

Contrasting characteristics of colored dissolved organic matter of the coastal and estuarine waters of Goa during summer

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The colored dissolved organic matter (CDOM) was investigated during the summer for the coastal and estuarine waters of Goa using the spectral absorption characteristics of CDOM. Accessions of CDOM were seen all along the estuary through multiple sources of CDOM with relatively insignificant sink, while in the coastal waters there was a sink due to photo bleaching. Measure of CDOM indicated by the absorption at reference wavelength $a_g(412)$ varied with a mean value of 0.470 m^{-1} in the Mandovi, 0.420 m^{-1} in Zuari and 0.176 m^{-1} in the coastal waters. Slope of CDOM $S_{250-600}$ was found to vary from 0.080-0.017 nm^{-1} in coastal waters and 0.017-0.020 nm^{-1} in the estuaries. High values of $S_{275-295}$ observed in the coastal waters were indicative of photobleaching. Point of inflection was observed at a distance of about 8 km from the mouth of the estuary at a salinity of about 34 psu.

[**Key words:** CDOM, Dissolved organic matter, Estuaries, Coastal waters, optical properties, resuspension, Goa]

Introduction

Dissolved organic matter (DOM) stores a large amount of organic carbon in the marine environment¹. Colored dissolved organic matter (CDOM) which is often known as gilvin, gelbstoff, yellow substances, is defined as that component of DOM that passes through 0.2 micron filter and interacts with UV and visible light of the solar spectrum. The contribution by CDOM to dissolved organic carbon (DOC) is estimated to be the highest in the coastal and estuarine waters². CDOM regulates the penetration of UV light in the water column and hence it can have a positive or negative impact on the aquatic system³⁻⁵. Rivers and estuaries form an important source transporting DOM from the terrestrial ecosystem to the coastal ocean. Transformations of CDOM are expected to have a significant impact on carbon cycling dynamics⁶⁻⁸. The coastal waters off Goa are net consumers of organic matter, rather than producers⁹. Seasonal algal blooms of which *Trichodesmium* are observed during summer, *Noctiluca* during winter and other varied species, which are episodic, have been reported in these waters¹⁰⁻¹⁵. These blooms have an impact on the coastal waters affecting the

biogeochemical cycles. These waters are affected by seasonal reversing currents, with strong temperature inversions being observed due to the transport of low salinity waters from the Bay of Bengal during winter¹⁶. Hypoxia is also observed in these coastal waters¹⁷, which is of biogeochemical and environmental importance. The Mandovi and Zuari estuaries on the west coast of India are the two estuaries of Goa, which are classified as monsoonal estuaries¹⁸. There is very less discharge from river runoff during the summer because of which the estuaries become an extension of the sea and remain vertically well mixed¹⁹⁻²³. During the summer, there is very less precipitation and the driving force in the estuary for mixing and circulations are solely controlled by the tides²²⁻²⁴. Although adjacent to each other the Mandovi and Zuari estuaries are influenced by different factors thus, each estuarine environment exhibits a wide variation in its physical and chemical features²⁵. The estuarine waters during summer are found to be highly productive^{9-11, 26}. There are mangroves present all along the banks of the estuaries that form a major reservoir of organic matters. These estuaries receives

autochthonous and large allochthonous inputs from different sources, such as terrestrial, riverine discharge, mangrove leachate, anthropogenic activities²¹⁻²⁵. Goa is a well-known tourist destination and there is a large influx of tourist during this season also there are various associated activities such as pleasure cruises and floating platforms for casinos in the Mandovi estuary, which could have an impact on the environment.

There have not been any studies carried out of CDOM covering both estuaries and coastal waters of Goa, which will help in a better understanding of the sources and sinks of CDOM for these waters. The earlier studies of the Mandovi and Zuari estuaries did not look into these aspects²⁷. Present study carried out during summer was an attempt to understand the spatial variations of CDOM, the various sources, and sinks in the estuarine and coastal waters.

Materials and Methods

The measurements were carried out in the Mandovi estuary, the Zuari estuary, and the coastal waters of Goa, India (15.43- 15.48° N latitude and 73.6 – 74.05° E longitude) during the summer months of March- May 2014. In the Mandovi estuary, there were 6 stations from the mouth up to 23 Km upstream and similarly there were 5 stations up to 25 km in the Zuari estuary. The mean depth of the estuaries was about 5 m. Coastal waters were sampled in two transects, INCOIS and CaTS which covered up to depths of

28 m (Fig. 1). INCOIS transect covered 2 stations and the CaTS covered 4 stations. There were 104 samples of which 23 samples were collected at the CaTS location, 6 at INCOIS, 34 in the Mandovi and 41 in the Zuari estuary. The details of the sampling stations, which include date, time, position and the phase of the tide, are included in Tab.1.

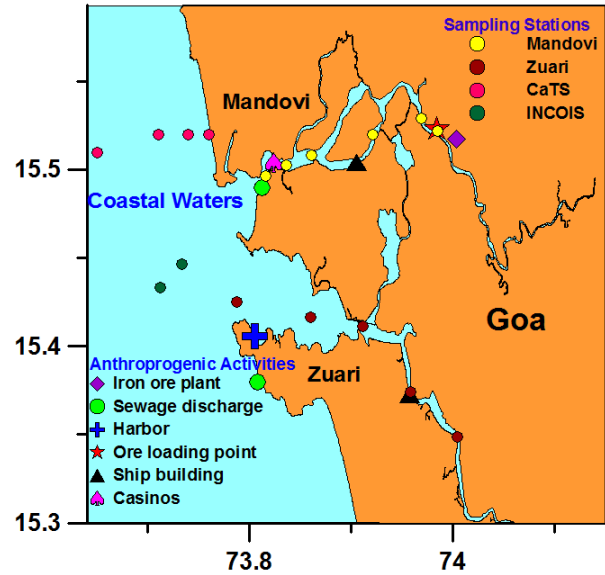


Fig.1 Shows the study area, (Goa on the west coast of India) with sampling stations, in the coastal waters and the two estuaries of Mandovi and Zuari and also the anthropogenic activities in the estuaries.

Table 1 . Sampling dates and tides

Date	Location	Latitude	Longitude	Station	Time (IST)	Tide
24/03/2014	Zuari	15.42523	73.78745	11	09:45	Low tide
24/03/2014	Zuari	15.4162	73.85947	12	11:30	Low tide
24/03/2014	Zuari	15.41183	73.91065	3	12:34	Low tide
24/03/2014	Zuari	15.37475	73.95806	13	13:37	Low tide
24/03/2014	Zuari	15.34806	74.00473	1	14:50	Low tide
27/03/2014	CaTS	15.51045	73.64964	4	10:04	High Tide
27/03/2014	CaTS	15.51994	73.71021	3	12:34	High Tide
27/03/2014	CaTS	15.52039	73.72102	2	14:10	Low tide
27/03/2014	CaTS	15.52034	73.75928	1	15:09	Low tide
16/04/2014	Mandovi	15.4958	73.81563	11	09:18	Low tide
16/04/2014	Mandovi	15.5027	73.83414	4	10:41	Low tide
16/04/2014	Mandovi	15.5041	73.85956	12	12:18	High tide
16/04/2014	Mandovi	15.52013	73.9202	2	13:36	High tide
16/04/2014	Mandovi	15.52858	73.96967	14	14:51	High tide
16/04/2014	Mandovi	15.52189	73.98385	1	15:55	High tide
24/04/2014	Zuari	15.42523	73.78745	11	09:34	High tide
24/04/2014	Zuari	15.4162	73.85947	12	11:31	High tide
24/04/2014	Zuari	15.41183	73.91065	3	12:13	Low tide
24/04/2014	Zuari	15.37475	73.95806	13	13:53	Low tide
24/04/2014	Zuari	15.34806	74.00473	1	15:01	Low tide
30/04/2014	CaTS	15.51045	73.64964	4	10:30	Low tide
30/04/2014	CaTS	15.51994	73.71021	3	12:07	High tide
30/04/2014	CaTS	15.52039	73.72102	2	13:55	High tide

30/04/2014	CaTS	15.52034	73.75928	1	14:56	High tide
13/05/2014	INCOIS	15.43326	73.71198	5	09:55	High tide
13/05/2014	INCOIS	15.44653	73.73364	4	12:05	High tide
27/05/2014	Mandovi	15.49583	73.81563	11	09:18	Low tide
27/05/2014	Mandovi	15.50272	73.83414	4	10:48	High tide
27/05/2014	Mandovi	15.5041	73.85956	12	11:35	High tide
27/05/2014	Mandovi	15.52013	73.9202	2	12:46	High tide
27/05/2014	Mandovi	15.52858	73.96967	14	14:02	High tide
27/05/2014	Mandovi	15.52189	73.98385	1	15:17	High tide
29/05/2015	Zuari	15.4162	73.85947	12	10:45	Low tide
29/05/2015	Zuari	15.41183	73.91065	3	11:38	High tide
29/05/2015	Zuari	15.37475	73.95806	13	12:51	High tide
29/05/2015	Zuari	15.34806	74.00473	1	15:00	High tide

Water samples collected at discrete depths were processed and analysed for CDOM, chlorophyll and total suspended matter (TSM). The water samples were filtered immediately on board following the standard SeaWiFS protocols²⁸. For CDOM analysis, water was filtered into the amber glass bottles using 0.2 micron polycarbonate membrane filter under low vacuum. Polycarbonate membrane was preconditioned by soaking in 10% HCl for 15min prior to filtration; this membrane was then rinsed with 100ml of MilliQ water. Water samples were then stored at ~4°C until spectrophotometric analysis in the laboratory²⁹. For the analysis of chlorophyll, 500 ml to 1 litre of water was filtered depending on the turbidity levels on to 0.7 micron GF/F filter and analysed using the Turner fluorometer following standard protocols³⁰. TSM was obtained by filtering 500 ml to 1 litre of water on to pre-weighed 0.4 micron polycarbonate membrane filter followed by washing with MilliQ water to remove sea salt and then dried at 105°C for 1 hour.

Apparent optical parameters in the water column were measured in-situ using the free falling profiler hyper spectral radiometer (Satlantic Inc, Canada). The in-situ spectral inherent optical parameters of absorption, beam attenuation and backscattering were measured using the instruments, AC-9 and BB3 respectively (WetLabs, USA).

Absorbance measurements of the samples were carried out after bringing the refrigerated samples to room temperature for the temperature corrections³¹. The absorption of CDOM was measured using a UV-visible Shimadzu 2600 dual beam spectrophotometer with a cuvette of 10cm path length. Fresh MilliQ water from Millipore Ultrapure water system was used as the reference for the analysis. Absorbance spectra were obtained from 250-850nm range at 1nm interval and were corrected for baseline by averaging the absorbance from 700-850 nm and subtracting it from all the absorbance values³².

Absorption by CDOM is usually modelled in terms of exponentially decreasing function^{33,34} and is given in Eqn. 1, where λ_0 is a reference wavelength and S (nm^{-1}) is the spectral slope parameter describing the relative steepness of the spectrum.

$$a_g(\lambda) = a_g(\lambda_0)e^{-S(\lambda-\lambda_0)} \quad (1)$$

The reference wavelength λ_0 chosen for our study was 412 nm. Spectral slope coefficient, S was estimated using a linear fit of the log-linearized $a_g(\lambda)$ spectrum (nm^{-1}). Absorption of CDOM at reference wavelength is often accepted as a proxy for the concentration of CDOM and the S for changes in the composition of CDOM, including the ratio of humic acids to fulvic acids^{35,36}. Using a narrow wavelength range to calculate S often provides additional information than that obtained with a broader range³⁷. Slopes derived in the narrow wavelength range of $S_{275-295}$, $S_{350-400}$ and spectral slope ratio S_R ($S_{275-295}/S_{350-400}$) were used to track the changes in the molecular weight of the organic matter as proposed by Helms et al, (2008)³⁸.

Short wavelength slope in the range 275-295 can be measured with better precision even in highly photobleached waters and is very sensitive to changes in molecular weight and sources of CDOM. The ratio of slopes S_R has been reported for monitoring shifts in molecular weights and has been used to characterise different water types³⁸.

Results

Optical proxies of CDOM such as absorption coefficient of CDOM at specific wavelengths, spectral slopes, and the ratio of slope along with other physical, biological and optical parameters were used to understand the diagenesis of CDOM in the coastal and estuarine waters of Goa. The variations in spectral characteristics of CDOM for the waters of the study are given in Tab. 2.

Table 2. Statistics of CDOM parameters

	Mandovi			Zuari			Coastal		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
$a_g(412)$	0.220	0.630	0.470	0.190	0.670	0.420	0.121	0.208	0.176
$S_{250-600}$	0.014	0.018	0.016	0.017	0.020	0.018	0.008	0.017	0.013
$S_{275-295}$	0.019	0.021	0.020	0.019	0.023	0.021	0.025	0.030	0.026
S_R	1.068	1.400	1.230	0.990	1.370	1.120	1.585	2.289	1.888

Salinity and temperature showed typical features as observed and reported by others²². Salinity in the coastal waters was the highest and increased offshore and varied from 35.10 to 35.60 (Fig. 2a). The salinity in the Mandovi and Zuari estuaries decreased uniformly upstream and it varied from a low value of 19.38 to 35.01. The salinity in the Mandovi estuary was slightly higher than that of the Zuari estuary (Fig. 2b). Temperature varied in a contrasting manner in the estuarine and coastal waters. In the estuaries, the temperature varied from 30.71 to 35.58°C and in the coastal waters, the temperature varied within a narrow range of 30.13 to 31.12 °C. The temperature in the Zuari estuary was observed to be higher than the Mandovi estuary.

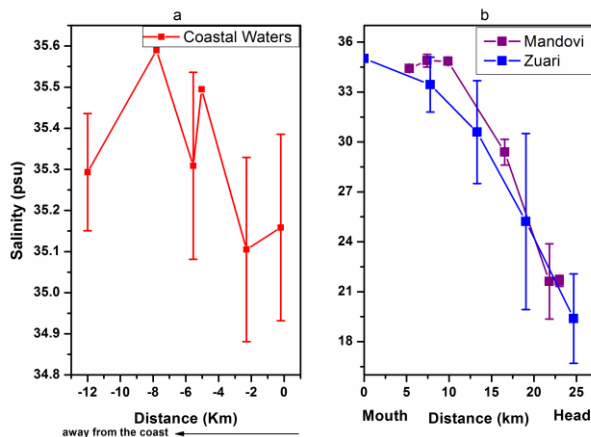


Figure 2: Spatial variation of salinity (a) coastal waters (Left) and (b) Mandovi and Zuari estuaries (Right). The distance shown in the estuaries are from the mouth of the estuary moving upstream and in the coastal waters, it is moving offshore.

In the coastal waters, the absorption was relatively less than estuaries and decreased offshore with a low value of 0.120 to 0.210m⁻¹. A drop in $a_g(412)$ was also observed at a distance of 2 to 4 Km from the coast (Fig. 3a). The $a_g(412)$ increased from the mouth towards upstream of both the estuaries. The $a_g(412)$ varied from 0.220 to 0.640 m⁻¹ in the Mandovi and 0.200 to 0.680 m⁻¹ in the Zuari estuaries. The $a_g(412)$ was found to be higher in the mid-stream region of the Mandovi estuary than the Zuari estuary (Fig. 3b).

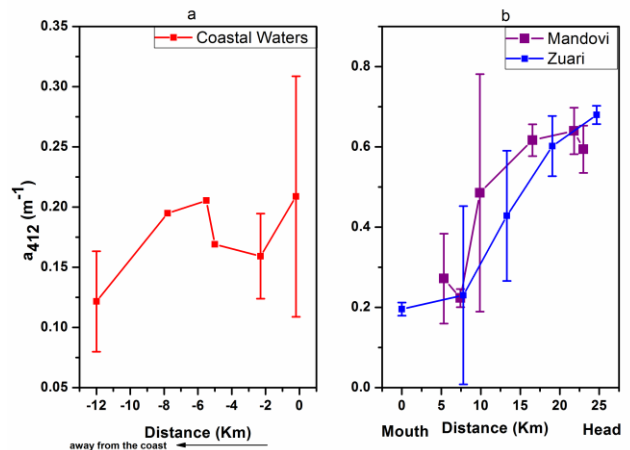


Figure 3: Spatial variations of CDOM absorption at 412 nm⁻¹ $a_g(412)$, (a) coastal waters (Left) and (b) Mandovi and Zuari estuaries (Right).

The slope taken over the wide spectral range of 250-600 nm has been used as a tracer to monitor changes in CDOM processes such as photochemical alteration, biological degradation, pH fluctuations and flocculation or coagulation processes^{35 3940}.

In the coastal waters, $S_{250-600}$ increased from the coast to a distance of 4 Km and then dropped sharply. The $S_{250-600}$ in the coastal waters was relatively lower than estuaries and varied from 0.008 to 0.017 nm⁻¹ (Fig. 4a).

In the Mandovi estuary, $S_{250-600}$ increased from the mouth to the head of the estuary and varied from 0.014 to 0.018 nm⁻¹ (Fig. 4b). A very low value of $S_{250-600}$ was observed at the mouth of this estuary. In the Zuari estuary, the $S_{250-600}$ varied from 0.017 to 0.021 nm⁻¹. A very high value was observed at about 8 Km in the Zuari and thereafter it decreased towards the head. A similar noticeable feature was also found in the Mandovi estuary. The $S_{250-600}$ in the Mandovi estuary was relatively lower than the Zuari estuary.

There was a marginal variation of slope $S_{250-600}$ with an increase in salinity up to 34 psu, and thereafter $S_{250-600}$ decreased.

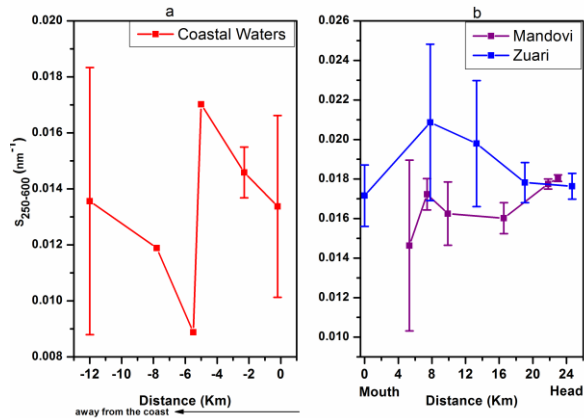


Fig 4: Spatial variations of slope, $S_{250-600}$ nm⁻¹ (a) coastal waters (Left) and (b) Mandovi and Zuari estuaries (Right).

$S_{275-295}$ has been used as a reliable proxy of CDOM average molecular weight (MW) and also as a potential indicator of photobleaching³⁸. In the coastal waters $S_{275-295}$ was low near the coast and increased significantly at a distance of 12 km offshore. The $S_{275-295}$ values were significantly higher in the coastal waters, as compared to the estuaries and varied from 0.025 to 0.030 nm⁻¹ (Fig. 5a). The $S_{275-295}$ in the Mandovi estuary was found to vary marginally within a narrow range of 0.019 to 0.021 nm⁻¹. At a distance of about 8 km from the mouth, $S_{275-295}$ was found to be very high in the Mandovi estuary. In the Zuari estuary, relatively larger variations of $S_{275-295}$ with values in the range of 0.019 to 0.024 nm⁻¹ were observed which decreased towards the head of the estuary (Fig. 5b).

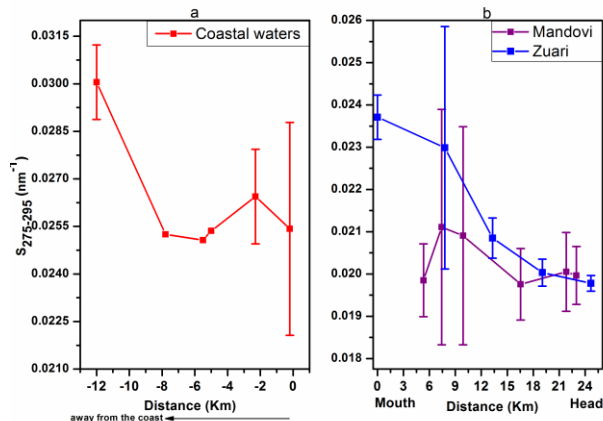


Fig 5: Spatial variations of slope in the narrow spectral range, $S_{275-295}$ nm⁻¹ (a) coastal waters (Left) and (b) Mandovi and Zuari estuaries (Right).

S_R , another proxy for the molecular weight of DOM has also been used as an indicator of photobleaching. In the coastal waters, S_R increased offshore. At a distance of 5 km from the

coast, a transition in S_R was observed. S_R in coastal waters varied from 1.58 to 2.30 (Fig. 6a). In the Mandovi estuary, S_R decreased linearly from the mouth to the head of the estuary and varied from 1.05 to 1.40. In the Zuari estuary, a sharp drop in S_R was observed at 7 km from the mouth and thereafter showed minimal variations towards the head of the estuary. S_R in the Zuari estuary varied from 1.00 to 1.38 (Fig. 6b).

The variation of S_R with salinity was found to be nearly invariant and varied within a small range of 0.90 to 1.20 until a salinity of 34, and thereafter S_R showed an increase in values as high as 2.4.

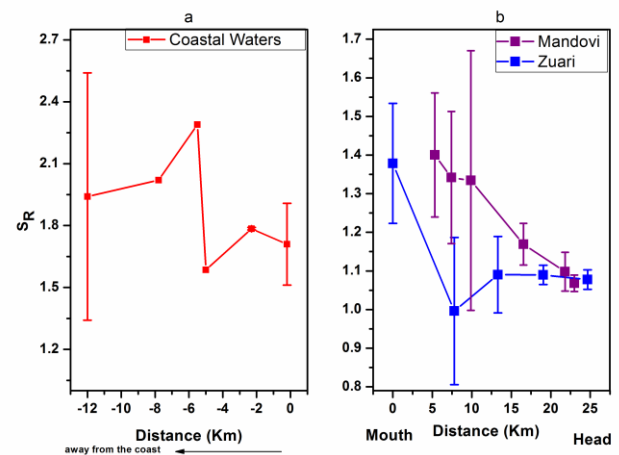


Figure 6: Spatial variations of the ratio of slopes, S_R (a) coastal waters (Left) and (b) Mandovi and Zuari estuaries (Right).

For studying conservative mixing salinity has often been used, as it was the best option to trace the mixing of water masses. In waters where there is mixing of saline marine water with fresh water, the behavior of CDOM on its conservative nature can be judged by examining the deviations from the linear relationship with salinity. Conservative mixing model is created by joining end points of highest salinity (sea water) and lowest salinity (freshwater) and the line is referred to as the theoretical dilution line³⁹. Here the conservative mixing model of CDOM using $a_g(412)$ with salinity for estuaries and coastal waters of Goa showed a trend of non-conservative behavior with most of the points falling above the mixing line and for higher salinity waters above 34 psu most of the points fall below the mixing line (Fig. 7). All those members which fall below are attributed to the sink or removal of the CDOM and other members above the line are flagged as sources or additions of CDOM^{39 41}. Such an inverse relation is typical of riverine and terrestrial sources⁴².

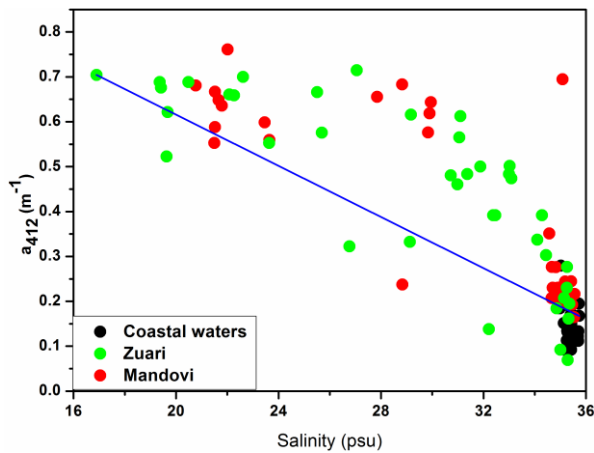


Fig 7: Conservative mixing model using $a_g(412)$ and salinity.

Discussion

It is essential to understand various factors and processes that influence the CDOM during summer. Estuarine and coastal waters of Goa during summer are under the influence of high solar radiations, surface temperature, salinity and wind speed. Spatial variations of temperature and salinity observed were typical of such estuaries in summer with salinity decreasing upstream and the temperature showing a reverse trend. Due to lack of rains during summer, the CDOM will not be regulated by the fresh water or riverine inputs and the circulations and mixing processes will be primarily controlled by the tides²². These coastal waters experience oligotrophic conditions and *Trichodesmium* blooms have been reported. The estuarine waters are relatively more productive and moving upstream in the estuaries the chlorophyll levels were found to increase. Contrary to the variations of chlorophyll, the suspended particles were found to decrease while moving upstream in the estuaries^{43 44}.

During this period of study, there were large spatial variations of CDOM and its spectral characteristics in the coastal and estuarine waters of Goa.

Sources of CDOM in the coastal waters were limited to being autochthonous and from the transport of CDOM by tidal circulations from the estuaries. The fate of CDOM in the coastal waters was influenced largely by the process of photobleaching as corroborated by high S_R and $S_{275-295}$ ^{33 45}. Such removals due to photobleaching have often been observed in high salinity areas of the estuaries and coastal waters^{46 47}. Hence the low levels of CDOM indicated by the absorption at 412 nm, $a_g(412)$ observed in the coastal waters could be due to the low-level inputs of CDOM

from limited sources and the removal by photobleaching.

CDOM optical properties of the coastal waters were closely examined to understand the mechanisms of production, removal and its characteristics. Though the CDOM in coastal waters were uniformly distributed, a noticeable dip in $a_g(412)$ was observed at ~ 6 Km offshore (Fig. 3a). Examining this region, it was found that this region had low $a_g(412)$, high $S_{250-600}$ (Fig.4a) and low S_R (Fig.6a) and relatively high chlorophyll. All these factors implied autochthonous production by phytoplankton accompanied by microbial degradation of freshly produced DOM^{4 38 48 49}. These low values of CDOM could not be entirely attributed to photobleaching, as the $S_{275-295}$ and S_R were relatively low. Although most of the losses of CDOM in coastal waters during summer were assumed to be through photoreactions, the process of microbial degradations also aids in the removal of CDOM. Since the productions of CDOM are at relatively lower level, this loss by photobleaching and microbial degradation becomes evident.

The CDOM in the Mandovi were relatively higher than in the Zuari. Generally, in the estuaries the sources of CDOM are of terrestrial origin and the same were observed for the estuaries of Goa which were indicated by low values of S_R ³⁸. Terrigenous nature of CDOM becomes more dominant further upstream which was evident from the decreasing values of S_R moving upstream with decreasing salinity^{38 50 51}. This newly produced CDOM having lower S_R imply a stronger linkage to terrestrial origin³⁸ (Fig.6b). The loss by the process of photobleaching was found to be obliterated to the large production and also it does not seem to be the prime mechanism of removal or sink in these estuaries, as the $S_{275-295}$ and S_R values were relatively lower. Slopes $S_{275-290}$ and $S_{250-600}$ were lower in Mandovi and S_R was higher compared to Zuari. This indicated that terrigenous sources dominated in the Zuari while in the Mandovi the high levels of CDOM were due to the anthropogenic sources. The CDOM characteristics were similar in nature at the heads of both the estuaries. Regions in the Mandovi as we move from the mouth upstream close to the capital city of Panjim show distinct variations in slopes, $S_{275-290}$, $S_{250-600}$ and the ratio of slopes S_R . Within these regions of the city limits, there were numerous sources of CDOM, which could include large-scale treated sewage discharges and

untreated discharges and drainages from settlements, factories, floating platforms of casinos (Fig. 1).

$S_{275-295}$ and S_R , which were reported to correlate negatively with the average molecular weight of DOM, were higher in the marine end than in the freshwater end, indicating an abundance of DOM with lower average molecular weight in the coastal waters.

Moving towards the mouth downstream of the estuary a gradual increase in salinity was observed and the CDOM characteristics such as S and S_R were invariant with salinity. However, there was a point of salinity beyond which there was a sudden change in the CDOM properties and this delimitation is known as the inflection point^{47 52 53 54}. Looking at the variations of S and S_R with salinity for the estuaries of our studies, the inflection point was at the region of salinity value of 34 psu. This intense mixing zone was at about 8 Km upstream from the mouth of the estuaries⁵⁵.

In the Zuari estuary at this region of inflection, there were distinct variations of the CDOM properties. Most of the CDOM and associated properties were at the extremum. The CDOM was found to be lowest, indicated by $a_g(412)$, the highest value of $S_{250-600}$ and S_R was the lowest (Fig.3b, 4b and 6b). Chlorophyll values were within the range of variation as it increased steadily from the mouth towards upstream. This region was observed to be under the influence of resuspension and turbulence, with abundant particulate matter, which was indicated by the highest values of TSM (mgm^{-3}), backscattering coefficient, b_{650} (m^{-1}) and fraction of particulate backscattering at 700 nm, B_p (m^{-1}) (Fig. 8). Lowest values of γ , the slope of particle size distribution (PSD) was observed here, which suggested that particulate matters were of relatively larger sizes. High values of refractive indices suggest that the abundance of these particles to be of mineral in nature. At such regions of turbidity maximum zone, resuspension and mixing have been reported, which help in CDOM production due to leaching from soil or sediment-derived suspended particles^{41 56 57 58}. The extreme turbidity levels were affirmed by the high diffuse attenuation coefficient and the presumption of bottom resuspension was substantiated by the high values of measured particulate beam attenuation near the bottom (Fig. 8). Such regions of inflection with high TSM also aid in the flocculation and microbial degradation

processes and thereby facilitate in the removal of CDOM^{59 60}. Hence the CDOM productions aided by resuspension were removed by flocculation or microbial activities at a faster pace to have any noticeable CDOM at these regions of turbidity maximum in these estuaries. The removal by the photolytic process was minimal indicated by the lowest values of S_R and relatively low value of $S_{275-295}$.

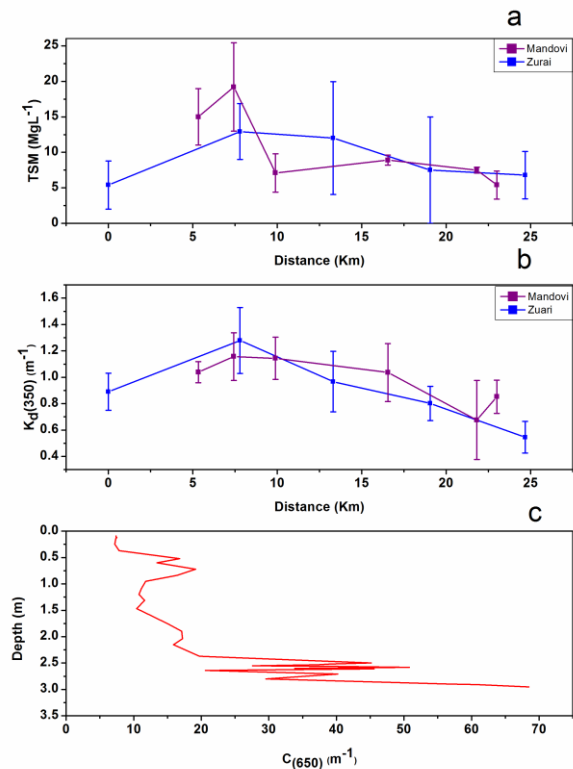


Fig 8: Variations of parameters in the estuaries of (a) total suspended matter (TSM) (Top), (b) diffuse attenuation coefficient at 350 nm ($K_d(350)$) in the estuary (Middle) and (c) depth profile of particulate beam attenuation $c_p(650)$ at point of inflection in the Zuari (Bottom).

A non-conservative behavior of CDOM with salinity was observed in the coastal and estuarine waters of Goa (Fig. 7). For a better understanding of this non-conservative behavior of CDOM, the study area was split into three regions of varying salinities, the first region from 18-24 psu, second region in the mid-section from 24- 34 psu and lastly at high salinity from 34- 35.5psu. Though the regions have been divided based on the ranges of salinities, the regions were also found to be geographically distinct.

The first region of low salinities occurs at the upstream of the estuaries. These regions in both the estuaries are under the influence of fresh water from various river run-offs but during summer it is minimal²². Quasi-conservative

behavior in this region suggests that the CDOM sources were unvarying. Mandovi and Zuari estuaries have mangroves along its banks which harbor sediments rich in organic matter⁶¹. Removal of CDOM by flocculation, adsorption or photobleaching was not observed from the optical characteristics of CDOM. Removal by flocculation could be negligible as the river runoff is minimal²¹ and the sediment load was observed to be low (Fig. 8). These regions were characterized by high molecular weight DOM as seen by lowest S_R (Fig. 6b) indicating a large amount of terrestrial source.

The second region occurs close to the most urbanized area. Largest deviations from the mixing line were observed in these regions, implying non-conservative behavior of CDOM mixing. The additions of CDOM could come from natural sources or anthropogenic origin. This region also has large mangroves habitats to be one of the sources of CDOM. Anthropogenic activities like construction of jetties, ship building and boat traffic (cruising), mining activities, sewage discharge, agricultural run-off, and industrial effluents have increased in these estuaries⁶²⁻⁶⁶ numerous floating casinos could also contribute to the enhancement of CDOM (Fig. 1). Sand mining was observed in these regions which disturb the benthic materials and could also contribute to CDOM. Moreover, industrial related activities were at a peak during October-May at several points along the estuary and discharge nutrients, heavy metals and other pollutants in the form of organic and inorganic industrial waste into the estuary^{65 67}.

Last regions with highest salinities were the coastal waters. The highest values of $S_{275-295}$ (Fig. 5a) and S_R (Fig. 6a) observed in the offshore waters indicated loss of CDOM by photobleaching^{37 44}. Lowest diffuse attenuation of light at 350 nm, $K_d(350)$ observed in these waters was also another proof of low CDOM, permitting the deep penetration of UV solar light (Fig.9).

Conclusion

Contrasting features, sources and sinks of CDOM were observed in the coastal and estuarine waters of Goa during summer when the estuaries receive the least influx from the rivers. In the coastal waters, though there was an autochthonous production of CDOM by phytoplankton, major

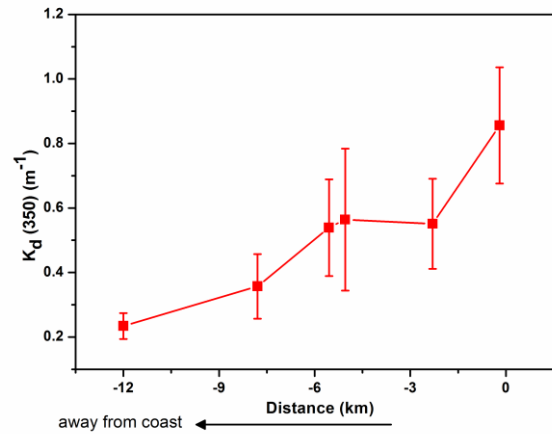


Fig 9: Variations of diffuse attenuation coefficient at 350 nm ($K_d(350)$) in the coastal waters.

contributions come from terrigenous and anthropogenic sources transported from the estuaries through tidal circulations. Environmental conditions favor photobleaching and microbial degradation and become dominant sinks, which lower the levels of CDOM present in the coastal waters resulting in deeper penetration of UV light in the water column (Fig. 10).

Large spatial variations of CDOM were observed in the estuaries. Spectral variations of CDOM were found to be almost similar at the head of both the estuaries. Sources of CDOM in the Mandovi and Zuari were found to be many, while the sinks were relatively insignificant. Sources in the estuaries are due to the terrigenous matter, leachate from the mangroves present along the banks, soil derived matter from resuspended sediments and a large amount of anthropogenic activity. Sinks in the estuaries were likely to be due to microbial degradation and flocculation. CDOM in Mandovi was higher as compared to that of the Zuari, which could be attributed to numerous sources of CDOM. Non-conservative behavior of CDOM was observed in these waters (Fig. 10)

One of the noticeable features was the point of inflection which had low CDOM with high turbidity and was found at about 8 Km upstream from the mouth of the estuary. High saline coastal waters were dominated by low molecular weight DOM probably due to photobleaching and microbial activity, whereas the low saline estuarine waters had high molecular weight DOM that can be linked to the terrigenous nature of DOM.

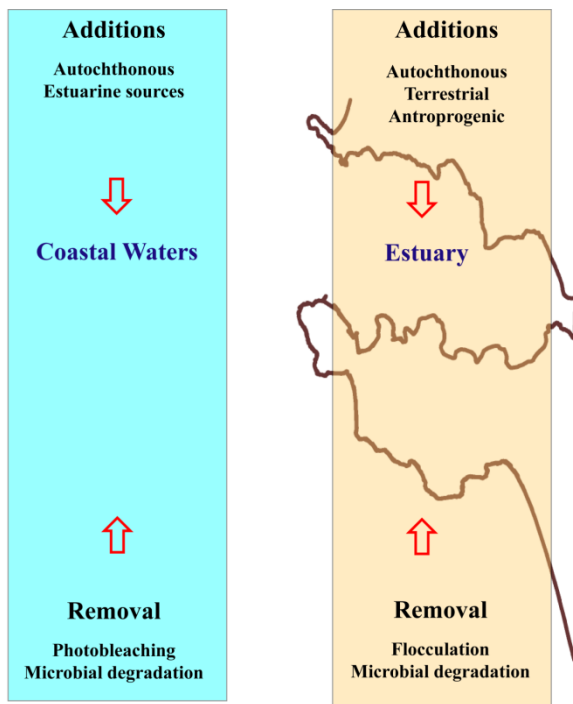


Fig 10: Schematic overview of the conclusions drawn from the study.

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