear relation with S (R= -0.69). This is also evident from the concentration of sediment prevailing in different zones of the estuaries during this season (table 2).

The salinity pattern along the axis of the estuaries categorizes them under homogeneous estuaries during this season (Fig 2a and Fig 2b). In a well mixed estuary, CDOM should have been more than in a partially mixed estuary developed during post-monsoon season (table 1). But this is not true in the present case. Pre-monsoon season being a period of clear sky, the area receives maximum irradiance and hence highest sea surface temperature during April and May (Qasim, 2003). Therefore, photo bleaching during this season might have reduced CDOM concentration in both the estuaries.

An entirely different relation is seen between the estuaries with respect to the relation of S with salinity. In Mandovi, the regression is linear and negative (R=-0.83) but in Zuari, though the relation is linear, it is positive (R = 0.69). This means advection of coastal saline waters brings CDOM in to the lower zone of Mandovi to a greater degree, but in Zuari estuary this contribution is not significant. This might be the reason for high mean CDOM in the lower zone of Mandovi than in the respective zone of Zuari estuary. This is also evident from the large standard deviation in the lower zone of Mandovi estuary during this period.

Devassy *et al.* (1979) reported trichodesmium blooms along the coastal waters of Goa (around 16^0 N) during April. In their studies, Madhupratap *et al.* (2001) reported that along the west coast of India (north of 15 ^{0} N) algal blooms are formed during pre-monsoon season. Hence CDOM pool builds up as the bloom senescence in May. A reversal in the direction of the current, from poleward to equatorward, might have advected CDOM rich waters to Mandovi to a greater degree. Bhargava and Dwivedi (1974) showed that influx of neritic waters in the lower zone of both the estuaries make the region more productive during pre-monsoon season. Hence the advection of CDOM from coastal region might be responsible for its greater incidence in the lower zones of the estuaries.

The advection of neritic waters is the sole source of CDOM in the lower zone of Zuari estuary while terrestrial input along with the advection of neritic waters are the sources of CDOM in the lower zone of Mandovi. In their observations on CDOM dispersion over the Florida shelf, Del Castillo *et al.* (2000) had indicated the role of mixing in the distribution of CDOM. The above discussion has clearly revealed that the spatial and temporal variations of CDOM in these estuaries are controlled by the mixing process.

4.2 Monsoon

During monsoon, the whole basin of the Mandovi is filled with fresh water and mixing with sea water takes place at the lower zone (salinity is 5 PSU). But in Zuari estuary, mixing is at the middle zone and the salinity is 19 PSU (Fig. 2c, 2d). Researchers found that limit of sea ward extent of terrestrially originated CDOM vary seasonally depending upon the magnitude of the fresh water (Vodaceck *et al.*, 1997; Rochelle-Newall and Fisher, 2002b). Uniform $a_{CDOM}(440)$ through out Mandovi estuary and a non-uniform distribution in Zuari estuary is a clear indication that river discharge is the major mechanism to distribute terrestrially originated CDOM throughout Mandovi estuary and up to middle zone of Zuari estuary.

An inverse linear relation between $a_{CDOM}(440)$ and salinity, with correlation coefficients -0.83 and -0.77 in Mandovi and Zuari estuaries respectively, further confirms the role of terrestrial input of CDOM to both the estuaries (Fig. 6a, 6b).

4.3. Post-monsoon

An elevated concentration of CDOM in the middle zone, compared to that in the lower and upper zones of both the estuaries, revealed that fresh water discharge is not the only source of CDOM during post-monsoon. The secondary mechanism to increase CDOM could be *in situ* production through disintegration of chlorophyll_a, resuspension of sediments or due to both the processes.

A good relation of a_{CDOM} (440) with chlorophyll_a (R=0.72) and sediment (R=0.81) in Mandovi estuary and a strong linear relation with both chlorophyll_a (R=0.85) and sediment (R=0.81) in Zuari estuary explicitly explains that both chlorophyll_a and sediment could contribute to CDOM absorption in both these estuaries (Table 3). Further, analysis revealed a negative linear relation between *S* and chlorophyll_a in Mandovi (R= -0.74) and Zuari (R=-0.84) estuaries. Better regression of *S* with sediment (R= -0.59) in Zuari than in Mandovi (R=-0.44) is also observed. This indicates that sediment can act as an additional source of CDOM in Zuari estuary.

On local scales, *in situ* production from phytoplankton decomposition and extraction from bottom sediments may be an important source of CDOM (Twardowski and Donaghay, 2001; Boss *et al.*, 2001). However, in their studies, Rochelle-Newall and Fisher (2002 a) showed that CDOM absorption doesn't correlate with chlorophyll_a content. Hence it has been proposed that phytoplankton does not produce CDOM directly but acts as a source of biomass which is transformed to CDOM via microbially - meditated process. This is also vivid from table 2. If the aforementioned processes are responsible for the increase of CDOM in the middle zones of both the estuaries, it is important to know the physical processes augmenting resuspension of bottom settled sediments at this zone

Since the estuaries converge in the upstream, they are narrow and shallow at the upper zone (Unnikrishnan *et al.*, 1997). But the degree of decrease of depth and width of the estuaries from lower to middle zone are different. At the lower zone, Mandovi estuary is 5.8m deep and 3.2 km wide. It decreases to 4.0 m and 0.8 km at the middle zone. Similarly, depth and width of Zuari estuary decreases to 3.0 m and 1 km at the middle zone from 8.0 m depth and 5.5 km width at the lower zone. The momentum balance in a shallow estuary is pressure gradient and friction. In the case of funnel shaped (converging type) estuaries like Mandovi and Zuari, where the cross sectional area decreases upstream, the amplification due to convergence of the channel cancels decay due to friction, leaving the amplitude unchanged over long distances along the channels (Friedrichs and Aubrey, 1994). In such estuaries when the fresh water discharge decreases, as monsoon recedes, the effect of tide (sea water flux) becomes significant and the frictional effect at the bottom of the estuaries generates turbulence which is sufficient to break the monsoonal (salt-wedge) characteristics of the estuaries and convert them into partially mixed during post-monsoon. This mixing helps in resuspension of the bottom settled sediments which in turn induce CDOM in the middle zone of both the estuaries and augments the concentration during this season.

This might also be responsible for the shedding of CDOM rich water from the middle zone of Zuari estuary (Fig. 4) towards the offshore region (salt-wedge extends up to middle zone in Zuari estuary). But this type of a secluded plume is not seen at the mouth of Mandovi estuary. As the salt-wedge is formed at the lower zone (depth 5.8 m) of Mandovi estuary, a momentum balance exists between the fresh water (pressure gradient) and friction. Hence the tide generated bottom turbulence is not sufficient to break the wedge and that results in the gradual diffusion of CDOM from the lower zone of Mandovi to the offshore region **.**

In their studies, Boss *et al.* (2001) suggested that sediment resuspension events driven by storms have also been observed to contribute to CDOM in bottom waters. In their attempt to analyze estuarine colour components during pre-monsoon season, Menon *et al.* (2006a) had observed high incidence of CDOM in the region of sediment plumes.

It is interesting to note an opposite relation of *S* with salinity between Mandovi and Zuari estuaries during this season. In Mandovi, the relation is negative and the regression coefficient is -0.75 while in Zuari it is positive and the coefficient is 0.48. This means coastal advection of saline waters is yet another source of CDOM contributing significantly to the lower zone of Mandovi estuary. Hence the combined effect of coastal advection, terrestrial input and *in situ* production caused the lower zone of Mandovi estuary to have more CDOM than the respective zone of the Zuari estuary during this season.

4.4. Reversal of current direction

Apart from the estuarine region, OCM data also revealed the CDOM build up at the coastal inshore waters south of Zuari estuary during October (Fig 4). It was reported that the area between 8^0 N and 15^0 N (south of 15^0 N), along the eastern Arabian sea, is productive during southwest monsoon (Madhupratap *et al.*, 2001). During the fall inter-monsoon (October and November) period, CDOM concentration increases due to the disintegration of chlorophyll_a. Moreover, the current reverses from equatorward to poleward during October. This might have acted as an agent to transport CDOM rich waters along the coastal inshore region south of Zuari estuary.

In their studies, Keith *et al.* (2002) indicated that phytoplankton utilizes accessory pigments at longer wavelengths when the CDOM absorption is high and values of *S* less than or equal to 0.02. This criterion holds well in the present case wherein Mandovi estuary has more CDOM concentration than Zuari estuary. It was reported that Mandovi estuary is less productive than Zuari estuary (Krishna Kumari *et al.*, 2002).

5. Conclusion

Remote analysis of CDOM using OCM data revealed that temporal and spatial variability of CDOM in Mandovi and Zuari estuaries is controlled by seasonal hydrodynamics. This is evident from the presence of more CDOM-rich waters in the lower zone and coastal inshore region of the estuaries by the end of pre-monsoon and accumulation of high CDOM waters in the middle zone of both the estuaries by the end of post-monsoon season. This is the first time that CDOM in these estuaries has been remotely analyzed for an entire year through an optical sensor having spatial resolution of 360 m. Of the two estuaries, Mandovi experiences higher CDOM concentration and maximum variability. The study could also assess the fate of secluded CDOM rich water (plume) in the offshore region during the initial phase of post-monsoon. Though monsoonal fresh water flux is the major source of CDOM in both the estuaries, its contribution is more predominant in Mandovi estuary than in Zuari estuary. The study revealed that it is possible to analyze the fate of CDOM synoptically through an optical sensor, if equipped with a good site- specific algorithm. Success in mapping CDOM and studying its temporal variation in estuaries will help in developing a basic tool to understand and monitor the discharge of dissolved organic matter from non-point sources which is responsible to make a coastal region hypoxic.

Acknowledgements

The authors would like to thank Indian Space Research Organisation (ISRO) for the project sanctioned under MOP programme. They also wish to thank Prof Dileep Deobagkar, Vice Chancellor, Goa University for all the facilities given during the the study.

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Legends to figures

Figure 1 Map of the study area showing hydrographic stations in different zones of Mandovi-Zuari estuaries of Goa.

Figure 2 Vertical sections of salinity along the axis of a) Mandovi and b) Zuari estuary during Pre-monsoon and c) Mandovi and d) Zuari estuary during Monsoon season.

Figure 3 Correlation between *in situ* and satellite derived a_{CDOM} (440) (the dotted line in the figure show 95% confidence level).

Figure 4 Synoptic distribution of a_{CDOM} (440) in Mandovi and Zuari estuaries from January to May and September to December 2005.

Figure 5 Regression between a_{CDOM} (440) and slope coefficient (S) in a) Mandovi and b) Zuari estuary.

Figure 6 Regression between a_{CDOM} (440) and salinity in a) Mandovi and b) Zuari estuary.

Table 1. Mean and Standard deviation of $a_{CDOM}(440)$ at upper, middle and lower zones of Mandovi and Zuari estuaries. 24 data points, derived seasonally for each zone of the two estuaries were used for the analysis.

		Mandovi E.			Zuari E.		
		Upper	Middle	Lower	Upper	Middle	Lower
Pre-Monsoon	Mean	0.67	0.67	1.02	0.71	0.67	0.86
	Stdev	0.44	0.48	1.00	0.26	0.26	0.47
Monsoon	Mean	0.66	0.66	0.66	0.38	0.53	0.11
	Stdev	0.19	0.19	0.49	0.07	0.49	0.08
Post-Monsoon	Mean	0.71	2.00	1.40	0.73	1.69	0.49
	Stdev	0.43	1.80	0.85	0.45	0.60	0.45

Table 2 Mean and Standard deviation of chlorophyll_a and sediment concentrations at upper, middle and lower zones of Mandovi and Zuari estuaries during different seasons. 24 data points, derived seasonally for each zone of the two estuaries were used for the analysis.

		Mandovi E.						Zuari E.					
		Chlorophyll (ug/l)			Sediment (mg/l)			Chlorophyll (ug/l)			Sediment (mg/l)		
		Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower
Pre-Monsoon	Mean	9.70	6.32	3.72	13.95	20.37	16.03	6.68	5.95	3.63	22.82	22.72	14.45
	Stdev	6.07	2.35	1.08	3.30	4.11	6.44	3.33	2.55	1.68	7.41	10.71	3.85
Monsoon	Mean	7.00	2.45	4.59	18.63	18.13	14.00	6.61	3.68	4.88	18.20	18.00	12.00
	Stdev	0.14	1.03	0.08	2.11	0.35	0.18	1.48	2.80	0.18	5.83	0.20	0.80
Post-Monsoon	Mean	3.13	2.90	1.50	5.48	8.41	10.15	2.37	2.14	1.41	10.21	16.74	8.27
	Stdev	2.51	1.13	0.95	2.49	1.35	1.56	2.01	0.97	1.01	3.63	6.30	3.67

Table 3. Regression coefficients, (R), between different parameters derived during pre-monsoon and post-monsoon seasons. Regression of $a_{CDOM}(440)$ with sediment and chlorophyll_a and regression of slope coefficient (*S*) with salinity, sediment and chlorophyll_a.

Parameters	Pre-monsoon		Post-monsoon	
	Mandovi	Zuari	Mandovi	Zuari
$a_{CDOM(440)}$ vs. sediment	R= 0.12 n=20 Linear	R= 0.38 n=20 Linear	R= 0.81 n=14 Power	R= 0.81 n=14 Linear
$a_{CDOM(440)}$ vs. chlorophyll a	R= 0.23 n=20 Linear	R= -0.42 n=20 Linear	R= 0.72 n=14 Power	R= 0.85 n=14 Linear
slope vs. salinity	R= -0.83 n=20 Linear	R= 0.69 n=17 Linear	R= -0.75 n=14 Linear	R= 0.48 n=14 Linear
slope vs. sediment	R= -0.29 n=20 Linear	R= -0.69 n=20 Linear	R= -0.44 n=14 Linear	R= -0.59 n=14 Linear
slope vs. chlorophyll a	R= -0.37 n=20 Linear	R= 0.10 n=20 Linear	R= -0.74 n=14 Linear	R= -0.84 n=14 Linear

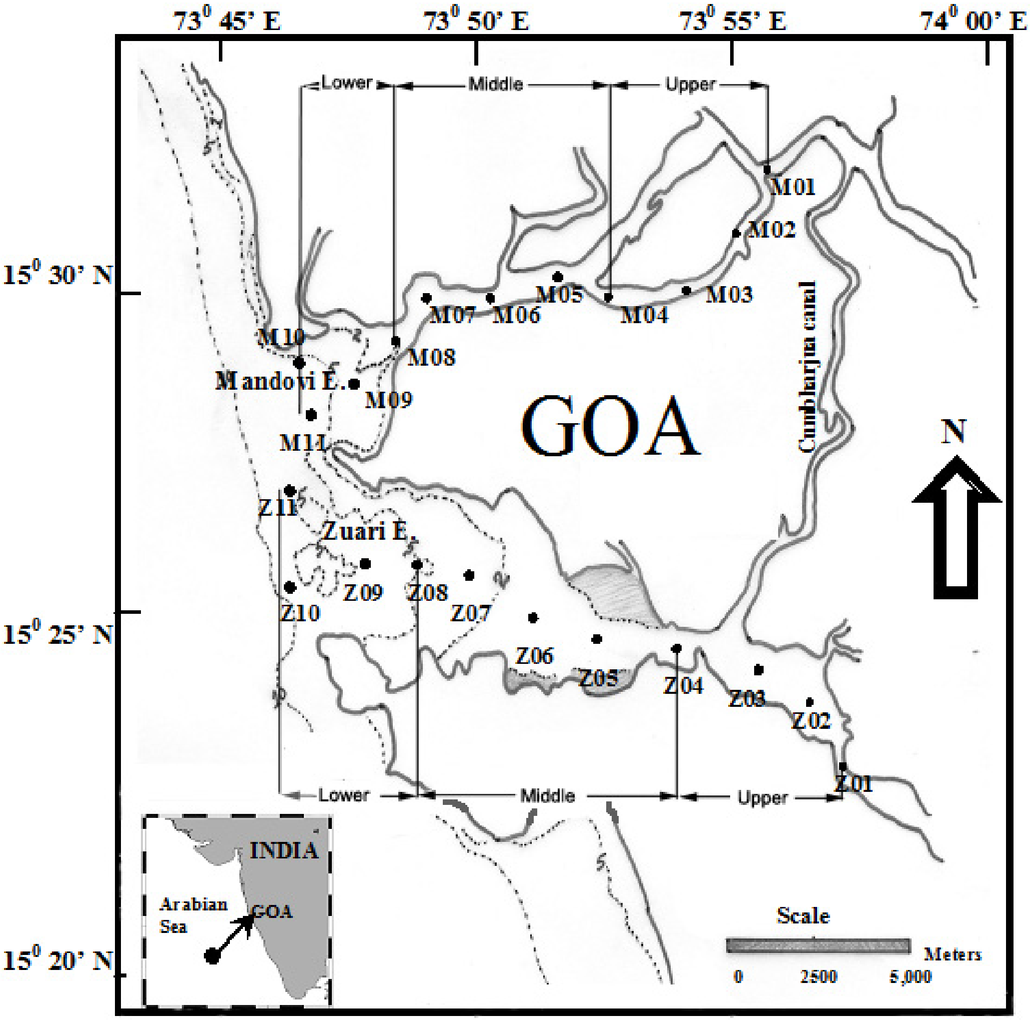
73⁰ 45' E
73⁰ 50' E
73⁰ 55' E
74⁰ 00' E
15⁰ 30' N
15⁰ 25' N
15⁰ 20' N
Lower
Middle
Upper
M01
M02
M03
M04
M05
M06
M07
M08
M09
M10
M11
Mandovi E.
GOA
Cumbharjua canal
N
Z11
Zuari E.
Z09
Z08
Z07
Z10
Z06
Z05
Z04
Z03
Z02
Z01
INDIA
Arabian Sea
GOA
Scale
Meters
0
2500
5,000

Figure 1

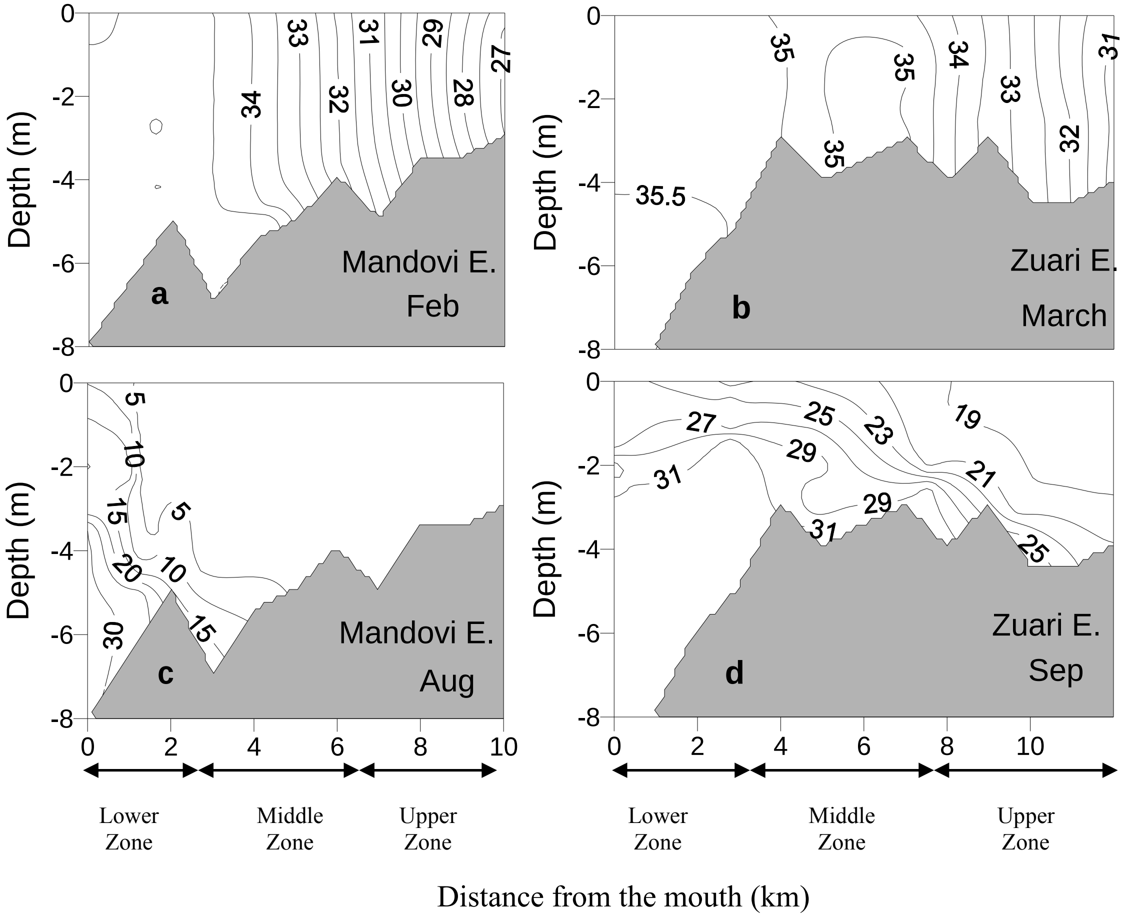
a
Mandovi E.
Feb
b
Zuari E.
March
c
Mandovi E.
Aug
d
Zuari E.
Sep
Depth (m)
0
-2
-4
-6
-8
34
33
32
31
30
29
28
27
35
35.5
35
35
34
33
32
31
5
10
15
5
20
10
15
30
27
25
23
19
29
21
31
29
31
25
0
2
4
6
8
10
Lower Zone
Middle Zone
Upper Zone
Distance from the mouth (km)

Figure 2

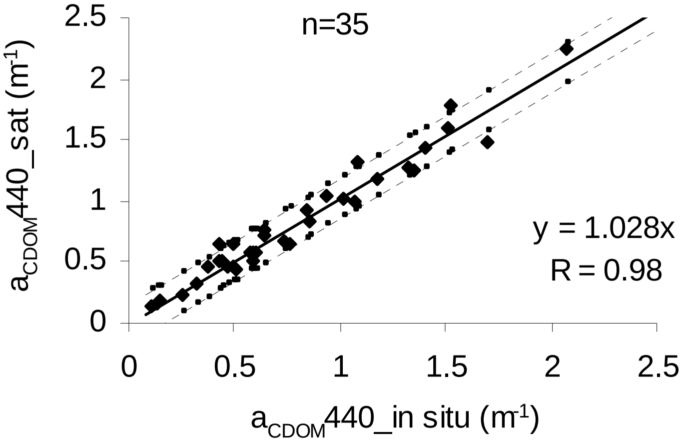
n=35
y = 1.028x
R = 0.98
$a_{CDOM}440\_sat$ (m^{-1})
$a_{CDOM}440\_in$ situ (m^{-1})
0
0.5
1
1.5
2
2.5
0
0.5
1
1.5
2
2.5

Figure 3

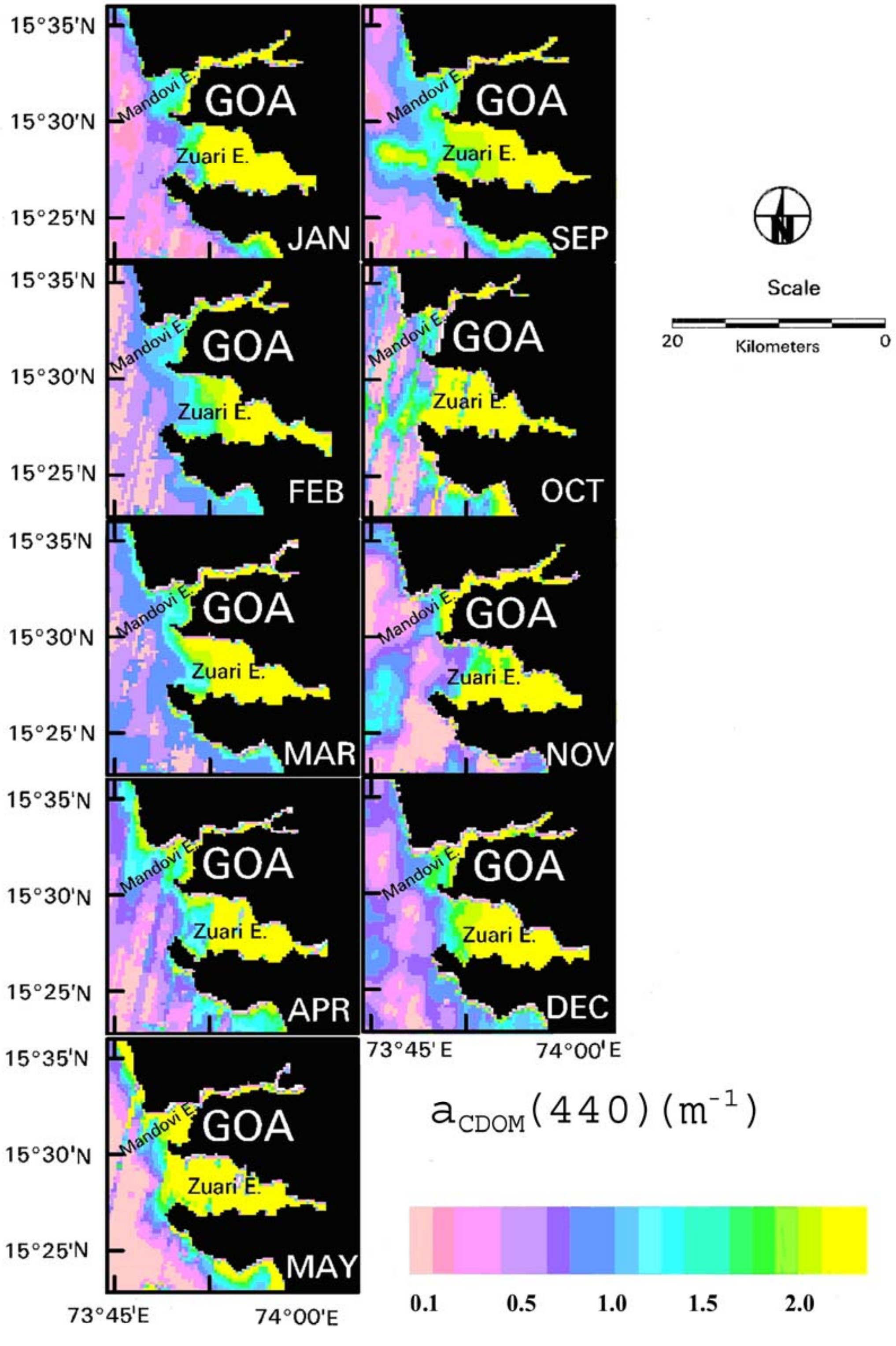
15°35'N
15°30'N
15°25'N
GOA
Mandovi E.
Zuari E.
JAN
SEP
FEB
OCT
MAR
NOV
APR
DEC
MAY
73°45'E
74°00'E
N
Scale
20
Kilometers
0
$a_{CDOM}(440)(m^{-1})$
0.1
0.5
1.0
1.5
2.0

Figure 4

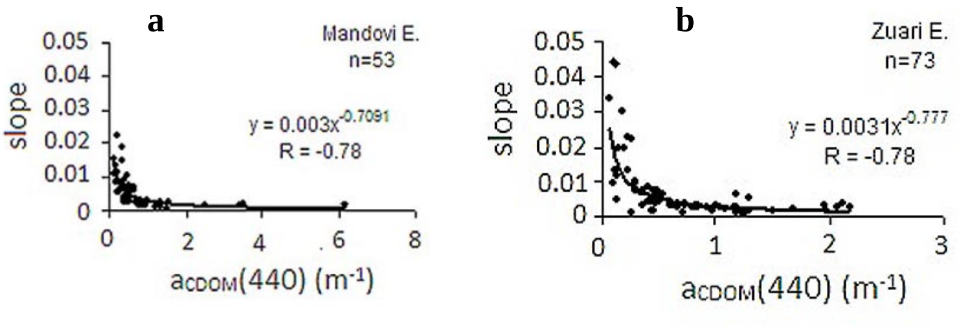

Figure 5

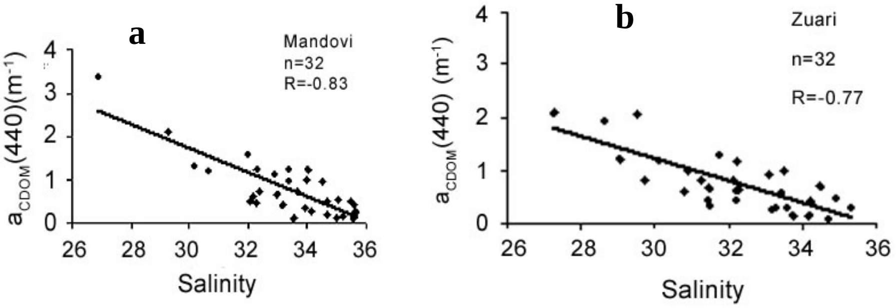

Figure 6