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Variations in concentrations and sources of bioavailable organic compounds in the Indian estuaries and their fluxes to coastal waters

B.S.K. Kumar, and V.V.S.S. Sarma*

CSIR-National Institute of Oceanography, Regional Centre, 176 Lawsons Bay Colony,
Visakhapatnam, India

*Corresponding author: sarmav@nio.org

Abstract:

Estuarine organic matter (EOM) supports heterotrophic carbon demand in the estuaries. However, the fraction of bioavailable organic compounds, which are easily assimilated by biological organisms, in the EOM is unclear. We hypothesize that a significant fraction of dissolved EOM is bioavailable and supports heterotrophic activity in the Indian estuaries. In order to test this hypothesis, 26 major, medium and minor Indian estuaries were sampled during wet and dry periods (2011-2012) for dissolved bioavailable organic compounds and dissolved organic carbon (DOC). The mean concentration of total dissolved carbohydrates (TDCHO) and total dissolved proteins (TDPRO) were higher during wet than dry period in contrary to the observations of dissolved free Amino Acids (DFAA). TDPRO:TDCHO and statistical analysis revealed that terrestrial organic matter contributed significantly to the EOM in the major and medium estuaries during wet period whereas fresh organic matter derived from *in situ* production contributed in all estuaries during dry period and minor estuaries during wet period. The lower concentrations of TDCHO and DFAA and their contribution to DOC were observed in the Indian than global estuaries suggesting that either efficient utilization of bioavailable organic compounds or less inputs (autochthonous/allochthonous) in the Indian estuaries. Indian estuaries transported an order of magnitude higher concentration of bioavailable organic compounds to the coastal Bay of Bengal ($490 \times 10^9 \text{ gC y}^{-1}$) than to the Arabian Sea ($50 \times 10^9 \text{ gC y}^{-1}$). The contribution of bioavailable organic compounds to the DOC export was 25% and 7% in the Bay of Bengal and Arabian Sea respectively. This study suggests that EOM contains a significant fraction of bioavailable organic compounds, as hypothesized, which might support heterotrophic carbon demand in the Indian estuaries as well as adjacent coastal waters.

Key words: carbohydrates, amino acids, proteins, DOC, dissolved organic carbon, river discharge, phytoplankton biomass, Indian estuaries

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Introduction

The global rivers discharge 370×10^{12} g of organic carbon to the ocean annually (Schlesinger and Melack 1981) and it is equivalent to <10% of the dissolved organic carbon in the ocean (Williams and Druffel 1987). The riverine (terrestrial) organic matter (TOM) is mainly derived from vascular plants, soils and it is a major source of organic matter to the estuaries and coastal environment (Onstad et al. 2000; Sanchez-Vidal et al. 2013). The TOM is one of the major energy sources to the aquatic organisms (Sedell et al., 1989; Wang et al. 2014). The transformation of TOM in the rivers and estuaries makes these regions as a strong source of carbon dioxide (CO₂) to the atmosphere (Regnier et al. 2013; Raymond et al. 2013; van Geldern et al. 2015; Sarma et al. 2011).

Heterotrophic respiration exceeds autotrophic production in the estuaries, where biologically reactive (labile) organic matter supports heterotrophic carbon demand (Raymond and Bauer 2000; 2001; Sarma et al. 2009). Labile fraction of the DOM pool comprises complex and aromatic residues (Fasching et al. 2014). Concentration of labile organic compounds in the aquatic system regulates the heterotrophic activity (Marques Junior et al. 2002). Labile (biochemical) organic compounds are derived from various processes including direct release by organisms (Hama and Yanagi 2001), microbial degradation of organic matter (Hellebust 1965), viral or bacterial lysis of phytoplankton cells (Jumars et al. 1989) and allochthonous material from rivers and soil (Gueguen et al. 2006). Amino acids are a major fraction of the freshly produced organic matter with preferential utilization by heterotrophic microorganisms leading to less preservation of OM in the water column and sediments (Tremblay and Benner 2006). Phytoplanktons are a significant source of labile organic compounds in the aquatic environment. High contribution of labile compounds to total organic matter in the estuarine phytoplankton (Achituv et al. 1994; Hussain et al. 2016), zooplankton (Ingole and Parulekar 1995; Condon et al. 2010) and bacteria (Zhu et al., 2014) are observed. High labile organic compounds are associated with high biomass of bacillariophyceae, dinophyceae and chlorophyceae in the estuarine environment (Snejana et al. 2003; Striquer-Soares and Chevolut 1996). The contribution of labile compounds are variable in different groups of phytoplankton, for instance, Chlorophyceae is known to be protein richer than other phytoplankton groups (Striquer-Soares and Chevolut 1996). Hence variations in phytoplankton composition may influence concentrations of labile organic compounds. Increased river discharge enhances suspended particulate matter (SPM) load which in turn shallows photic depth and decreases abundance of

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estuarine phytoplankton and zooplankton (Heip et al.1995; Caffrey 2004; Gazeau et al. 2004; 2005; Ram et al. 2003; Sarma et al. 2009). Hence magnitude of discharge determines not only plankton abundance but also the concentration of freshly produced labile organic matter. It was noticed that discharge is a significant source of river-borne organic matter to the estuary (Wollast and Mackenzie 1989; Smith and Hollibaugh 1993; Wollast 1998; Sarma et al. 2014), but it is considered to be refractory and unavailable for metabolic breakdown (Charles et al., 1998). In contrast, Sarma et al. (2009) estimated that 40-90% of the heterotrophic carbon demand is met from TOM in the Godavari estuary and that the contribution of TOM was more during discharge period when phytoplankton production was low. Sarma et al. (2012) noticed super-saturation of partial pressure of carbon dioxide (pCO₂) in the Indian estuaries due to decomposition of TOM. Perennial dominance of heterotrophy over autotrophy in the Indian estuaries (Sarma et al. 2009; Gupta et al. 2008; 2009) was inferred to be supported by TOM.

Very few studies were conducted to examine the concentration of labile compounds in the Indian estuaries. For instance, Khodse et al. (2010) estimated 11 to 60% of dissolved organic carbon (DOC) is contributed by total carbohydrates (TCHO) in Mandovi estuary, central west coast of India. Recently Krishna et al. (2015) estimated that 1.82 and 0.55 Tg of DOC is transported from Indian estuaries annually to the Bay of Bengal and Arabian Sea respectively, but the contribution of labile fraction remains unknown. Sarma et al. (2014) noticed significant spatial variations in magnitude of river discharge and phytoplankton biomass in the Indian estuaries due to variations in rainfall over Indian subcontinent. For instance, southwestern India receives higher rainfall (~3000 mm) followed by northeastern (1000-2500 mm) and the least rainfall occurs over the southeast (300-500 mm) and northwestern India (200-500 mm) (Soman and Kumar 1990). It was observed that the variations in suspended particulate matter (SPM) and magnitude of discharge determine the phytoplankton biomass and vegetation in the watershed that governs the composition and quality of TOM in the Indian estuaries (Sarma et al. 2014). This may result in spatial variations in contribution of labile organic compounds to DOM pool in the Indian estuaries. We hypothesize that a significant fraction of TOM may be labile that supports heterotrophic carbon demand in the Indian estuaries. It is difficult to measure all labile organic compounds in the DOM pool as it comprises complex and aromatic organic compounds (Fasching et al. 2015). Hence, we concentrated to study some of the bioavailable organic compounds, such as total dissolved carbohydrates (TDCHO; semi-labile), dissolved free amino acids (DFAA; labile) and total dissolved proteins (TDPRO; semi-labile). We

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called in this study these compounds as labile organic compounds, which indeed represent some of the bioavailable organic compounds in the aquatic environment. In order to test the above said hypothesis, samples were collected in 26 Indian estuaries during wet (discharge) and dry periods to examine the sources of bioavailable organic matter and estimate their export fluxes to the adjacent coastal regions.

Material and methods

Study area

India houses 14 major, 44 medium and 162 minor estuaries, which are influenced by monsoonal rainfall, hence they are called monsoonal estuaries. Indian estuaries have characteristic runoff periods, mostly from June to September, when Indian subcontinent receives rainfall, and exhibit non-steady state behavior (Vijith et al. 2009; Sridevi et al. 2013; 2015). This study is a part of the major project in the Indian estuaries and part of the data was published elsewhere on particulate organic matter (Sarma et al., 2014), dissolved organic carbon (Krishna et al., 2015), nutrient fluxes (Krishna et al., 2016), and trace gases fluxes (Sarma et al., 2012; Rao and Sarma 2013; 2016; Viswanadham et al., 2016).

Sampling and analysis

Since most of the Indian estuaries are shallow (2 to 5 m), water samples were collected from surface in 26 estuaries (Fig. 1) during wet (28 July to 18 August 2011) and dry (10 January to 1 February 2012) periods using a mechanized boat. Since no significant spatial gradients are observed between upstream and downstream with reference to salinity (Sridevi et al. 2015) and biogeochemical properties (Sarma et al. 2009; 2010) during wet (discharge) period due to heavy discharge, and unidirectional flow (from river to sea), water sampling was conducted at 5 locations covering upstream to down stream. In contrast, significant salinity gradients were observed during dry period due to dominance of marine water intrusion caused by ceasing of freshwater discharge (Sarma et al.,

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2012; Sridevi et al., 2015), sampling was carried out at 5 to 10 locations covering entire salinity range (0 to 30) from upstream to down stream. River discharge data were obtained from Kumar et al. (2005) and also from the dam authorities (Table 1a).

Water column temperature and salinity was measured using portable Conductivity-Temperature-Depth profiler (CTD; SBE-19 plus, Sea-Bird Electronics, USA). Water samples were collected using 5 L Niskin bottles. Extreme care was taken to avoid contamination of organic carbon samples during subsampling from Niskin bottle. Glass tube was connected to the filter holder, fitted with pre-combusted (450° C; 6h) 0.7 µm pore size glass fiber filter (GF/F), and the other end of the filter holder is opened to pre-acid clean glass bottle for collection of DOC and bioavailable organic carbon compounds samples. Once filled to three-fourth volume, the sample bottle was closed with glass stoppers and frozen until analysis for DOC, TDCHO, DFAA and TDPRO. In the case of DOC samples, 0.2 ml of 10% suprapure ortho-phosphoric acid was added as a preservative.

A 500 ml to 1 L water sample was filtered through 0.7 µm GF/F filter (Whatman) and phytoplankton biomass retained on the filter was extracted with N,N, dimethyl formamide, at 4°C in dark for 12 h, and the fluorescence in the extract was measured using spectrofluorophotometer (Varian Eclipse spectrofluorometer, USA) following Suzuki and Ishimaru (1990). The analytical precision for Chl-*a* analysis was ±4%. The SPM was measured based on weight difference of the particulate matter retained on 0.22 µm pore size polycarbonate filter after drying at 60°C for 48 h. Ammonium was measured following standard colorimetric procedure of Grashoff et al. (1992) with a precision of ± 0.02 µmol L⁻¹. Total viable bacteria count (TVC) was measured following the method described by Nagvenkar and Ramaiah (2009).

Phytoplankton cell abundance was carried out by cell counting method. The qualitative enumeration of phytoplankton was measured by sedimentation technique (Hasle 1978). Phytoplankton were identified following standard protocols (Santra 1993; Tomas 1996; Baker 2012) using BX51 OLYMPUS microscope (Olympus, Japan) and it is expressed in terms of cells per litre and pooled them into different groups of phytoplankton. Mesozooplankton samples were collected by horizontal towing of bongo net of 200 µm mesh and the volume of water filtered by the net was measured with

a calibrated flow meter (Hydrobios, USA) mounted at the mouth of the net. Mesozooplankton biomass was estimated by the standard displacement volume method (Harris et al. 2000) and the biomass was expressed in milli litres per cubic meter (ml. m^{-3}).

At the shore laboratory, the acidified (with 0.2 ml of supra-pure ortho-phosphoric acid in 50 ml of sample) DOC samples were sparged with ultrapure oxygen (99.995%) to remove inorganic carbon as carbon dioxide (CO_2). The DOC in the inorganic carbon free water was measured using TOC analyzer (TOC-VCSH, Shimadzu, Japan) following high temperature catalytic oxidation method (Benner and Hedges, 1993; Spyres et al. 2000). Precision of the DOC measurements was better than 4%. The measurement of DOC was calibrated using Certified Reference Material supplied by Dr. D.A. Hansell. The accuracy of the DOC measurements were <6%.

For TDCHO, about 1 ml of filtered water sample (with GF/F filter) was taken in a clean dry glass test tube and 1 ml of 5% phenol and 5 ml of 96% sulphuric acid was added. At the hot (exothermic) condition, resulted from addition of sulfuric acid to sample, polysaccharides, di-saccharides and oligissaharides are converted to monossacharides, which are then dehydrated to hydroxylmethyl furfural. This forms a orange-yellow colored complex with phenol. The reaction test tube kept in a water bath having temperature of 25°C for 20-30 min and the absorbance of the solution was measured at 490 nm using UV-Visible spectrophotometer following Dubois et al. (1956). The detection limit for carbohydrates as evaluated by glucose is from 1 - 120 mg/l.

For measurements of DFAA, about 2 ml of filtered water sample was taken and 2 ml of mixed reagent (Borate buffer (pH of 10.5), 1% o-phthalaldehyde in methanol and 0.1% 2-mercapto ethanol) was added and fluorescence of the isoindole derivatives was measured at excitation and emission at 342 nm and 452 nm respectively using spectrofluorophotometer (Parson et al. 1984). The detection limit for DFAA varied between 0.0007 and 7.5 mg/l of glycine. In the case of total dissolved proteins (TDPRO), about 2 ml of filtered sea water samples were heated at 80°C for 30 min in alkaline medium (0.5 ml of 1N NaOH) to dissolve proteins. After cooling, aliquot of 2.0 ml was transferred into test tube and 5.0 ml of carbonate-tartrate-copper solution was added and mixed. After 10 min, 1.0 ml of Folin-Ciocalteu reagent was added and absorbance of the complex was measured at 650 nm using spectrophotometer (Lowry et al. 1951). The detection limit for proteins is 0.01 - 1 mg/l (Bovine Serum Albumin). Samples were analyzed in duplicate and reported as mean

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values. Precisions for TDCHO, DFAA and TDPRO were ± 0.11 , ± 0.01 and ± 0.2 μM , respectively based on standard deviation of analysis of 10 aliquots of same sample.

Partial pressure of carbon dioxide (pCO_2) data was taken from Sarma et al. (2012) which was estimated from dissolved inorganic carbon and pH using dissociation constants of Millero et al. (2006). The detailed discussion of measurement of dissolved inorganic carbon and pH were given elsewhere (Sarma et al. 2012). The software Grapher was used for two dimensional graphical representation of the data and statistical analysis was performed using Statistica.

3. Results

The data collected in the Indian estuaries displayed a range of different hydrological conditions, from low freshwater flow and longer residence time to high freshwater flow and shorter residence time. The rate of mean annual discharge into the Indian estuaries varied between ~ 28 and $3505 \text{ m}^3 \text{ s}^{-1}$ (Table 1a) and they were classified as major ($>500 \text{ m}^3 \text{ s}^{-1}$), medium (>100 to $<500 \text{ m}^3 \text{ s}^{-1}$) and minor estuaries ($<100 \text{ m}^3 \text{ s}^{-1}$; Table 1a) following Sarma et al. (2014).

3.1. Hydrographic properties, suspended load (SPM) and phytoplankton biomass (Chl-a) in the Indian estuaries

Salinity in the Indian estuaries varied from near freshwater (0.06) to marine (28.7) during the wet period (Table 1a). The mean salinity of major, medium and minor estuaries was 2.93 ± 1 , 5.92 ± 2 and 12.1 ± 3 respectively (Fig. 2). Salinity displayed inverse relationship with magnitude of discharge (Table 2) during wet period. In contrast, salinity varied from 3.7 to 26.8 with the higher mean salinity in the minor (12.6 ± 1) than medium (11.4 ± 1) and major estuaries (9.8 ± 1) during dry period (Fig. 2).

The concentrations of SPM varied with reference to space and time, with relatively higher concentrations in Narmada, Tapi, Godavari and Haldia ($>200 \text{ mg l}^{-1}$) than other Indian estuaries

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sampled ($<150 \text{ mg l}^{-1}$; Table 1a) during wet period. The concentration of SPM displayed significant positive relation with river discharge (Table 2) in the Indian estuaries. Higher SPM was noticed in Narmada and Tapti (209 ± 56.3 and $417.7 \pm 25.3 \text{ mg l}^{-1}$ respectively) than other estuaries sampled ($<100 \text{ mg l}^{-1}$) during dry period (Table 1b). The mean concentrations of SPM were higher in the major ($169.2 \pm 55 \text{ mg l}^{-1}$) compared to medium ($71.8 \pm 17 \text{ mg l}^{-1}$) and minor estuaries ($30.3 \pm 8 \text{ mg l}^{-1}$) during wet period and similar pattern was observed (81.6 ± 22 , 42.2 ± 5 and $36.4 \pm 4 \text{ mg l}^{-1}$ respectively) during dry period. The concentration of Chl-*a* varied widely between wet (0.8 to 6.5 mg m^{-3}) and dry periods (0.8 - 28.1 mg m^{-3}). The concentration of Chl-*a* was higher in the minor ($7.3 \pm 1 \text{ mg m}^{-3}$) than medium ($6.0 \pm 1 \text{ mg m}^{-3}$) followed by major estuaries ($3.4 \pm 1 \text{ mg m}^{-3}$) during wet and 11.5 ± 3 , 4.5 ± 1 and $9.9 \pm 2 \text{ mg m}^{-3}$ during dry periods respectively (Fig. 2). Ammonium concentration was found to be higher in major estuaries ($5.1 \pm 3 \text{ }\mu\text{M}$) followed by medium ($3.9 \pm 1 \text{ }\mu\text{M}$) and minor estuaries ($2.0 \pm 1 \text{ }\mu\text{M}$) during wet period and the highest was found in major ($6.4 \pm 3 \text{ }\mu\text{M}$) followed by minor ($4.7 \pm 1 \text{ }\mu\text{M}$) and medium estuaries ($2.2 \pm 0.6 \text{ }\mu\text{M}$) during dry period.

3.2. Spatial variations in concentrations of DOC and bioavailable organic compounds in the Indian estuaries

3.3.1. Dissolved organic carbon (DOC)

The concentrations of DOC varied from 239 to 1079 μMC during wet period in the Indian estuaries (Table 1a). Relatively higher concentration of DOC was observed in the minor ($482 \pm 24 \text{ }\mu\text{MC}$) than major ($426 \pm 54 \text{ }\mu\text{MC}$) and medium estuaries ($352 \pm 23 \text{ }\mu\text{MC}$) during wet period (Fig. 2). DOC concentrations varied from 200 to 950 μMC (Table 1b) with higher concentrations were also observed in minor ($530 \pm 92 \text{ }\mu\text{MC}$) followed by major ($509 \pm 60 \text{ }\mu\text{MC}$) and medium ($268 \pm 77 \text{ }\mu\text{MC}$) estuaries during dry period (Fig. 2). The mean concentration of DOC in the Indian estuaries ($449 \pm 204 \text{ }\mu\text{MC}$) is higher than Mississippi ($307 \text{ }\mu\text{MC}$; Wang et al., 2013) but lower than Congo estuary ($604 \text{ }\mu\text{MC}$; Probst and Suchet 1992).

3.3.2. Total Dissolved Carbohydrates (TDCHO)

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The concentration of TDCHO varied from 2.3 to 26.8 μMC (Table 1a) during wet period with relatively higher concentration in the major ($10.9\pm 1.1 \mu\text{MC}$) than medium ($7.4\pm 1.2 \mu\text{MC}$) and minor estuaries ($6.9\pm 2.1 \mu\text{MC}$) (Fig. 2). High concentrations of TDCHO ($>10 \mu\text{MC}$) were observed in estuaries that received high discharge ($>1000 \text{ m}^3 \text{ s}^{-1}$). The concentration of TDCHO was relatively low and uniform in all Indian estuaries (2.2 to 9.5 μMC) during dry period (Table 1b).

The TDCHO displayed positive relation with discharge and SPM in the major ($r=0.89$; $p<0.001$ and $r=0.91$; $p<0.001$ respectively) and medium estuaries ($r=0.45$; $p<0.05$; and $r=0.68$; $p<0.001$ respectively) during wet period (Table 2). Significant relation was observed between TDCHO and Chl-*a* ($r=0.71$; $p<0.001$; $r=0.59$; $p<0.01$) only in the minor estuaries during wet and dry periods and medium estuaries during dry period (Table 2). Insignificant relation of TDCHO was observed with discharge and SPM in the minor estuaries. A significant inverse relation was found between TDCHO and total viable bacteria counts (TVC) in all estuaries (Table 2) and moderate relationship with pCO_2 and TDCHO in the major estuaries during wet period.

TDCHO displayed a significant linear relationship with salinity ($r=0.78$; $p<0.001$) and SPM ($r=0.62$; $p<0.001$) and insignificant relationship with Chl-*a* ($r=0.22$; $p<0.12$) in the major estuaries during dry period (Table 2). In contrast, TDCHO displayed significant relation with Chl-*a* ($r=0.32$; $p<0.005$) whereas significant relation with salinity and SPM was found during dry period in the medium estuaries.

3.2.3. Dissolved free amino acids (DFAA)

The concentrations of DFAA in the Indian estuaries varied from 0.1 to 2.7 μMC and 1.3 to 3.9 μMC during wet and dry periods respectively (Table 1a,b). The average concentration of DFAA was almost double during dry ($2.4\pm 1 \mu\text{MC}$) compared to wet period ($1.2\pm 1.0 \mu\text{MC}$) with weak spatial variability. The concentration of DFAA in major and minor estuaries was slightly higher (1.5 ± 0.2 and $1.9\pm 0.2 \mu\text{MC}$ respectively) than medium estuaries ($0.9\pm 0.1 \mu\text{MC}$) during wet period, in contrast, poor spatial variations were observed during dry period (2.3 to 2.9 μMC ; Fig.2).

Similar to TDCHO, the concentrations of DFAA displayed strong relation with discharge ($r=0.52$; $p<0.05$) and SPM in the major ($r=0.41$; $p<0.05$) and medium estuaries ($r=0.42$; $p<0.05$) but inverse relation was observed with salinity ($r=-0.48$; $p<0.05$) during wet period. Strong a significant linear relationship was observed between DFAA and Chl-*a* ($r=0.91$; $p<0.001$) in the minor estuaries during wet period (Table 2). DFAA showed significant linear relation with Chlorophyceae in all estuaries ($r=0.62$; $p<0.05$) except southeaten estuaries, such as Penna, Ponnayaar, Ambalyaar, Cauvery, Vaigai, where it was correlated with Bacillariophyceae ($r=0.53$; $p<0.05$; Table 2). A significant inverse relation of DFAA was observed with TVC and pCO_2 and linear relation with zooplankton abundance in medium estuaries but such relation was absent in major and minor estuaries where zooplankton abundance was low (Table 2). The concentration of DFAA displayed significant linear relationship with salinity ($r=0.5$; $p<0.01$), SPM ($r=0.53$; $p<0.01$) and Chl-*a* ($r=0.52$; $p<0.01$) in the major estuaries whereas significant relation was observed only with Chl-*a* ($r=0.38$; $p<0.05$) in the medium estuaries during dry period.

3.3.4. Total Dissolved Proteins (TDPRO)

The TDPRO concentrations varied from 1.2 to 16.6 μ MC (Table 1a) during wet and 2.5 to 7.9 μ MC during dry period in the Indian estuaries (Table 1b) with relatively higher concentrations during former than latter period in the minor estuaries. The concentration of TDPRO was higher in the major estuaries (7.2 ± 1.1 μ MC) than medium (6.1 ± 1.2 μ MC) and minor estuaries (5.7 ± 1.1 μ MC) during wet period and similar trend exists during dry period (6.6 ± 1.6 , 5.2 ± 0.3 and 3.2 ± 0.3 μ MC respectively; Fig. 2). TDPRO in the major and medium estuaries correlated linearly with discharge ($r=0.85$; $p<0.001$; $r=0.49$; $p<0.05$) and SPM ($r=0.62$; $p<0.01$; $r=0.44$; $p<0.05$), but inversely with salinity ($r=-0.52$, $p<0.05$; $r=-0.38$; $p<0.05$) during wet period. Strong linear relation was observed with Chl-*a* ($r=0.92$; $p<0.001$) and salinity ($r=0.82$; $p<0.001$) in the minor estuaries. The TDPRO displayed inverse correlation with TVC (Table 2), ammonium ($r=-0.55$, $p<0.1$) and pCO_2 ($r=-0.63$; $p<0.01$ and $r=-0.75$; $p<0.001$ in major and medium estuaries respectively) during wet period.

During the dry period, TDPRO linearly correlated with salinity ($r=0.38$; $p<0.05$; $r=0.63$; $p<0.001$; $r=0.72$; $p<0.001$), and Chl-*a* ($r=0.41$; $p<0.05$; $r=0.35$; $p<0.05$; $r=0.6$; $p<0.01$) in major, medium and minor estuaries and with SPM ($r=0.66$; $p<0.001$; $r=0.41$; $p<0.01$) in the major and medium estuaries only. DFAA and TDPRO are inversely correlated during wet period and except major estuaries during dry period (Table 2).

4. Discussion

4.1. *Variability and controlling factors of bioavailable organic compounds in the Indian estuaries during wet (discharge) period*

The Indian estuaries display a range of hydrological conditions driven by variable freshwater flows and flushing rates during wet period (Table 1a). The spatial variations in discharge are controlled by precipitation and also the origin of the river. Some peninsular rivers, such as Godavari, Mahanadi and Krishna, are originated in the western India and flow towards east by covering distance between 900 and 1465 kms. Hence the discharge of these rivers follow precipitation pattern in the western India. The western India receives the highest precipitation (Soman and Kumar 1990), the length of west flowing rivers, such as Mandovi, Zuari, Kali, are short (~100 km) leading to low discharge. Penna, Cauvery, Ponnayyar and Vaigai are located in the southeastern India (south of 16°N), which originated in central India where less precipitation occurs (Soman and Kumar 1990). Therefore, size of the river, location, and precipitation pattern controls the magnitude of discharge into the coastal ocean that may influence the magnitude of modification of organic matter within the river.

The dissolved and particulate organic carbon in the Indian estuaries was governed by the magnitude of river discharge and SPM load during wet period (Sarma et al. 2014; Krishna et al. 2015). A significant relation of organic compounds (TDCHO, DFAA and TDPRO) with discharge and salinity indicates that possible contribution of terrestrial sources to the major and medium estuaries during wet period (Table 2). The relation between SPM and organic compounds indicated possible source from sediments as the flow of river was several folds higher during wet than dry period (Sridevi et al. 2015) resulting in resuspension of surface sediments into overlying water. High SPM severely limits

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phytoplankton production during wet period (Sarma et al. 2009) resulting in insignificant relation between bioavailable organic compounds and phytoplankton biomass (as Chl-*a*) in the major and medium estuaries during wet period. However, a significant relation was observed between TDPRO and Chl-*a* in medium estuaries and a weak relation in major estuaries suggesting some contribution from *in situ* processes as well. The intensive observations made on variability on DFAA over a period of 3 years in the Godavari estuary (Kumar 2014) indicated that DFAA displayed inverse relation with total bacterial abundance suggesting bacterial metabolism as a major sink. On the other hand, the concentrations of TDCHO, DFAA and TDPRO in the minor estuaries were controlled by phytoplankton biomass (i.e., Chl-*a*) (Table 2) during wet period due to weak discharge leading to low SPM, that facilitates high phytoplankton growth. Sarma et al. (2009) noticed formation of phytoplankton blooms in the Godavari estuary during the onset and termination phase of the discharge due to enhanced nutrient inputs, strong stratification and relatively low SPM levels. Similar features are also observed in other Indian estuaries such as, Mandovi-Zuari estuarine system (Pednekar et al. 2011) and Kochi estuary (Gupta et al. 2008) on the west coast of India.

Coffin (1989) compared winter and summer uptakes of DFAA by bacteria. The summer uptakes were higher due to warm temperatures when the bacterial metabolism is higher. The significant inverse relation of DFAA with TVC (Table 2) and ammonium suggest that amino acids are preferentially utilized by bacteria than TDPRO, leading to release of ammonium during wet period. Sediments and phytoplankton are major sources of DFAA to the aquatic system and both of these sources would lead to higher amino acid concentrations in the shallow, high productive and low salinity regions of the estuary (Jorgensen 1982). Thus, bacterial cells in the nitrogen-rich (low salinity) regions of the estuary utilize a larger portion of the amino acid as energy source than less nitrogen (high salinity) region of the estuary (Jorgensen 1982). The low concentrations of DFAA in Mahisagar and Narmada ($0.3 \pm 0.2 \mu\text{MC}$) estuaries were associated with high bacterial abundance ($2.3 \pm 3.1 \times 10^8$ cells/ml) whereas high DFAA concentrations ($1.0 \pm 1.5 \mu\text{MC}$) in southern Indian estuaries (Penna, Krishna, Ponnayyar, Vellar, Cauvery, Ambalayar, Vaigai, Chalakudi and Kochi back waters) were associated with low bacterial cell abundance ($0.009 \pm 0.01 \times 10^8$ cells/ml) suggesting high bacterial utilization of DFAA could be potential reason for variability in their concentrations.

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Sarma et al. (2009; 2011; 2012) observed that Indian estuaries are heterotrophic throughout the year and computed that 40 to 90% of heterotrophic carbon demand is met from TOM with higher contribution during wet period when phytoplankton production was the least. Increase in total bacterial counts and respiration rates was also noticed in the Godavari estuary associated with peak discharge leading to increase in pCO₂ levels to as high as >30,000 μatm (Sarma et al. 2011). Higher pCO₂ levels, above the atmospheric value, were noticed in the Indian estuaries during wet period and it was attributed to decomposition of organic matter (Sarma et al. 2012). This is further confirmed by inverse correlation of DOC with pCO₂ (r=-0.71; p<0.001) and TDCHO, DFAA and TDPRO with pCO₂ (Table 2) during wet period indicating that decomposition of organic matter is the major source of pCO₂ in the Indian estuaries. The inverse relation of TDCHO, DFAA and TDPRO with pCO₂ suggest these compounds have been utilized by microbial organisms to meet their carbon needs in the Indian estuaries making Indian estuaries as source for atmospheric CO₂ (Sarma et al., 2011; 2012). The principal component analysis revealed that discharge and SPM contributed to TDCHO and TDPRO while inversely by salinity and phytoplankton biomass (Chl-*a*) in the major estuaries during wet period (Fig. 3). TDPRO is positively correlated with salinity and Chl-*a* suggesting that both mixing and biological production are major sources. TDCHO is linearly correlated with SPM and discharge during wet period in the medium estuaries indicating terrestrial and sedimentary sources are important. All parameters contributed to DFAA during wet period in the major and medium estuaries. In case of minor estuaries, discharge, Chl-*a* and SPM governed concentrations of TDCHO and DFAA while mixing contributed to TDPRO. This analysis suggests that discharge brought significant amount of terrestrial borne TDCHO, DFAA and TDPRO to the Indian estuaries that supported heterotrophic carbon demand leading to formation of high pCO₂ and flux to the atmosphere.

In order to understand the influence of environmental properties on distribution of bioavailable organic compounds (TDCHO, DFAA and TDPRO) in the Indian estuaries, dendrogram was drawn based on total measured bioavailable organic compounds (sum of TDCHO, DFAA and TDPRO). Three clusters have been formed at 70% level with reference to magnitude of discharge, i.e., major, medium and minor estuarise. This suggests that the concentration of total measured bioavailable organic compounds displayed similarity with reference to magnitude of discharge in the Indian estuaries (Fig. 4a).

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4.2. Variability and controlling factors of bioavailable organic compounds in the Indian estuaries during dry period

The concentrations of bioavailable organic compounds during dry period are lower compared to wet period. The significant relationship of TDCHO, DFAA and TDPRO with salinity, and SPM suggests re-suspension of bottom sediments by tidal currents as major source while weak relation with Chl-*a* indicates minor contribution through *in situ* production in the major estuaries (Table 2). In contrast, significant relation of TDCHO, DFAA and TDPRO with salinity and Chl-*a* in the medium and minor estuaries suggest both mixing and *in situ* processes contributed (Table 2). In addition to this, high zooplankton abundance was noticed in the medium and major estuaries during dry period (Venkataramana et al., 2017) suggesting that enhanced grazing might have influenced their production in these estuaries. The strong relation of zooplankton abundance with TDCHO and TDPRO suggests significant role in the major ($r=0.86$ and $r=0.98$; $p<0.001$ respectively) and medium ($r=0.50$ and $r=0.89$; $p<0.001$ respectively; Table 2) estuaries. Zooplankton contains high content of TDCHO (10-20%) and TDPRO (40-60%) in their body hence increase in their abundance and their degraded products enhance labile organic compounds to the water (Ingole and Parulekar 1995; Condon et al. 2010). The role of zooplankton could not be determined in the minor estuaries due to lack of data. DFAA displayed significant relationship with TDPRO in medium and minor estuaries indicating that these two pools are well coupled. TDCHO and TDPRO did not display significant correlation with Chl-*a* in the major and minor estuaries while weak relationship in medium estuaries indicates that the contribution from biological production is relatively low. The strong relation of TDCHO and TDPRO with SPM in major estuaries suggests resuspension is a major source during dry period. This could be potentially caused by higher tidal amplitude between flood and ebb tide in some of the major estuaries such as Narmada, Tapi, Haldia and Mahanadi (2.8 to 11 m) resulting in relatively higher resuspension of bottom sediments (Table 2).

In addition to this, the concentrations of these compounds in the ground water were significantly higher (by 5 to 230%, 8 to 152% and 5 to 103% for TDCHO, DFAA and TDPRO respectively) than that of estuarine waters in Godavari estuary (Kumar 2014). Using exchange rates estimated based on Radium isotopes (Rengarajan and Sarma 2015), Kumar (2014) estimated that 16-48% of the

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estuarine TDCHO, DFAA and TDPRO are contributed through ground water exchange in the Godavari estuary during dry period. However, such estimations were not carried out in other estuaries due to lack of data. A significant contribution of these compounds from ground water may probably weaken the relationship with estuarine properties. However, it must be proved through measurements of biochemical compounds in the groundwaters in the future. The principal component analysis suggests that TDCHO and DFAA are controlled by SPM, salinity and Chl-*a* in the major estuaries while TDCHO is mainly contributed by SPM and Chl-*a* and DFAA is produced through biological processes (Chl-*a*) in the medium estuaries. On the other hand, TDCHO and TDPRO are governed by salinity in the minor estuaries (Fig. 3). Therefore, this study strongly suggests that variations in magnitude of discharge, tidal currents, nutrient levels, abundance of bacteria, phytoplankton and zooplankton abundance from one estuary to another estuary have significance impact on the TDCHO, DFAA and TDPRO concentrations in the Indian estuaries.

In order to understand the influence of environmental properties on distribution of bioavailable organic compounds (TDCHO, DFAA and TDPRO) in the Indian estuaries, dendrogram was drawn based on total measured bioavailable organic compounds (sum of TDCHO, DFAA and TDPRO). Two clusters have been formed at 50% level with reference to magnitude of discharge. Medium estuaries formed one group, except Vaigai, and minor and major estuaries formed another group. Again at 70% level, the second group formed again two clusters, i.e., minor and major estuaries. This suggests that the concentrations of total measured bioavailable organic compounds in the Indian estuaries are impacted by magnitude of discharge in the Indian estuaries (Fig. 4).

4.3. Sources of bioavailable organic compounds to the Indian estuaries

The concentrations of carbohydrates and proteins reflect the growth phase of phytoplankton, as they develop actively synthesized proteins yielding enhanced TDPRO:TDCHO ratio as observed in

various ecosystems (Aleya 1991; Michard et al. 1995; Iola and Alessandra 2008; Kumar et al. 2013). Cowie and Hedges (1984) suggested possible means for distinguishing sources of organic matter through total carbohydrates. The rationale for this approach is that terrestrial plants contain relatively higher carbohydrates than plankton or bacteria. Protein:Carbohydrates ratio has been used as an index to determine the origin of material in the sediments in the Galacian coast (NW Spain; Cividanes et al., 2002), and Eastern Mediterranean Sea (Danovaro et al., 1993). The lower protein:carbohydrates ratio is a typical feature of terrigenous sources (Danovaro, 1996) and vice versa is *in situ* production as proteins are more readily used by bacteria than carbohydrates (Williams and Carlucci, 1976; Newell and Field, 1983; Danovaro et al., 1993). However, these ratios should be interpreted with caution as estuaries contain some fraction marine sources and also dilution of carbohydrate-poor terrigenous carbon from charcoal, soil etc.

Lower TDPRO:TDCHO ratios were observed (<1) (Table 1a) during wet period probably indicating significant contribution of terrestrial and dead organic matter to the major and medium estuaries. In contrast, higher ratios (>1; Table 1a) were observed in the minor estuaries indicating larger contribution from *in situ* production (freshly produced) facilitated by enhanced phytoplankton growth due to lower SPM. In addition to this, lower bacterial abundance was also recorded in the minor estuaries further indicating that less modification of organic matter enhanced TDPRO:TDCHO ratios. Therefore, nature of organic matter in the Indian estuaries is governed by magnitude of river discharge, and phytoplankton biomass. During dry period most of the estuaries have TDPRO:TDCHO >1 except estuaries like Rushikulya, Vamsadhara, Nagavali, Sabarmati, Mahisagar, Cauvery, Ambalayaar and Vaigai (Table 1b) which had TDPRO:TDCHO <1 indicating that *in situ* production contributed significantly in the former estuaries and modified or degraded organic matter contributed in the latter estuaries (Table 1b). These results are consistent with the statistical analysis discussed in the former section.

In addition to this, the source of the organic matter also modifies TDPRO:TDCHO ratios as relatively higher proteins are observed in the C₃ plants than C₄ (Barbehenn et al. 2004). Sarma et al. (2014) identified that the contribution of organic matter from C₃ plants dominated in the northern estuaries, north of Krishna estuary, while C₄ plants in the southern estuaries based on isotopic

composition of carbon and nitrogen in particulate organic matter. The higher TDPRO:TDCHO ratios in the northern estuaries could also be due to higher contribution of C₃ plants compared to south.

4.4. *Comparison of bioavailable organic compounds and their contribution to DOC in Indian estuaries with global estuaries*

The measurements of bioavailable organic compounds in the global estuaries are rather scarce. However, TDCHO and DFAA were measured in some American, European and Chinese estuaries along with DOC. Table 3 compares the concentrations of TDCHO+ DFAA and their contribution to DOC in the global and Indian estuaries. The TDCHO+DFAA ranged between 17.1 and 79.6 μ MC with higher concentrations in the Mississippi River and this range is significantly higher than that of Indian estuaries (2.8 to 26.7 μ MC). The mean concentrations TDCHO+DFAA in the global estuaries was higher (16.3 \pm 3 μ MC) than Indian estuaries (10.2 \pm 2 μ MC). On the other hand, the contribution of TDCHO+DFAA to DOC varied from 4.8 to 31.8% with higher value from Adriatic Sea and lower values in Delaware and Mississippi river (4.2-4.8%). The global mean of contribution of TDCHO+DFAA to DOC was 5.1% which is twice higher than that of the mean of Indian estuaries (2.2%). The lower contribution of measured bioavailable compounds to DOC in the Indian estuaries could be due to less production/source from the upstream river or higher microbial decomposition as higher bacterial respiration rates are reported in the Indian estuaries due to warmer temperatures resulted in record levels of pCO₂ in the Indian estuaries (Sarma et al. 2011; 2012; Gawade et al., 2017). More studies are required to provide evidence for possible reasons for lower contribution of measured bioavailable organic compounds to DOC in the Indian estuaries.

4.5. *Contribution of measured bioavailable organic compounds from Indian estuaries to the adjacent coastal regions and its possible impact on coastal food web*

The transport load of TDCHO, DFAA and TDPRO from individual monsoonal estuaries to the adjacent coastal waters was calculated by multiplying the mean concentration at the mouth of the estuary with the volume of discharge ($m^3 y^{-1}$). The annual mean export flux from the Indian estuaries was 430 x 10⁹, 22 x 10⁹, 35 x 10⁹ g C to the Bay of Bengal and 30 x 10⁹, 0.9 x 10⁹, 11 x 10⁹ g C to the

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Arabian Sea in the form of TDCHO, DFAA and TDPRO respectively. Indian estuaries transport 10 times higher concentrations of measured bioavailable organic compounds to the coastal Bay of Bengal ($\sim 490 \times 10^9 \text{ gC y}^{-1}$) than to the Arabian Sea ($\sim 50 \times 10^9 \text{ gC y}^{-1}$). It is consistent with the higher concentrations of DOC in the upper water column of the Bay of Bengal (150-200 μM ; Fernandes et al. 2008) than in the Arabian Sea (80-100 μM ; Hansel and Peltzer 1998). Such higher concentration of DOC in the Bay of Bengal is attributed to riverine sources (Fernandes et al. 2008). Recently Krishna et al. (2015) estimated that higher amount of DOC ($1820 \times 10^9 \text{ gC y}^{-1}$) from Indian estuaries enters into the Bay of Bengal than to the Arabian Sea ($550 \times 10^9 \text{ gC y}^{-1}$). This study suggests that $\sim 25\%$ and 7% of the DOC exported to the Bay of Bengal and Arabian Sea was contributed by bioavailable compounds respectively. This is consistent with the higher bacterial abundance in the coastal Bay of Bengal than the Arabian Sea (Gauns et al. 2005) suggesting that labile organic matter transported by the rivers support bacterial activity in the coastal Bay.

The estimation of fluxes of bioavailable organic compounds to the adjacent coastal waters may carry significant error as the observations were carried out one time during each season. In order to examine the variations in bioavailable organic compounds within each period, monthly bioavailable organic compounds data collected in the Godavari estuary for the year 2009 to 2011 was analyzed (Kumar 2014). This analysis revealed that the concentrations of TDCHO, DFAA and TDPRO displayed strong temporal variability with relatively higher concentrations during discharge (wet) period than no discharge (dry) period. The variability in TDCHO, DFAA and TDPRO concentrations within the discharge period was about 9.7%, 9.5% and 4.6% respectively based on the monthly observation carried out in the Godavari estuary. Though this variability is estuary dependent, however, the possible error associated with our estimations of flux of bioavailable organic compounds to the coastal ocean may carry an error in the tune of 10% due to temporal variations. Since error estimation was done based on monthly variability in one estuary and the flux of organic compounds are more sensitive to the discharge variations, the estimated flux may be over/under estimated due to lack of high-time-resolution data. Therefore, the exact error on the flux estimation may be more than evaluated above.

5. Summary and conclusions

In order to examine the spatial and temporal variations in bioavailable organic compounds (TDCHO, DFAA and TDPRO) and their sources, a study was conducted in 26 major, medium and minor estuaries along the Indian coast during wet and dry periods. Relatively higher concentrations of bioavailable organic compounds were observed during wet compared to dry period. Based on statistical and principal component analysis, the discharge is the major source of bioavailable organic compounds to the Indian estuaries during wet period while *in situ* production and tidal resuspension during dry period in the major and medium estuaries. Bacterial utilization of bioavailable compounds led to supersaturation of pCO₂ in the major estuaries during wet period as evidenced from the strong inverse relation between pCO₂ and bioavailable organic compounds. The ratio of TDPRO: TDCHO suggest that Indian estuaries receive degraded organic matter during wet period and *in situ* (freshly produced) processes contributed organic matter during dry period. Nevertheless both these sources of bioavailable compounds significantly supported microbial carbon demand in the Indian estuaries. The amount of dissolved bioavailable organic compounds transported to the Bay of Bengal is an order of magnitude higher (~490x10⁹ g C) than in the Arabian Sea (~50x10⁹ g C) and it is consistent with the higher DOC concentration in the Bay of Bengal during wet period. It was further noticed that about 25% and 7% of the DOC flux to the Bay of Bengal and Arabian Sea were contributed by bioavailable organic compounds respectively. This study suggests that bioavailable organic compounds transported to the estuary and coastal ocean support microbial activity and thus food web dynamics in the northern Indian Ocean, as hypothesized. In addition to this, higher bacterial abundance supports microzooplankton (20-200 μm) population in the western Bay of Bengal due to existence of microbial loop (Gauns et al. 2005; Jyothibabu et al. 2008; Prasanna Kumar et al. 2010). Therefore this study further suggests that river discharge may increase bacterial abundance that may have significant impact on the coastal heterotrophy and food web dynamics.

Discharge of Indian rivers is being modified due to inter-connecting rivers and construction of more dams to conserve freshwater during non-monsoon period. Reduced discharge is expected to eutrophicate Indian estuaries (Acharyya et al. 2012) and intensify coastal upwelling (Sarma et al. 2015). On the other hand, decrease in river discharge may reduce bioavailable organic carbon inputs to coastal waters that might have significant impact on abundance of bacteria and microzooplankton that may influence coastal fisheries. Therefore, more work is needed to confirm impact of variations in magnitude of discharge on coastal ecosystem through long-term observations.

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Table 1(a): Average and standard deviation (Avg±SD) of discharge, surface area, tidal amplitude, salinity, SPM, Chl-*a*, DOC, TDCHO, DFAA, TDPRO and ratio of TDPRO:TDCHO (P/C) in the Indian estuaries during wet period.

Estuary	Discharge (m ³ /Sec)	Surface area (10 ³ Km ²)	TA*(m) [§]	Salinity (psu)	SPM (mg/l)	Chl- <i>a</i> (mg/m ³)	DOC (µMC)	TCHO (µMC)	DFAA (µMC)	TPRO (µMC)	P/C [¶]
Rivers draining into bay of Bengal- Peak discharge period (wet period)											
Haldia	1600	10	7	0.71±0.1	229.7±52.0	2.9±0.8	321±58	12.2±2.7	0.9±0.7	4.5±3.9	0.35±0.27
Subarnalekha	392#	19	-	3.92±0.5	50.8±19.0	1.8±0.2	339±102	6.3±1.4	0.8±0.4	13.8±2.2	2.04±1.38
Baitarani	903#	14	-	0.12±0.2	149.7±124.0	3.3±0.4	357±89	14.7±4.5	1.6±0.3	1.7±1.3	0.14±0.13
Mahanadi	2121#	142	2.8	0.10±0.8	16.4±3.0	3.2±0.8	528±156	8.7±3.6	1.6±0.3	5.4±0.6	0.73±0.39
Rushikulya	61	9	-	20.74±0.2	18.4±2.0	1.1±0.2	421±189	9.9±4.5	1.5±0.2	9.3±1.7	1.56±1.30
Vamsadhara	111	11	-	13.23±0.5	31.7±5.0	4.3±0.7	301±52	3.5±0.3	1.1±0.6	10.2±2	2.89±0.81
Nagavali	63	9	2.1	28.74±1.0	43.4±12.0	1.4±0.3	314±86	4.3±1.0	0.2±0.01	15.1±1.8	3.65±1.33
Godavari	3505#	313	2.1	0.1±0.1	691.5±46.0	1.8±0.2	341±54	19.3±2.8	2.7±0.6	14.7±0.7	0.78±0.14
Krishna	577#	259	1.9	5.21±0.3	15.8±2.0	5.5±0.8	368±72	24.6±0.3	0.9±0.5	3.9±0.9	1.32±0.61
Penna	200#	55	-	10.23±0.5	26.1±25.0	6.2±0.5	344±65	3.3±0.1	1.3±0.5	4.3±2.0	1.26±1.43
Ponnayaa	51	16	-	0.23±0.1	32.2±30.0	3.1±3.2	350±56	17.1±5.6	2.3±1.1	6.9±1.6	0.5±0.2
Vellar	29	9	1.5	11.53±0.8	44.5±16.0	4.1±0.8	276±78	4.1±0.1	1.1±0.2	6.5±2.8	1.10±0.9

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Cauvery	677#	88	-	11.32±0.8	28.7±9.0	6.5±1.0	380±88	7.5±4.5	1.6±0.7	5.5±1.3	0.9±0.78
Ar	28		-	4.22±0.2	67.5±60.0	1.7±0.3	1179±189	26.8±0.2	1.5±0.3	14.9±3.2	0.8±0.2
Vaigai	36	7	-	24.65±1.0	29.2±19.0	1.9±0.6	239±53	2.6±2.2	1.3±0.3	9.8±2.1	1.80±1.20
Rivers draining into Arabian sea- Peak discharge period (wet period)											
Kochi backwaters	391	-	1.3	3.85±0.6	70.3±48.0	3.4±0.7	274±65	4.8±0.9	1.6±0.2	3.4±1.1	0.78±0.81
Chalakuudi	61	2	-	0.10±0.1	13.3±4.0	2.6±0.4	419±92	4.4±1.9	1.5±0.3	1.2±1.6	0.36±0.3
Bharatapuzha	161	6	-	0.13±0.1	6.5±1.0	2.7±0.2	429±102	2.6±0.3	0.5±0.3	1.3±0.3	0.51±0.22
Netravathi	351	3	-	0.15±0.1	140.2±17.0	3.5±0.5	360±59	20.1±4.2	0.7±0.1	9.1±0.4	0.46±0.08
Kali	152	4	-	5.82±0.5	31.6±4.0	3.8±0.2	248±67	2.4±1.4	0.3±0.1	1.6±0.1	0.75±0.36
Zuari	103	1	2.7	6.41±0.6	33.7±11.0	2.6±0.3	370±65	2.6±1.3	0.8±0.2	3.4±2.5	1.75±0.85
Mandovi	105	4	2.7	0.44±0.1	17.0±4.0	1.7±0.3	434±88	2.3±0.3	0.9±0.3	1.9±0.2	0.46±0.06
Narmada	1447#	99	11	0.21±0.1	905.2±18.0	0.8±0.2	353±78	24.6±0.1	0.2±0.1	16.6±1.6	0.68±0.00
Tapti	472#	65	-	0.11±0.1	441.1±148.0	1.0±0.2	716±112	18.1±7.7	0.8±0.1	10.6±1.7	0.62±0.17
Sabarmati	120#	22	-	0.11±0.1	145.2±29.2	1.2±0.1	288±45	5.6±0.1	0.6±0.1	10.7±0.1	0.41±0.01
Ir	349	26	7.6	0.13±0.1	138.1±17.0	1.2±0.3	537±65	8.8±2.2	0.1±0.1	5.3±1.1	0.61±0.04

- Data not available

represents data taken from *Kumar et al.*, 2005 and others taken from Dam authorities of respective river.

§ Dr. S.R. Shetye Personal communication.

*TA-Tidal Amplitude

¥P/C: Protein to Carbohydrate ratio

Table 1(b): Average and standard deviation (Avg±SD) of Salinity, SPM, Chl-*a*, DOC, TDCHO, DFAA, TDPRO and ratio of TDPRO:TDCHO (P/C) in the Indian estuaries during dry period.

Estuary	Salinity (psu)	SPM (mg/l)	Chl- <i>a</i> (mg/m ³)	DOC (µMC)	TCHO (µMC)	DFAA (µMC)	TPRO (µMC)	P/C [‡]
Rivers draining into bay of Bengal								
Haldia	4.72±0.9	58.2±35.2	4.9±6.2	283±56	5.9±1.9	2.3±0.7	6.3±2.2	2.20±1.20
Subarnalekha	4.25±0.6	29.8±6.9	5.2±3.1	391±66	4.8±2.4	2.4±0.8	5.1±0.9	1.17±0.31
Baitarani	18.32±3.8	56.4±13.4	3.2±1.2	400±84	3.3±0.7	2.5±1.2	7.0±1.2	2.23±0.61
Mahanadi	7.94±3.8	26.8±1.9	4.8±2.4	475±95	5.2±2.9	1.3±0.5	4.3±1.9	1.01±0.54
Rushikulya	20.45±5.9	15.1±6.3	2.5±2.5	450±87	7.5±0.6	1.5±1.1	5.7±1.2	0.75±0.11
Vamsadhara	12.42±11.1	21.6±7.9	2.2±0.7	566±75	7.4±0.5	1.6±0.3	4.8±0.9	0.65±0.13

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Nagavali	6.42±10.2	8.1±3.7	4.1±2.1	633±68	7.2±0.8	1.6±0.7	3.9±0.7	0.55±0.18
Godavari	20.81±5.9	50.6±10.2	3.1±2.5	316±45	5.9±1.0	3.5±2.1	4.5±2.5	0.26±0.05
Krishna	20.50±7.1	71.5±20.7	9.1±4.2	566±89	2.5±0.4	2.1±1.0	3.7±0.9	1.51±0.40
Penna	6.61±6.7	33.8±41.6	3.3±3.1	708±82	2.9±0.3	1.7±0.2	3.8±2.1	1.26±0.62
Ponnayaar	4.62±7.6	97.3±72.1	15.2±4.5	633±68	3.0±0.4	2.4±1.0	3.0±2.1	1.02±0.68
Vellar	7.52±8.9	65.4±45.2	28.1±5.3	558±54	3.1±0.8	3.±2.3	3.5±1.4	1.21±0.56
Cauvery	6.92±9.4	24.5±8.8	20.2±10.1	583±55	2.8±0.6	2.3±0.5	2.5±0.2	0.91±0.14
Ambalayaar	15.25±5.3	17.1±13.9	0.8±0.2		4.4±2.0	2.5±0.4	2.7±0.08	0.69±0.32
Vaigai	10.52±6.9	70.2±13.6	7.6±6.2	808±112	6.4±2.9	3.0±1.2	4.4±0.5	0.92±0.72
Rivers draining into Arabian Sea								
Kochi back waters	8.82±9.3	75.7±29.1	12.5±5.6	308±58	3.1±1.0	2.7±1.4	3.6±1.5	1.22±0.51
Chalakudi	14.61±11.9	16.9±16.2	2.2±1.4	216±49	2.5±1.1	2.4±0.9	3.3±1.3	1.44±0.72
Bharatapuzha	15.42±10.2	32.1±18.1	6.2±6.2	200±52	3.2±0.4	3.9±1.0	3.3±0.8	1.03±0.18
Netravathi	8.03±12.5	28.5±24.7	4.3±2.5	250±48	2.2±0.6	3.2±1.3	3.5±1.1	1.63±0.54
Kali	14.11±9.5	63.0±3.65	5.1±6.5	225±59	2.3±0.9	2.5±1.5	3.6±1.7	1.55±0.32
Zuari	21.76±11.6	50.7±16.5	3.4±3.3	291±85	3.5±0.6	2.6±0.6	7.3±1.8	2.22±0.85
Mandovi	22.64±7.3	37.9±16.5	3.6±3.2	225±45	3.9±0.9	1.7±0.4	7.9±1.1	2.10±0.62
Narmada	3.75±8.4	209.2±56.3	1.2±2.0	683±75	8.9±0.8	3.6±1.7	3.7±1.2	1.42±0.8
Tapti	9.01±15.2	417.7±25.3	2.1±1.2	766±85	9.0±1.9	3.2±2.3	2.6±2.9	1.35±0.8
Sabarmathi	26.82±2.3	22.2±16.2	11.6±1.9	915±98	9.2±3.8	3.3±2.1	6.2±2.1	0.79±0.56
Mahisagar	25.12±2.5	27.5±21.3	10.8±2.3	883±88	9.5±3.3	2.1±1.0	3.8±1.3	0.41±0.16

³P/C: Protein to Carbohydrate ratio

Table 2: Rank Correlation matrix (Spearman's; r) of different properties in the Indian estuaries (#, ## and ### indicates p<0.001, 0.01 and 0.05 respectively. The number in the bracket denotes degrees of freedom.

Parameters	Major Estuaries		Medium Estuaries		Minor Estuaries	
	Wet Period	Dry Period	Wet Period	Dry Period	Wet Period	Dry Period
Discharge vs Salinity	-0.86(8) [#]	ND	-0.55(9) ^{##}	ND	-0.65(7) ^{###}	ND
Discharge vs SPM	+0.89(8) [#]	ND	+0.52(9) ^{##}	ND	+0.06(7)	ND
Discharge vs Chl- <i>a</i>	-0.75(8) [#]	ND	-0.35(9)	ND	+0.15(7)	ND
Salinity vs SPM	-0.56(19) ^{###}	+0.6(74) [#]	+0.23(27)	+0.06(86)	+0.33(21)	+0.2(66)
Salinity vs Chl- <i>a</i>	+0.21(24)	+0.4(66) ^{###}	+0.52(24) ^{##}	+0.05(62)	+0.17(18)	+0.25(65)
SPM vs Chl- <i>a</i>	+0.35(24)	+0.3(52)	+0.01(27)	+0.08(71)	+0.07(14)	+0.41(70) ^{###}
TDCHO vs Discharge	+0.89(8) [#]	ND	+0.45(9) ^{###}	ND	+0.06(7)	ND
TDCHO vs Salinity	-0.56(19) ^{###}	+0.78(80) [#]	+0.19(27)	+0.5(90) [#]	+0.21(21)	+0.82(70) [#]
TDCHO vs SPM	+0.91(24) [#]	+0.62(74) [#]	+0.68(27) [#]	-0.01(50)	+0.01(21)	-0.24(70)
TDCHO vs Chl- <i>a</i>	+0.32(24)	+0.22(52)	+0.1(27)	+0.32(69) ^{###}	+0.71(21) [#]	+0.59(63) ^{##}
TDCHO vs Zoo Plankton	+0.05(24)	+0.86(30) [#]	+0.29(27)	+0.50(30) [#]	ND	ND
TDCHO vs pCO ₂	-0.48(18) ^{###}	+0.08(56)	+0.2(27)	+0.18(62)	+0.34(21) ^{###}	+0.22(64)
TDCHO vs TVC	-0.61(22) ^{##}	ND	-0.5(18) ^{###}	ND	-0.3(12) ^{###}	ND
DFAA vs Discharge	+0.52(8) ^{###}	ND	-0.52(9) ^{##}	ND	+0.02(8)	ND
DFAA vs Salinity	-0.48(17) ^{###}	+0.5(69) ^{##}	-0.12(27)	+0.52(85) [#]	+0.21(21)	+0.84(70) [#]
DFAA vs SPM	+0.41(19) ^{###}	+0.53(71) ^{##}	+0.42(19) ^{###}	+0.1(53)	+0.1(21)	+0.15(65)
DFAA vs Chl- <i>a</i>	+0.24(24)	+0.52(72) ^{##}	+0.07(27)	+0.38(75) ^{###}	+0.91(21) [#]	+0.62(65) ^{##}

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DFAA vs PCO2	-0.62(24) ^{##}	-0.29(49)	-0.39(14) ^{###}	-0.74(86) [#]	-0.8(21) [#]	-0.55(62) ^{##}
DFAA vs Zoo Plankton	+0.16(24)	+0.01(32)	+0.79(27) [#]	+0.24(22)	ND	ND
DFAA vs TVC	-0.68(24) ^{##}	ND	-0.58(26) ^{##}	ND	-0.49(21) ^{##}	ND
DFAA vs TDPRO	-0.59(20) ^{###}	+0.26(75)	-0.42(19) ^{###}	-0.72(90) [#]	-0.65(21) ^{###}	-0.85(70) [#]
DFAA vs Bacillariophyceae	ND	ND	+0.53(21) ^{###}	ND	ND	ND
DFAA vs Ammonium	+0.71(24) [#]	+0.25(52)	+0.69(27) [#]	+0.19(55)	+0.35(21) ^{###}	ND
TDPRO vs Discharge	+0.85(8) [#]	ND	+0.49(9) ^{###}	ND	+0.12(7)	ND
TDPRO vs Salinity	-0.52(18) ^{###}	+0.38(63) ^{###}	-0.38(15) ^{###}	+0.63(90) [#]	+0.82(21) [#]	+0.72(70) [#]
TDPRO vs SPM	+0.62(24) ^{##}	+0.66(80) [#]	+0.44(20) ^{###}	+0.41(82) ^{##}	+0.54(18) ^{###}	+0.28(61)
TDPRO vs Chl- <i>a</i>	+0.42(19) ^{###}	+0.41(64) ^{###}	+0.65(27) [#]	+0.35(72) ^{###}	+0.92(21) [#]	+0.6(65) ^{##}
TDPRO vs Zoo Plankton	+0.23(24)	+0.98(32) [#]	+0.88(27) [#]	+0.99(27) [#]	ND	ND
TDPRO vs pCO2	-0.63(24) ^{##}	-0.31(62)	-0.75(27) [#]	-0.33(69) ^{###}	-0.4(21) ^{##}	-0.67(70) [#]
TDPRO vs TVC	-0.55(18) ^{###}	ND	-0.41(18) ^{###}	ND	-0.52(19) ^{###}	ND
TVC vs Ammonium	+0.61(24) ^{##}	+0.22(55)	+0.58(27) ^{##}	+0.20(53)	+0.51(18) ^{###}	+0.11(50)

ND-nodata

-: No significant correlation

Table 3: Mean concentrations of TDCHO, DFAA, DOC and contribution of bioavailable compounds to DOC in the world estuaries.

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Estuary	TDCHO (μM)	DFAA (μM)	DOC (μM)	Contribution of TDCHO to DOC (%)	Contribution of DFAA to DOC (%)	Reference
Delaware Estuary	16.7	16.7	355.7	4.7	0.1	Coffin et al., 1989; Witter and Luther, 2002
N. Adriatic Sea	47.5	47.5	250	19	12.8	Pettine et al., 2001; Pettine et al., 2007
Lena River	21.9	5	612	3.6	0.6	Lara et al., 1998
Siberian River	37	0.9	346	0.4	0.3	Lara et al., 1998; Shen et al., 2012
Mississippi River	75.5	0.3	307	24.6	0.1	Shen et al., 2012; Wang et al., 2013; Duan and Bianchi, 2007
Pearl River Estuary	20.3	1.0	307	24.6	0.5	He et al., 2010; Wang et al., 2013; Present Study
Major Estuaries	10.9	1.5	426.1	3.1	0.5	Duan and Bianchi, 2007
Medium Estuaries	7.4	0.3	32.6	3.1	0.5	He et al., 2010; Present Study
Minor Estuaries	6.9	0.1	1.5	2.5	0.3	Present Study
Major Estuaries	19	1.9	407.3	4	1.5	Present Study
Medium Estuaries	7.4	1.7	352			
Minor Estuaries	6.9	1	482			
Major Estuaries	19	1.9	407.3			
Medium Estuaries	7.4	1.7	352			
Minor Estuaries	6.9	1	482			
Major Estuaries	19	1.9	407.3			
Medium Estuaries	7.4	1.7	352			
Minor Estuaries	6.9	1	482			

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Legend to Figures:

Figure 1: Map showing estuaries sampled in this study. Black line displays main river flow. The rivers with bigger, italic and smaller font of river names denote major, medium and minor rivers respectively.

Figure 2: Mean of a) Salinity (psu), b) SPM (mg/l), c) Chl-*a* (mg/m³), d) DOC (μMC) e) TDCHO (μMC), f) DFAA (μMC), g) TDPRO (μMC) in the major, medium and minor estuaries during wet and dry periods. The standard deviation of variability is given as a error bar.

Figure 3: Principal component analysis of different controlling factors in the Indian estuaries during wet and dry periods: a), b) and c) represents wet period and d), e) and f) represents dry period. Since no discharge occurs, we did not include discharge during dry period.

Figure 4: Dendrogram showing similarity of total measured bioavailable organic compounds in the Indian estuaries during a) wet period and b) dry period.

Figure 1:

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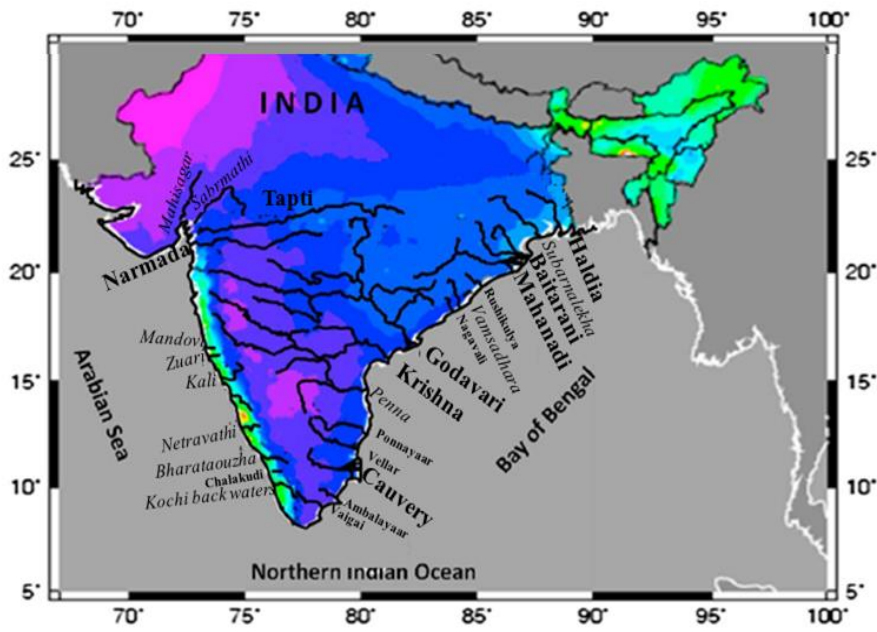
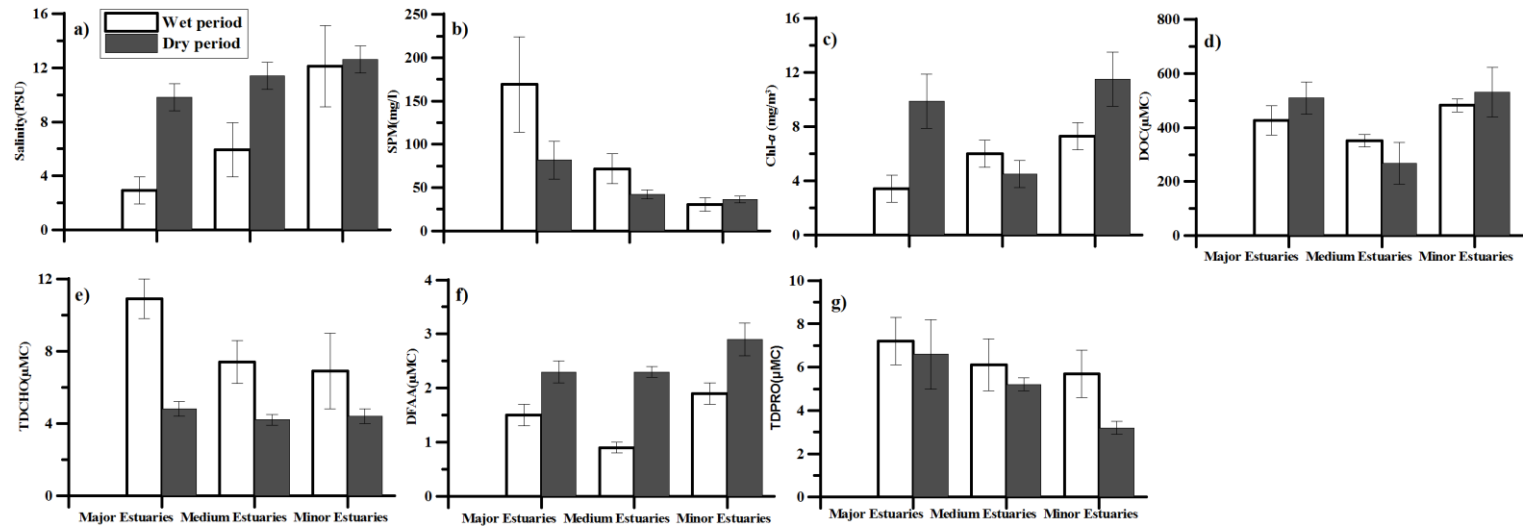


Figure 2:



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Figure 3:

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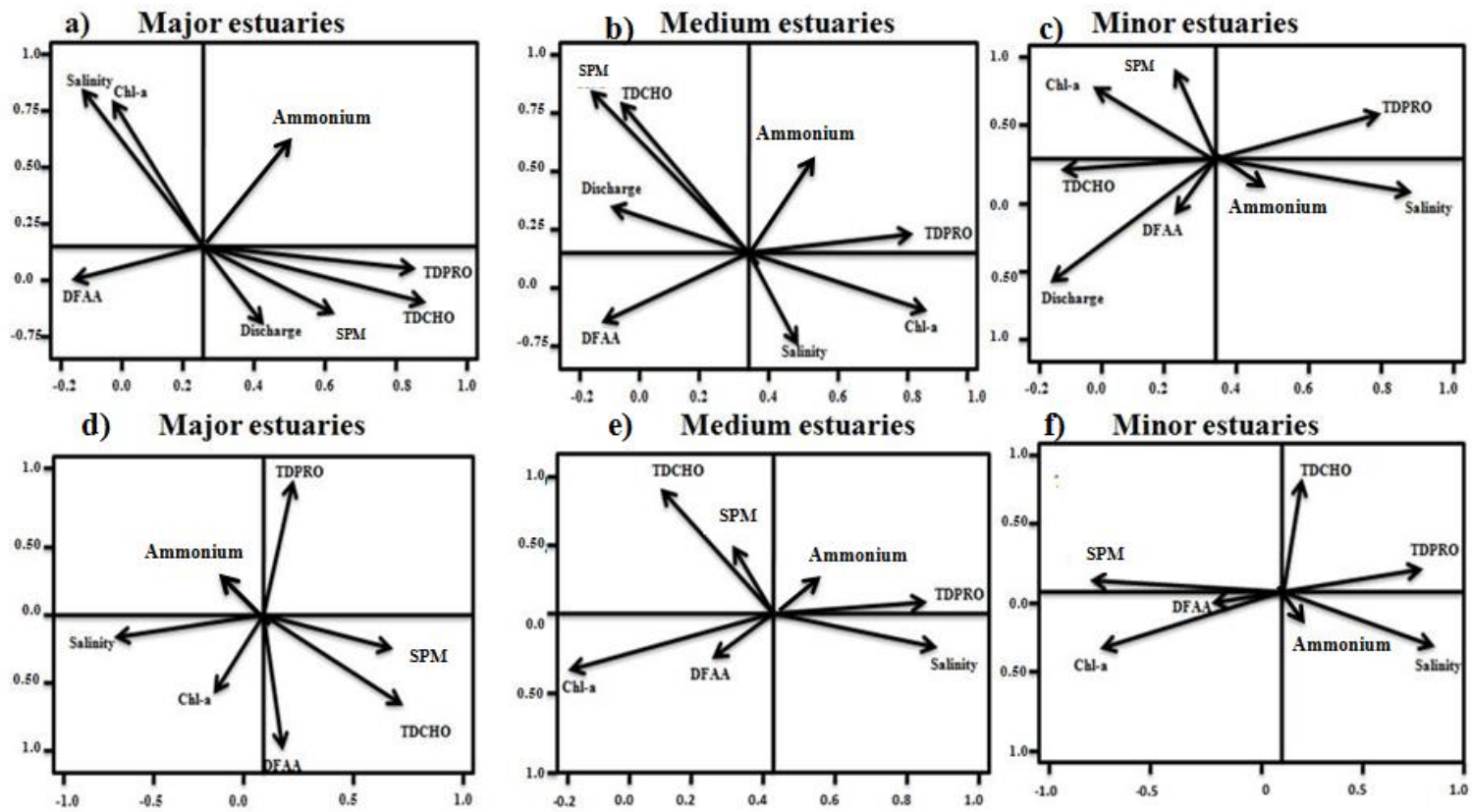
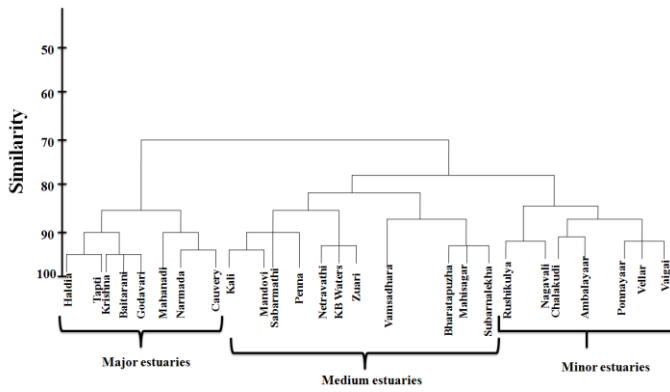


Figure 4:

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a)



b)

