scientific reports

OPEN

Role of synthetic fertilizers on stable isotope ratios of particulate organic matter in the Godavari River

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In this study, we examined the major sources of particulate organic matter (POM) in the Godavari River during high flow and low flow periods, to understand the impact of excess nitrogen (N)-fertilizers used in agricultural fields. $\delta^{13}C$ of particulate organic carbon (POC) and $\delta^{15}N$ of particulate nitrogen (PN), elemental carbon (C) to N ratio and POC:Chl-a ratios indicated that *in-situ* sources predominantly contributed (~60%) during low flow period, whereas, terrestrial sources largely contributed during high flow period (75–80%). This is attributed to prevailing conducive conditions such as low flow, better light availability due to low suspended matter and availability of nutrients for phytoplankton growth during former period, whereas increased transport of particulate and dissolved materials from land to river during the latter period. $\delta^{15}N_{PN}$ during low flow (7.4 ± 2.9‰) and high flow (9.4 ± 2.1‰) periods demonstrate that contribution of POM produced from N-fertilizers ($\delta^{15}N_{PN}$: 0 ± 1‰) is not significant, rather than hitherto hypothesized. It could be due to seepage of excess N-fertilizers used in agricultural fields into groundwaters rather than transporting to rivers and/or transformation to another from through nitrification/denitrification processes within soils.

Keywords Stable isotopes, Organic carbon, Nitrogen, Particulate organic matter, Freshwater algae, Godavari

Rivers are the major means of transport of dissolved and particulate material from land to sea *via* estuaries[1,2]. Rivers carry significant amounts of particulate organic matter (~150 to 200 Tg yr^{-1})[2–4] and suspended sediments[5] along with dissolved inorganic nutrients[6,7], dissolved organic matter[8,9] and various types of pollutants[10,11] to the global ocean. Riverine export of land-driven nutrients in large quantities, mainly due to anthropogenic activities, such as the use of excess synthetic fertilizers in agricultural and aquacultural practices, domestic and industrial sewage, often causes 'eutrophication', in estuaries and coastal waters[12,13]. Formation of eutrophication ultimately leads to the development of 'dead zones' in coastal waters. Maure et al.[14] reported that about 1.15 million km^2 area of global coastal waters (depth: <200m) are eutrophic potential.

India is the second largest consumer of synthetic fertilizers in the world, with an annual consumption of 26.5 Tg, after China (48.8 Tg), with a global share of 15.3% in N-fertilizer consumption[15]. The most commonly used N, phosphorus (P) and potassium (K) fertilizers in agriculture practices in India for restoration of soil nutrients and increasing the crop yield are Urea (46% N), Diammonium phosphate (DAP; 46% P and 18% N), Muriate of Potash (60% K) and other complex (NPK) fertilizers in different ratios such as 10:26:26, 19:19:19 and 12:32:16 etc. Excess fertilizers used in agriculture and aquaculture activities are expected to reach rivers, estuaries and coastal oceans. Impact of these fertilizer nutrients on ecosystem in Indian rivers, estuaries and coastal waters remain poorly understood. Occurrence of oxygen minimum zone (OMZ) due to seasonal upwelling along west coast of India is reported to be intensified, and leads to eutrophication due to transport of fertilizer nutrients to coastal ocean[16]. Expansion of OMZ (both horizontally and vertically) in the Arabian Sea was attributed to increased organic matter loading to deeper depths. This increase of organic matter could be due to either wind-driven coastal upwelling or supply of anthropogenic nutrients from coastal cities along west coast of India[17]. Bristow et al.[18] reported that OMZ in the Bay of Bengal is at its tipping point, and it will become dead zone if primary production in the overlying water column increases by transport of anthropogenic nutrients and/or intensification of summer monsoon. Although many studies attributed various biogeochemical processes in the Arabian Sea and Bay of Bengal to anthropogenic nutrients (agricultural, industrial and domestic sewage) from

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the Indian subcontinent, quantitative studies on anthropogenic nutrients budget and identification of nutrient sources are very limited. Krishna et al.[7] reported that Indian monsoonal rivers annually export only 0.22 ± 0.05 Tg (1Tg = 10^{12} g) of dissolved inorganic nitrogenous nutrients to the northern Indian Ocean, and such a low fluxes were attributed to efficient (~ 91%) elimination/retention of nutrients before reaching the coastal ocean.

In this study, we investigated the major sources of particulate organic carbon (POC) and particulate nitrogen (PN) in the Godavari river from the place of its origin (Nasik) to the place at which it confluences with the Bay of Bengal (Yanam), covering a stretch of ~1600 km, during both low flow and high flow periods. The Godavari is the largest monsoonal river that exports highest amount of POC ($2.81*10^6$ tons yr^{-1}), PN ($0.29*10^6$ tons yr^{-1}), DOC ($0.45*10^6$ tons yr^{-1}), DON ($0.085*10^6$ tons yr^{-1}) and suspended load (~$170x10^6$ tons)[8,19,20] among the monsoonal rivers in India. It accounts for ~1.7% of the total POC export by major rivers in the world[3].

Elemental ratios of carbon to nitrogen (C:N ratio), POC:Chl-a ratios and stable isotopic signatures of POC ($\delta^{13}C_{POC}$) and PN ($\delta^{15}N_{PN}$) are well established tracers to delineate the major sources of organic matter in rivers[21,23–25], estuaries[26], coastal[27] and open ocean regions[28,29]. However, a caution is required while using these tracers for identification of POM sources because decomposition of POM by heterotrophic organisms modifies isotopic signatures in the residual POM[30–32]. The $\delta^{13}C_{POC}$ values indicate source of inorganic carbon used for production of POC, and therefore have distinctly different $\delta^{13}C_{POC}$ values for freshwater phytoplankton (-33.2‰ to -27.5‰)[33] and terrestrial POC (-28‰ to -26‰)[32]. Similarly, $\delta^{15}N_{PN}$ depends on $\delta^{15}N$ of nitrogenous nutrients used for production of PN. However, various internal processes such as nitrification, denitrification, N_2 fixation influence $\delta^{15}N_{PN}$ values due to preferential uptake of lighter isotope (^{14}N) over heavier isotope (^{15}N) in these processes[34,35]. Nutrients derived from diverse sources have distinctly different $\delta^{15}N$ values. For instance, PN produced from sewage nutrients has relatively enriched $\delta^{15}N$ (~14±4‰)[36] compared to PN supported by synthetic N-fertilizers (0±1‰)[37–39] and N_2 fixation (-2‰ to 1‰)[40,41]. The $\delta^{15}N_{PN}$ values are thus indicate nutrient sources used for primary production. The main objectives of our study are (i) to investigate the major sources of POC and PN, and their seasonal variability and (ii) to understand the impact of synthetic N-fertilizers on POC and PN in the Godavari River.

Study region and sample collection

Study region

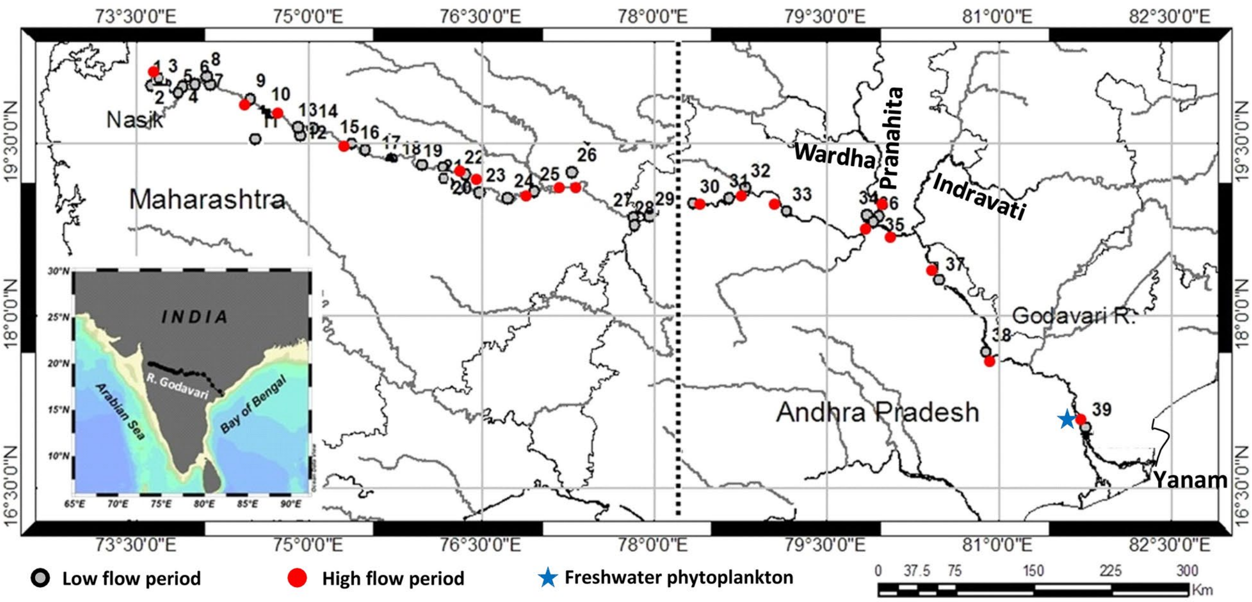
Godavari River is the 3rd largest river (after Ganges and Brahmaputra) in India that originates in the Western Ghats at Triambak near Nasik City at an altitude of ca. 1600 m. It flows eastward for about 1600 km across the Indian peninsula before it drains into the Bay of Bengal. The Godavari River discharges ~ 110 km^3 yr^{-1} of fresh water and 170 million tons yr^{-1} of suspended sediment to the Bay of Bengal[3,20]. The Godavari River basin extends from 73°26'E to 83°07'E and from 16°16'N to 22°36' N (Fig. 1), with an area of ~ 3.1×10^5 km^2 [19]. The river drains mainly Deccan Trap basalts and metamorphic rocks (Pre-Cambrian) in upper and lower reaches of the river, respectively. Due to strong seasonal variability in rainfall pattern over the catchment, with > 80% of the annual rainfall during SW monsoon, the high flow of water in the river confine only to SW monsoon season (Fig. 2). Lower basin of the river receives intense rainfall (1600 to > 3200 mm yr^{-1}) than upper basin (< 800 to 1200 mm yr^{-1}) within SW monsoon period[42]. Semi-arid and monsoonal climate prevails over the basin. Maximum and minimum temperatures are higher in lower basin than in upper basin[43]. Dominance of vegetation in the Godavari basin changes from grassland/cropland in upper basin to forest and shrub in lower basin of the river. Along the entire stretch, about 25 tributaries join the Godavari River and create an extensive delta on east coast of India[44]. A total of 921 dams of different sizes were constructed so far on the Godavari River and its tributaries mostly for irrigation purposes, and only a few for hydro-electric power generation (water resources information system of India, http://india-wris.nrsc.gov.in). Population density in the basin ranges from as low as 25–50 persons km^{-2} to 500–1000 persons km^{-2}, with a mean value of 194 persons km^{-2}.[45].

Sample collection

Surface water samples were collected using 5L Niskin samplers at 39 locations along entire stretch (~ 1600 km) of the Godavari River from its headland waters to mouth (Fig. 1a) during low flow (non-monsoon) period (November–December 2011). However, samples were collected only at 18 locations along entire stretch of the river during high flow (southwest monsoon) period (Fig. 1a) because many of the locations were not accessible for sample collection during this period. Land use and land cover map of the Godavari River is shown in Fig. 1b. Surface water samples were collected for dissolved inorganic nutrients, dissolved oxygen (DO), chlorophyll-a (Chl-*a*), total suspended matter (TSM), POC and PN. Surface water samples were collected in middle of the river-channel using mechanized boats to minimize contamination from river banks. Samples for freshwater phytoplankton were collected in the lower reaches of the river (Fig. 1a). Different parts (leaf, part of stem and part of root) of the abundant C_3 plants (rice, cotton, turmeric and wheat) and C_4 plants (sugarcane, maize, bajra and sorghum) and surface soils (0-10 cm) were collected in drainage basin of the river. Location details, $\delta^{13}C$ and $\delta^{15}N$ values of soils, C_3 and C_4 plants collected in drainage basin of the river were given elsewhere[46]. Rainfall and temperature data in the Godavari basin was taken from Central Water Commission, Ministry of Earth Sciences, Government of India[43]. Study region was divided into two parts for discussion based on geological characteristics and spatial variability in rainfall intensity and environmental conditions of the river basin. Upper reaches of the river extend up to ~ 1100 km from origin of the river, and lower reaches extend from ~ 1100 km to mouth of the river.

Methodology

About 500 ml of water sample was filtered through a non-combusted GF/F filter (nominal pore size: 0.7 µm; Whatman) under vacuum, and the material retained on filter was extracted into N,N, dimethyl formamide



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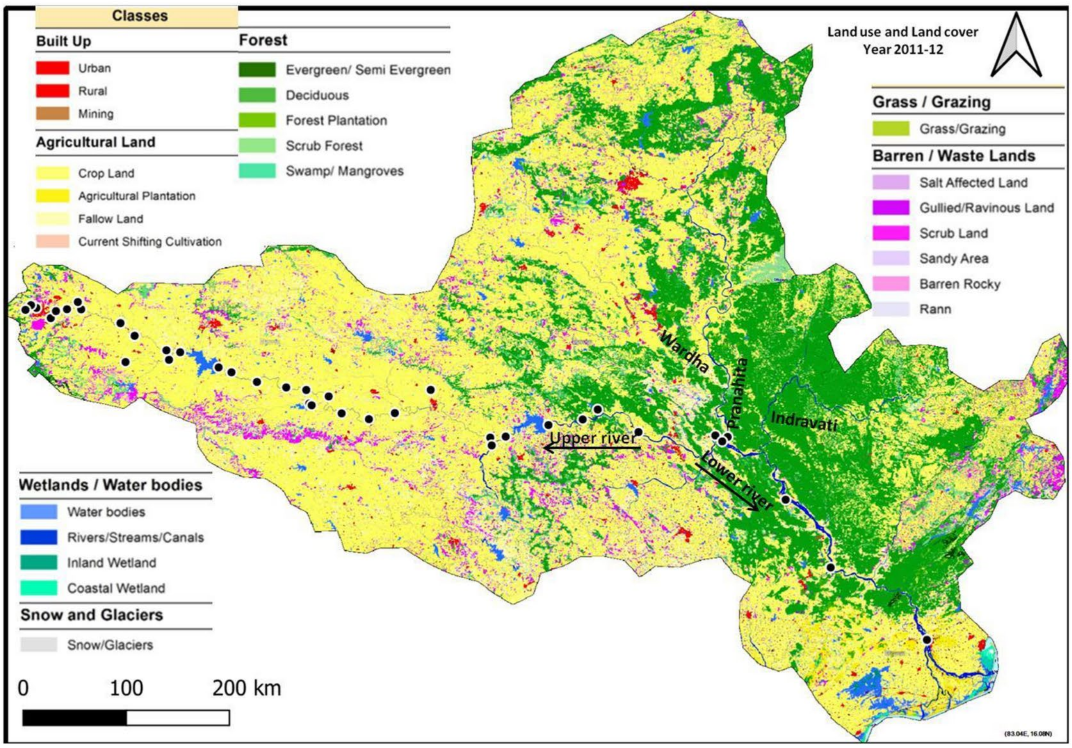

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Figure. 1. (**a**)Map showing Godavari River from its origin at Nasik to its mouth at Yanam. Sampling locations during high flow and low flow periods were shown by filled circles of red and grey colour, respectively. India map with Godavari River is shown in inset. Station at which freshwater phytoplankton collected is shown by cyan colour star. Major tributaries, Wardha, Pranahita and Indravati in the lower reaches of the river are also shown. (**b**) Land use and land cover map of the Godavari River basin. Sampling stations along the course of the river are marked by filled (blue colour) circles. Major tributaries, Wardha, Pranahita and Indravati, in lower reaches of the river are also shown.

(DMF). Concentration of Chl-*a* in the extract was measured using spectrofluorophotometer (Carry Eclipse, Varian, USA) following Suzuki and Ishimaru[47]. Analytical precision for the method, expressed as standard deviation, was ± 4%. DO was determined by Winkler's titration method of Carritt and Carpenter[48] using potentiometric end point detection (Metrohm, Switzerland) at a temporary field laboratory on the same day

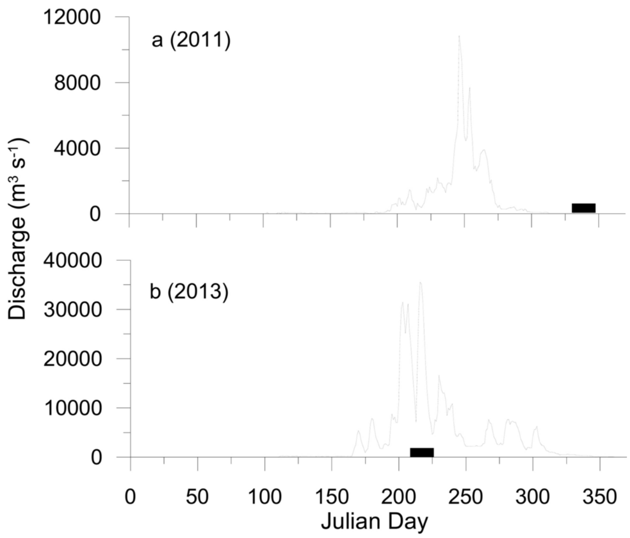

Figure. 2. Freshwater discharge from the Godavari River (**a**) during 2011 and (**b**) during 2013. Rectangular boxes filled with black colour indicate the sampling period. Gray colour shaded area represents the southwest (SW) monsoon (June – September) period.

of collection. Analytical precision, in terms of standard deviation, was ± 0.07%. Total suspended matter (TSM) was determined by the weight of material retained on filter (0.22 µm, polycarbonate) after filtering 300–500 ml of water sample followed by drying in an oven (50 °C, 48 h). Dissolved inorganic nutrients were analysed by the standard colorimetric method following Grashoff et al.[49] using an auto analyzer (SAN^{++}, Skalar, The Netherlands). Based on repeated analysis of standards and samples, precision of the method was found to be ± 0.02, 0.02, 0.01 and 0.02 µM for ammonium, nitrite + nitrate, phosphate and silicate, respectively.

Content and isotopes of POC and PN

For POC analysis, water sample (~ 500 ml) was passed through a pre-combusted (300 °C; 6 h) GF/F filter (nominal pore size: 0.7 µM; diameter: 47 mm; Whatman) under vacuum at a field laboratory, and preserved in ice for further processing at shore laboratory. After drying at 60 °C (24 h) in an oven at institute's laboratory, part of the filter was used directly for determination of concentration and isotopic composition of PN using an elemental analyzer (Flash EA, Thermo) coupled to isotope ratio mass spectrometer (IRMS, Delta V Plus, Thermo Electron, Germany) via Conflo IV. Part of the filters was acid fumigated to remove traces of inorganic carbon, and analyzed for concentrations and stable isotope ratios of POC using EA-IRMS instrument. The international atomic energy agency (IAEA) standards and laboratory standards such as glutamic acid, alanine, organic analytical standard (OAS) were used for calibration. Long term precision of the instrument was ± 0.2‰ for both C and N isotopes. Concentrations of POC and PON were reported in mg L^{-1} while their stable isotope ratios were expressed in per mil deviation from VPDB (Vienna Pee Dee Beleminte) for carbon, and atmospheric air for nitrogen as given below.

$$\delta^{13}C\left(or\delta^{15}N\right)=\left[\frac{\mathrm{X_{samp}}-\mathrm{X_{std}}}{\mathrm{X_{std}}}\right]\text{ x 1000?}$$

where, X_{samp} stands for $^{13}C/^{12}C$ and $^{15}N/^{14}N$ of a sample for carbon and nitrogen, respectively. The X_{std} represents $^{13}C/^{12}C$ and $^{15}N/^{14}N$ of standard, i. e., VPDB and atmospheric air, respectively. Measurement of $\delta^{13}C$, $\delta^{15}N$ and C:N ratios of freshwater phytoplankton (group level) was described elsewhere[46]. Software program "Grapher" (version 5) was used for graphical representation of data. Two tailed homoscedastic t-test was used to examine statistical significance of difference for various parameters between upper and lower reaches of the river.

Quantification of proportional contributions from major sources

Bayesian isotope mixing model SIAR (Stable Isotope Analysis in R) was used to estimate proportional contributions of OM from major sources to POM in the Godavari River. SIAR is an open source R package and available at Comprehensive R Archive Network (CRAN) site (http://cran.r-project.org). SIAR model uses Markov Chain Monte Carlo (MCMC) method for simulating the probable values for fitting algorithms[50,51]. The model includes covariance structure that defines the ability of model to separate various sources through the diagnostic matrix plot. Actual correlation coefficient of posterior distributions in the matrix plot describes the closeness of different sources. Lower correlation coefficient denotes well isolation of contributions from different sources, while the negative correlation indicates end-member values of possible sources are close to each other or overlapping[51]. Inclusion of the residual error term is an additional advantage of this model compared to the other Bayesian mixing models[51]. The model has already been used for quantification of proportional contributions of OM from major sources to POM in estuaries[46,52] and coastal systems[53,54]. Since 'SIAR' is a dual isotope mixing model that uses both $\delta^{13}C$ and $\delta^{15}N$, it gives a better quantification of source apportionment of OM than single isotope based models. Selection of end member values is crucial for isotope mixing models because output of the model mainly depends on $\delta^{13}C$ and $\delta^{15}N$ values of end members.

Measured $\delta^{13}C$ and $\delta^{15}N$ values of microscopically separated freshwater phytoplankton groups collected from lower reaches of the river (-31.2 ± 0.6‰ and 6.2 ± 0.5‰, respectively) were used as freshwater phytoplankton end member values. Mean $\delta^{13}C$ and $\delta^{15}N$ values of abundant terrestrial C_3 plants (rice, cotton, turmeric and wheat) (-25.9 ± 1.2‰ and 5.1 ± 2.1‰, respectively) and C_4 plants (sugarcane, maize, bajra and sorghum) (-13.1 ± 1.2‰ and 4.4 ± 2.1‰, respectively), and surface soils (-19.1 ± 2.4 and 10.1 ± 2.7‰, respectively) in the Godavari basin[46] were used as end members for terrestrial C_3 and C_4 plants and soil derived OM, respectively. $\delta^{15}N$ of sewage is typically enriched, and ranges between 12‰ to 25‰[55,56]. Mean $\delta^{13}C$ and $\delta^{15}N$ values of the sewage collected from Bombay (-31.5 ± 1.0‰ and 15.8 ± 1.6‰, respectively)[57], the major city near upper reaches of the river were used as sewage end member values. Similar $\delta^{15}N$ values are also reported for sewage from Visakhapatnam City near the lower reaches of the river (~ 14 ± 4‰)[36].

Results

Seasonal variability (low flow and high flow periods)

Dissolved inorganic nutrients such as ammonium, nitrite + nitrate and silicate concentrations were higher during high flow period (3.7 ± 5.1, 53.2 ± 20.9 and 49.7 ± 14.5 µM, respectively) compared to low flow period (0.4 ± 0.2, 15.5 ± 18.6, and 40.6 ± 11.7 µM, respectively) (Figs. 3a&b). However, phosphate concentrations were nearly equal ($p = 0.72$) during low flow (12.0 ± 7.6 µM) and high flow (12.3 ± 8.2 µM) periods (Figs. 3a&b; Table 1). Chl-*a* distribution was relatively less heterogeneous during low flow period (mean 11 ± 6 mg m^{-3}) compared to high flow period (20 ± 19 mg m^{-3}, Table 1). TSM concentrations varied between 2.0 and 38.6 mg L^{-1} (except higher concentration of 72 mg L^{-1}) during low flow period, whereas it varied widely between 1 and 186 mg L^{-1} during high flow period (Table 1). Percent of organic carbon in TSM (%OC) was higher ($p = 0.04$) during low flow period (mean 11.5 ± 8.4%, range: 0.9–35.7%) compared to high flow period (6.3 ± 6.3% and 0.5–20.3%, respectively) (Figs. 4a&b).

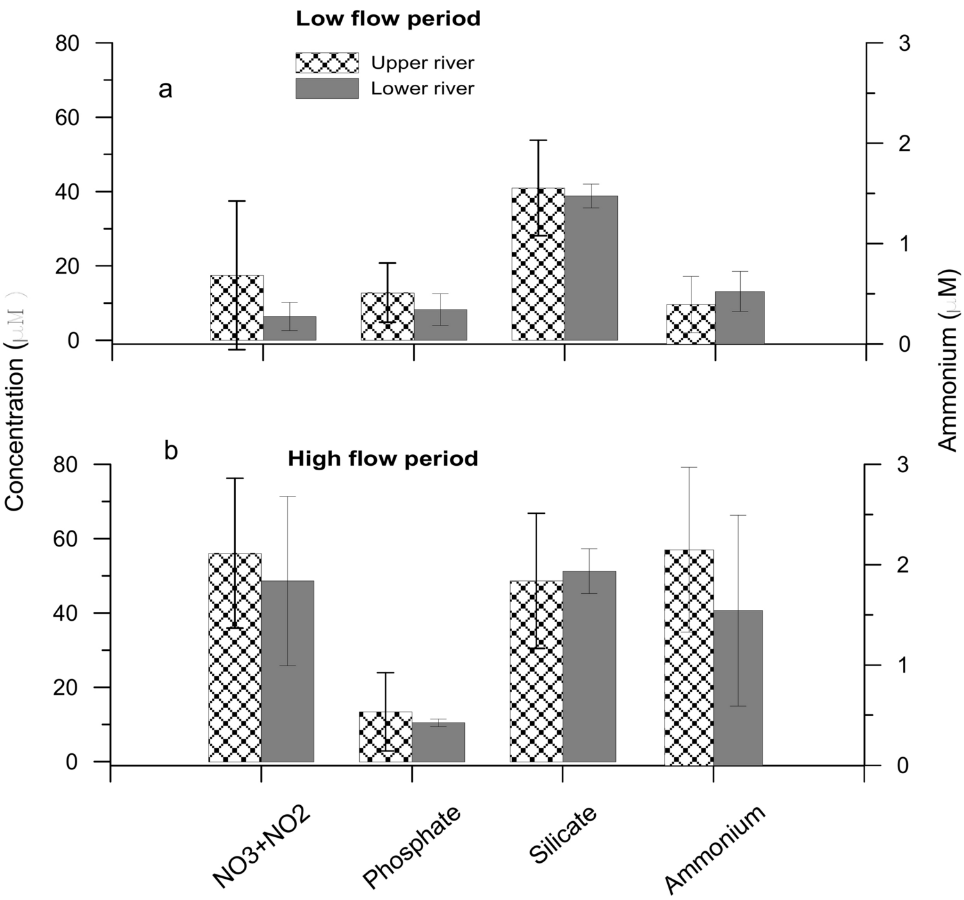

Figure. 3. Mean concentrations of dissolved inorganic nutrients such as nitrite+nitrate (NO_2^-+NO_3^-, µM), phosphate (µM), silicate (µM) and ammonium (µM) in upper and lower reaches of the Godavari River during (**a**) low flow period and (**b**) high flow period. Concentrations of ammonium were shown on right side y-axis while the other nutrients were shown on left side y-axis.

Parameter	Low flow period		High flow period	
	Range	*Mean (± SD)*	*Range*	*Mean(± SD)*
Ammonium (μM)	n.d – 5.3	0.4 ± 0.2	0.7–22.1	3.7 ± 5.1
Nitrate + Nitrite (μM)	1.9–71.6	15.5 ± 18.6	12.5–83.6	53.2 ± 20.9
Phosphate (μM)	2.9–33.0	12.0 ± 7.6	5.2–42.8	12.3 ± 8.2
Silicate (μM)	5.8–88.9	40.6 ± 11.7	24.1–74.4	49.7 ± 14.5
Chlorophyll-a (mg m^{-3})	1.7–24.3	10.4 ± 6.3	1.4–46.9	20.6 ± 19.1
TSM (mg l^{-1})	2.0–72.0	12.4 ± 14.2	1–186	59 ± 65
%OC in TSM	0.9–35.7	11.5 ± 8.4	0.5–20.3	6.3 ± 6.3
POC (mg l^{-1})	0.4–2.1	0.8 ± 0.3	0.2–1.8	0.9 ± 0.5
PN (mg l^{-1})	0.05–0.35	0.1 ± 0.05	0.01–0.11	0.06 ± 0.03
POC: Chl-*a* ratio	32–275	106 ± 65	13–677	155 ± 225
Elemental C:N ratio	3–22	9 ± 4	10–29	18 ± 4
$\delta^{13}C_{POC}$ (‰)	-32.8 to -20.7	-28.9 ± 2.6	-30.9 to -22.8	-25.8 ± 2.6
$\delta^{15}N_{PN}$ (‰)	1.2–15.0	7.4 ± 2.9	5.7–13.1	9.4 ± 2.1

Table 1. Range and mean (± SD) values of dissolved inorganic nutrients, ammonium, nitrite + nitrate, phosphate and silicate, phytoplankton biomass (chlorophyll-a), total suspended matter (TSM), percent organic carbon (%OC), particulate organic carbon (POC), particulate nitrogen (PN), ratios of POC:Chl-a and elemental C:N and stabile isotope ratios of carbon ($\delta^{13}C_{POC}$) and nitrogen ($\delta^{15}N_{PN}$) during low flow and high flow periods.

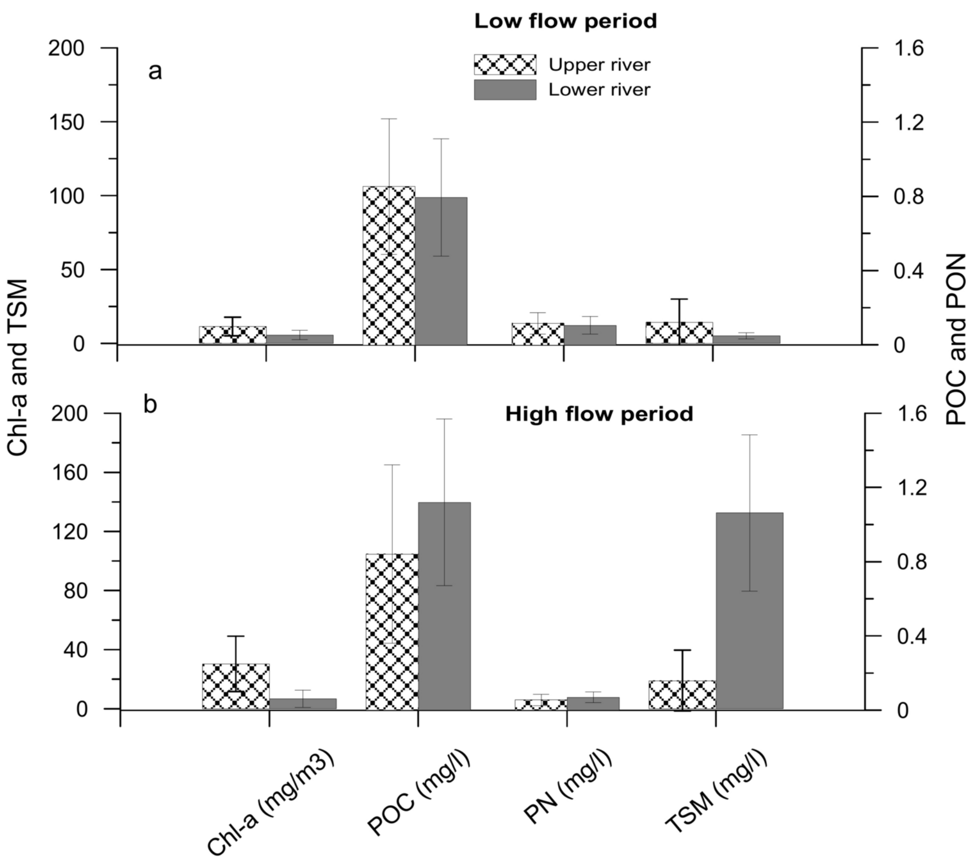

Figure. 4. Mean concentrations of Chlorophyll-a (Chl-a, mg m^{-3}), particulate organic carbon (POC, mg L^{-1}), particulate nitrogen (PN, mg L^{-1}) and total suspended mater (TSM, mg L^{-1}) in upper and lower reaches of the Godavari River during (**a**) low flow period and (**b**) high flow period. Concentrations of POC and PON were shown on the right side y-axis and the remaining parameters were shown on the left side y-axis.

POC concentrations ranged from 0.4—2.1 mg L^{-1} and 0.2 – 1.8 mg L^{-1} during low flow and high flow periods, respectively (Table 1). Concentrations of POC found in this study are similar with those reported earlier in the Godavari River[19,22]. Relatively higher range of PN concentrations were found during low flow period (0.05 – 0.35 mg L^{-1}) compared to high flow period (0.01 – 0.11 mg L^{-1}). Elemental C:N ratios ranged from 3 to 22 and 10 to 29 during low flow and high flow periods, respectively (Table 1), with lower mean ratios during former than latter period (Figs. 5a&b) (t-test; $p<0.001$). POC:Chl-a ratio, an indicator of contribution from phytoplankton biomass to total POC, varied from 32 to 275 during low flow period, whereas it varied widely between 13 and 677 during high flow period (Table 1). The $\delta^{13}C_{POC}$ varied from -32.8‰ to -20.7‰ and from -30.9‰ to -22.8‰ during low flow and high flow periods, respectively (Table 1). Relatively depleted mean $\delta^{13}C_{POC}$ values were observed during low flow (-28.9 ± 2.6‰) compared to high flow period (-25.8 ± 2.6‰) (t-test; $p<0.001$). The $\delta^{13}C_{POC}$ values observed in this study during low flow (mean -28.9 ± 2.6‰) and high flow (-25.8 ± 2.6‰) periods are similar to those reported earlier in the Godavari River[58] and elsewhere in the world, for example, Danube (-32.3 to -24.76‰)[59], Congo (-27.8 to -26.3‰)[60], Mekong (-29‰)[61] and Orinoco (-29.5 to -24.4‰)[62]. $\delta^{15}N_{PN}$ values broadly varied from 4.8‰ to 15.0‰ and from 5.7‰ to 13.1‰ during low flow and high flow periods, respectively, except three stations near origin of the river where depleted $\delta^{15}N_{PN}$ (1.2—2.9‰) were observed during low flow period.

Spatial variability (upper and lower reaches of the river)

Both nitrite + nitrate and phosphate concentrations were higher in upper than lower reaches of the river during low flow period (Figs. 3a&b), however, this variation is not statistically significant ($p=0.22$ and $p=0.18$, respectively). During both low flow and high flow periods, upper reaches of the river recorded relatively high mean Chl-a (27.5 and 12.2 mg m^{-3}, respectively) compared to lower reaches of the river (6.8 and 6.3 mg m^{-3}, respectively) (t-test, $p<0.05$ and $p<0.05$, respectively) (Fig. 4a&b). Higher mean TSM concentrations were found in upper (14.4 ± 15.5 mg L^{-1}) than lower reaches of the river (5.1 ± 2.1 mg L^{-1}) during low flow period, but the difference is not statistically significant. Contrastingly, lower TSM concentrations were observed in upper (21 ± 20 mg L^{-1}) than lower reaches of the river (133 ± 53 mg L^{-1}) (t-test; $p<0.001$) during high flow period (Fig. 4a&b). Percent organic carbon in TSM (%OC) was low in upper (10 ± 8%) compared to lower reaches (17 ± 5%) of the river during low flow period ($p=0.05$), whereas an opposite pattern was found during high flow period, with higher values in upper (9.6 ± 5.9%) compared to lower reaches of the river (0.9 ± 0.3%) ($p=0.002$) (Figs. 4a&b). Mean POC concentrations were similar in upper and lower reaches of the river during low flow period (Fig. 4a). Whereas, lower reaches of the river recorded high POC concentrations compared to upper

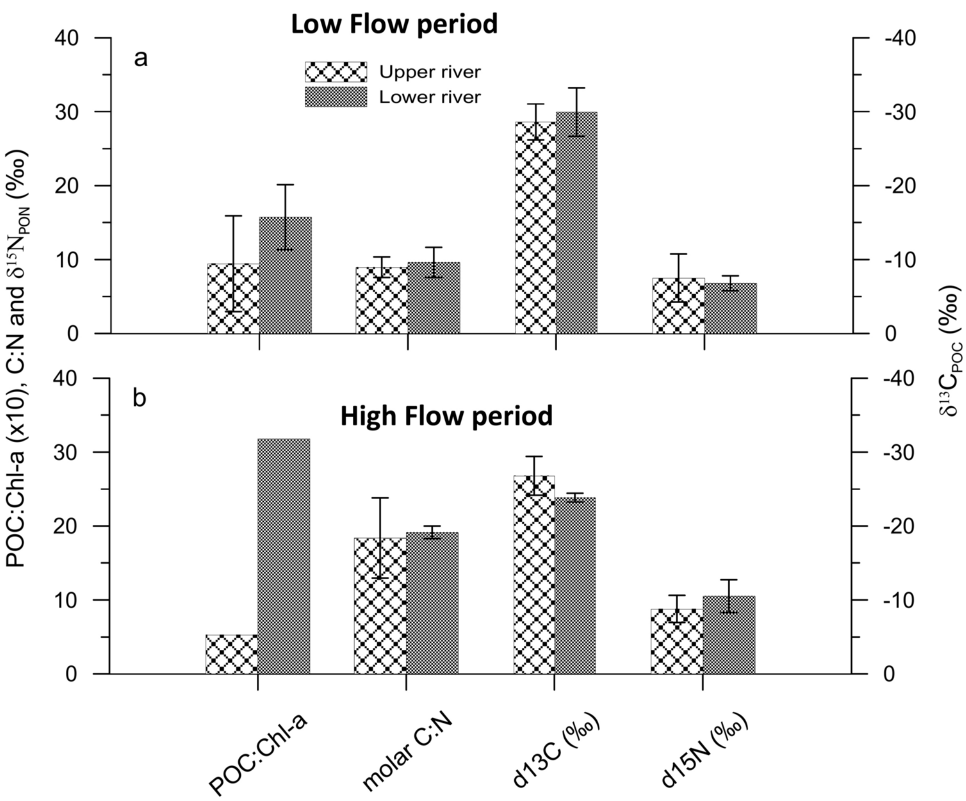

Figure. 5. Mean values of POC:Chl-a and molar C:N ratios, stable carbon isotopes of POC ($\delta^{13}C_{POC}$, ‰) and stable nitrogen isotopes of PN ($\delta^{15}N_{PN}$, ‰) in upper and lower reaches of the Godavari River during (**a**) dry period and (**b**) wet period. The $\delta^{13}C_{POC}$ values were shown on the right side y-axis and the remaining parameters were shown on the left side y-axis.

reaches during high flow period (Fig. 4b), however, it is not statistically significant (t-test; $p = 0.12$). Upper and lower reaches of the river recorded similar PN concentrations during both low and high flow periods (Figs. 4a&b).

Mean C:N ratios were similar in upper and lower reaches of the river during both low flow and high flow periods ($p = 0.54$ and $p = 0.82$, respectively) (Fig. 5a&b). Mean POC:Chl-a ratios were marginally lower in upper (98 ± 67) compared to lower reaches of the river (146 ± 36) during low flow period (Fig. 5a), however, it is significantly lower during high flow period (53 ± 64 and 318 ± 300, respectively) as shown in Fig. 5b (t-test, $p < 0.05$). Mean $\delta^{13}C_{POC}$ values were similar in upper (-28.6‰) and lower reaches (-29.9‰) of the river during low flow period (Fig. 5a). Whereas, depleted $\delta^{13}C_{POC}$ values were found in upper (-26.8‰) compared to lower reaches of the river (-23.8‰) during high flow period (Fig. 5b). $\delta^{15}N_{PN}$ showed relatively less spatial variability during low period, however, relatively enriched $\delta^{15}N_{PN}$ were found in lower reaches (10.5 ± 2.0‰) than upper reaches (8.7 ± 1.8‰) of the river during high flow period (Fig. 5b).

Discussion

Seasonal variations in the sources of POC and PN

Surface runoff during southwest (SW) monsoon transports land borne nutrients (from soils) to rivers. Drainage basin of the Godavari River receives > 80% of its annual rainfall only during four months period of SW monsoon (June–September)[19]. Intense rainfall during this period leaches nutrients, POC, PN and other dissolved materials from soils, leaf litter, debris of land plants and agricultural crops, excess fertilizers used in agricultural fields and sewage etc., and transports to rivers. Intense rainfall also enhances soil erosion in the drainage basin, leading to enhanced transport of particulate material to rivers[63]. Relatively higher TSM concentrations during high flow period (59 ± 65 mg L^{-1}) compared to low flow period (12.4 ± 14.2 mg L^{-1}) in this study indicate that significant input of terrestrial material to rivers during former period. However, such a difference was not noticed in POC concentrations which showed similar concentrations during high flow (0.8 ± 0.3 mg L^{-1}) and low flow (0.9 ± 0.5 mg L^{-1}) periods. This is attributed to significant amount of POC contribution from in-situ sources during low flow period because of prevailing conducive conditions for phytoplankton growth such as better light availability (low TSM; 12.4 ± 14.2 mg/L; Table 1) and stable water column (low flow) during this period. Lower TSM concentrations allow light penetration to deeper depths in the water column and thus enhance the light availability to phytoplankton leading to high primary production. Relatively high PN concentration during low flow (mean: 0.11 mg L^{-1}) than high flow period (0.06 mg L^{-1}) also suggest that major contribution of POM is from N-rich in-situ sources during former period, and N-poor terrestrial sources during latter period. This is because POM derived from in-situ sources predominantly contain N-rich proteins than N-poor cellulose, whereas, terrestrial POM mainly derived from vascular plants largely contain N-poor cellulose than N-rich proteins[64,65].

Mean C:N ratios found during low flow period (9 ± 4) are close to the range of C:N ratios of POM produced by phytoplankton (6–10)[26,66], (6.7)[67], (6–8)[68,69] indicating that predominant contribution of POM is possible from freshwater phytoplankton. On the other hand, C:N ratios during high flow period (18 ± 4) are close to typical C:N ratios of terrestrial POM (> 12)[2,32,70] and measured C:N ratios of soils in the Godavari basin (19 ± 4), but lower than measured C:N ratios of dominant C_3 plants (41 ± 32) and C_4 plants (53 ± 41) in drainage basin of the Godavari river. These results indicate that soil OM may be one of the major sources of POM in the river during high flow period. Although soils contain debris of C_3 and C_4 plant material, the lower C:N ratios of soils than C_3 and C_4 plants are due to bacterial colonization[32], and humification and mineralization processes[71] during decomposition of terrestrial POM in soils that result in C:N ratios of soils in the range of 8–20[72]. The POC:Chl-a ratios of < 200 and > 200 were used to characterize POC of phytoplankton and terrestrial origin, respectively[73,74]. Broad range of POC:Chl-*a* ratios during low flow period (32–275, mean 106 ± 65) and high flow period (13–677, 155 ± 225) likely indicate that both freshwater phytoplankton and terrestrial sources contribute to POM, with a predominance of the former during low flow period and the latter during high flow period.

The range of $\delta^{13}C_{POC}$ observed during low flow period (-32.8 to -20.7‰) is close to $\delta^{13}C$ of phytoplankton in the Godavari River (-31.2 ± 0.6‰), typical range of freshwater phytoplankton (-33.2 to -27.5‰)[33], sewage (-31.5 ± 1.0‰)[57] and terrestrial POM (-28 to -26‰)[32,75], and measured $\delta^{13}C$ of C_3 plants (-27.4 to -24‰) and soils (-23.5 to -15.3‰) in the Godavari basin (Fig. 6). These results suggest that both in-situ and terrestrial sources, including sewage, likely contribute to POM during low flow period, with a predominance of the former than the latter. On the other hand, $\delta^{13}C_{POC}$ values during high flow period (-30.0 to -22.8‰) are close to $\delta^{13}C$ of typical terrestrial POM and measured terrestrial C_3 plants of the Godavari basin, and slightly different from that of $\delta^{13}C$ of freshwater phytoplankton and sewage (Fig. 6), suggesting that POM is contributed by both terrestrial and in-situ sources, with a predominance of the former than the latter.

Broad range of $\delta^{15}N_{PN}$ during low flow period (4.8 to 15.0‰; mean 7.8 ± 2.6‰) indicates that predominant contribution of POM is from phytoplankton (5 to 8‰), with minor contribution from terrestrial sources, such as C_3 plants (5.1 ± 2.1‰), C_4 plants (4.4 ± 2.1‰) and soils (10.1 ± 2.7‰) (Fig. 6), corroborating with $\delta^{13}C_{POC}$ results. However, mean $\delta^{15}N_{PN}$ values during high flow period (9.4 ± 2.1‰; range: 5.7—13.1‰,) are very close to $\delta^{15}N$ of soils (10.1 ± 2.7‰) in the drainage basin, and significantly enriched than $\delta^{15}N$ of C_3 plants (5.2 ± 2.1‰) and C_4 plants (4.4 ± 2.1‰) plants. These results likely indicate that terrestrial sources, mainly soil derived POM, contribute to POM with minor contribution from in-situ sources during high flow period. Contrary to this, Chl-a concentrations were lower during low flow (11 ± 6 mg m^{-3}) than high flow period (21 ± 19 mg m^{-3}). This discrepancy mainly arises from the large spatial variability in Chl-a and TSM concentrations between upper and lower reaches of the river within the high flow period. Upper reaches of the river showed higher Chl-a (27.5 ± mg m^{-3}) and lower TSM (21 ± 20 mg L^{-1}) than the lower reaches of the river (6.8 ± mg m^{-3} and 133 ± 53 mg L^{-1}, respectively). Due to the joining of large tributaries, such as Wardha, Pranahita and Indravati in the middle course of the river (Fig. 1), the flow is strong and waters are turbid (TSM: 133 ± 53 mg L^{-1}) leading to low Chl-a

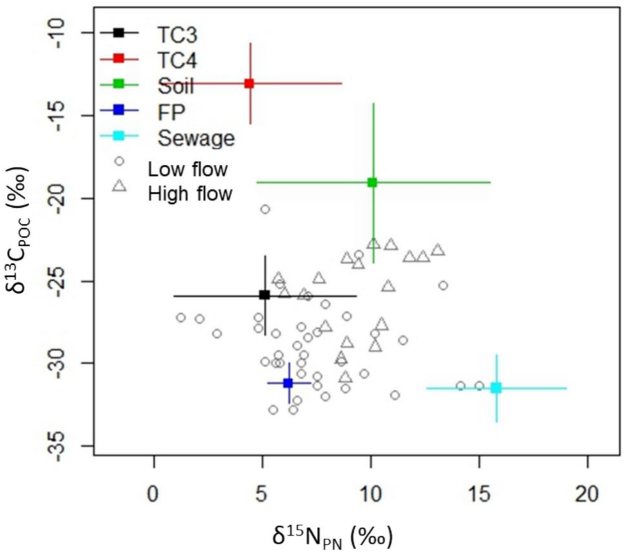

Figure. 6. Isospace plot of the $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ in suspended particulate matter of the Godavari River during low flow period (hollow circles) and high flow period (hollow triangle). End member ranges of both $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ of possible major sources of organic matter such as terrestrial C_3 plants (TC3, black coloured lines) and C_4 plants (TC4, red), soils (green), freshwater phytoplankton (blue) and sewage (cyan coloured lines) to suspended particulate organic matter (POM) in the Godavari River were also shown.

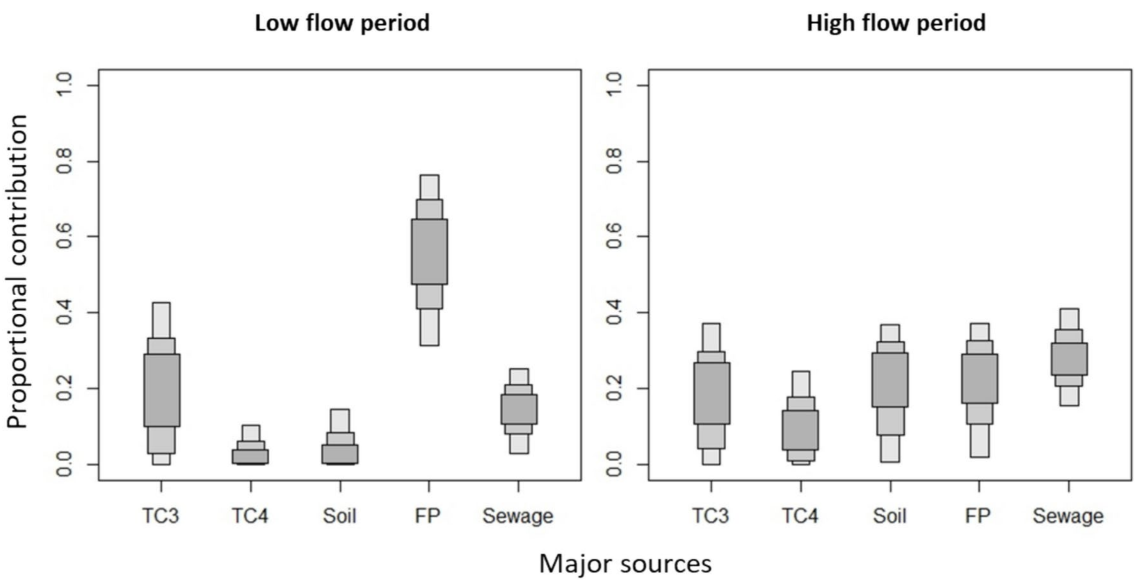

Figure. 7. Proportional contributions from terrestrial C3 and C4 plants (TC3 and TC4, respectively), soil organic matter (soil OM), freshwater phytoplankton (FP) and sewage derived organic matter (sewage) to POM pool in the Godavari River during low flow and high flow periods.

in the lower reaches of the river within the high flow period. No significant relationship of POC with either TSM or Chl-a confirm that both terrestrial and in-situ sources are contributing to POM[1,25].

SIAR model results showed that freshwater phytoplankton contributes up to 60% during low period while contribution from terrestrial sources is predominant (~75–80%) during high flow period (Fig. 7). Prevailing conducive conditions, such as nutrient availability, stable water column (low flow) and better light availability (low TSM) to phytoplankton are attributed for major contribution from phytoplankton during low flow period. Consistent with our observation, predominance of phytoplankton derived POM during low flow periods was also reported in the Godavari River[19,22] and some of the major rivers in the world, for example, Mississippi, Colorado, Rio Grande and Columbia[21], Oubangui[24], Umpqua[76], Alsea[77], Danube[78], Garonne, Loire and Rhone[79]. On the other hand, predominant (~75–80%) contribution of POM from terrestrial sources, mainly sewage (~25–30%), soils (~20%), C_3 plants (~20%) and C_4 plants (~10%), during high flow period is attributed to export of POM from soils, debris of C_3 and C_4 plants and sewage in drainage basin to the river by intense runoff during this period[80]. Also, less contribution from phytoplankton (20–25%) due to high TSM (67 ± 66 mg L^{-1}) that limits light availability to phytoplankton.

Spatial variations in the sources of POC and PN

Both POC and PN concentrations were similar in upper and lower reaches of the river during low flow period (Fig. 5a). However, significant spatial variability was observed during high flow period. During this period, relatively higher POC concentrations (1.2 mg L^{-1}) associated with higher TSM (133 ± 53 mg L^{-1}) and lower Chl-a (6.8 ± mg m^{-3}) were found in the lower reaches of the river. On the other hand, relatively lower POC (0.8 mg L^{-1}) associated with lower TSM (21 ± 20 mg L^{-1}) and higher Chl-a (27.5 ± mg m^{-3}) were observed in the upper reaches of the river. Intense rainfall (1600 to > 3200 mm yr^{-1})[42], dominance of sandy clay loam soils[81] and higher soil OC in northern part of the basin which drains into lower reaches of the river through the major tributaries, Wardha, Pranahita and Indtravati are attributed for the observed high POC and TSM concentrations in lower reaches of the river. Sandy clay loam soils are more susceptible to erosion by intense rainfall during SW monsoon due to higher soil detachment capacity[82] and restrict infiltration of water[83]. In addition, high temperatures[45], anthropogenic activities such as deforestation and increased agricultural activities in lower basin[84] also support erosion of soils. Balakrishna and Probst[22] reported high concentrations of TSM in tributaries of the Godavari River in lower basin, Wardha (129 mg L^{-1}), Pranahita (113 mg L^{-1}) and Indravati (79 mg L^{-1}) than tributaries in upper basin of the river during high flow period. Although, upper basin is dominated by black soils and grasslands, lower TSM concentrations in upper reaches of the river could be due to less intensity of rainfall (< 800 to1600 mm yr^{-1}) than lower basin of the river (1600 to > 3200 mm yr^{-1})[42]. Higher TSM concentrations (133 ± 53 mg L^{-1}) significantly decreases the light penetration depth in the water column and thus restricts the light availability to phytoplankton leading to low primary production in lower reaches (Chl-a: 6.8 mg m^{-3}). On the other hand, lower TSM concentrations (21 ± 20 mg L^{-1}) in the upper reaches of the river allows light penetration to deeper depths and thus enhances the light availability to phytoplankton leading to high primary production (Chl-a: 27.5 mg m^{-3}). These results demonstrate that in-situ sources predominantly contribute to POM pool in upper reaches while terrestrial sources in lower reaches of the river during high flow period. It is also evidenced from significantly high %OC in TSM in upper (9.6 ± 5.9%) than lower reaches of the river (0.9 ± 0.3%). However, based on $\delta^{13}C$ (-24.5 ± 0.3‰) and low yield of lignin phenols (Λ8), Pradhan et al.[58] concluded that algal POM is predominant in lower reaches of the river during high flow period. Even though, lignin phenols (Λ8) are specific markers for terrestrial sources of POM, they cannot differentiate contribution from lignin free algal POM and lignin degraded soil OM. Hence, lower yield of lignin phenols (Λ8) in lower reaches of the Godavari River during high flow period[58] could be due to significant contribution from soil OM. SIAR model estimated that contribution from soil OM is ~ 30% and it is higher than freshwater phytoplankton contribution (~ 10%). Spatial variability in sources of POM in the Godavari River is therefore intimately linked to the intensity of soil erosion that is controlled by strong rainfall in the lower reaches (1600 to > 3200 mm yr^{-1}) than the upper reaches (< 800 to1600 mm yr^{-1}) of the river.

Impact of excess fertilizers use in agricultural activities

The $\delta^{15}N_{PN}$ signatures have not shown any evidence for significant contribution of POM produced from synthetic N-fertilizers in the Godavari River. The $\delta^{15}N$ of synthetic fertilizer nitrogen was reported to be depleted (~ 0 ± 1‰)[37,39,85] because they are manufactured from atmospheric N_2. The $\delta^{15}N$ of N-fertilizers such as KNO_3, NH_4NO_3, Urea, $(NH_4)_2SO_4$ and NPK (20:10:10) etc., manufactured by different companies were found to be in the range of -5.9 to 2.6‰, with a mean $\delta^{15}N$ of -0.2‰[85]. Even though, India consumes 26.5 Tg yr^{-1} of synthetic fertilizers, and it accounts for 15.3% of the global N-fertilizer consumption[15], $\delta^{15}N_{PN}$ values of this study (< 4.8‰) are enriched compared to typical $\delta^{15}N$ of POM derived from fertilizer nitrogen (0 ± 1‰). These results demonstrate that impact of synthetic N-fertilizer usage in agricultural fields in drainage basin may be minor on ecosystem in the Godavari River. It could be due to retention and/or elimination of fertilizer nutrients due to their low utilization efficiency; only ~ 30 to 35% of the fertiliser nutrients applied is taken up by plant[86,87]. For instance, most commonly used nitrogen fertilizer, Urea, have the utilization efficiency of ~ 50% and the remaining 50% lost in different pathways; 2–20% through volatization, 15–25% reacting with organic compound in soils and 2–10% leaching into water[88]. Central Ground Water Board of India[89] reported that concentrations of nitrate in ground waters of many Indian states are higher than 45 mg L^{-1}, and attributed it to seepage of excess N-fertilizer used in agricultural activities into ground waters[21,90,91]. Rahman et al.[91] reported elevated NO_3^- concentrations in ground waters of Rajasthan state, India and attributed to anthropogenic sources. Based on land use map and NO_3^- concentrations in ground waters (1 to 415 mg L^{-1}) of Tamilnadu state, India, Jayarajan and Kuriachan[92] confirmed that use of excess fertilizers and sewage are the major sources of elevated NO_3^- concentrations in ground waters. Several other studies also reported elevated NO_3^- concentrations in ground waters of different river basins and attributed to N-fertilizer usage[93,94]. Based on multiple stable and radioactive isotopes tracers, recently, Harris et al.[95] demonstrated that ground water NO_3^- is originated from fertilizers in the western and eastern banks of the Nogoa River, Queensland, Australia. Recently, Kiran et al.[96] reported concentrations and $\delta^{15}N$ of nitrate ($\delta^{15}N_{NO3-}$) along the bank of the Godavari estuary during high and low flow periods, and found similar values of $\delta^{15}N_{NO3-}$ during both the periods and attributed to the homogenization through mineralization/immobilization of NO_3^- in the ground water. The authors[96] concluded that submarine groundwater discharge of denitrified NO_3^- is one of the major pathways of NO_3^- to the Godavari estuary. The $\delta^{15}N_{PN}$ values found in our study demonstrate that impact of N-fertilizer on POM in the Godavari River is not significant, rather than hitherto hypothesized. Further studies on $\delta^{15}N$ of NO_3^- in the ground waters of the drainage basin are required to confirm the impact of N-fertilizers on ground waters N-nutrients in the Godavari drainage basin.

Conclusions

Major sources of POM, and their spatial and seasonal variations were investigated in the Godavari River using isotopic signatures of carbon and nitrogen in suspended particulate matter. Elemental C:N and POC:Chl-a ratios, and $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ of suspended particulate matter clearly indicated that POM is predominantly contributed by water column phytoplankton (~60%) and terrestrial sources (75–80%) during low flow and high flow periods, respectively. Predominant contribution from phytoplankton is attributed to prevailing conducive conditions for phytoplankton growth during low flow period. On the other hand, major contribution from terrestrial sources is attributed to export of soils, debris of land plants, agricultural crops and sewage from drainage basin by the intense runoff during high flow period. Spatial variations in rainfall intensity, soil characteristics, land use change and agricultural activities in drainage basin of the river govern spatial variability in major POM sources. Relatively enriched $\delta^{15}N_{PN}$ ratios suggest that impact of N-fertilizers usage in agricultural fields of drainage basin is not significant on POM in the Godavari River. It is attributed to seepage of excess N-fertilizers into ground waters rather than their transportation to rivers.

Data availability

The data used in this study is available with the corresponding author (M.S. Krishna) and will be provided on reasonable request by e-mail (moturi@nio.org).

Received: 4 July 2024; Accepted: 18 April 2025
Published online: 19 May 2025

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Acknowledgements
We thank the Director, Council of Scientific and Industrial Research (CSIR)-National Institute of Oceanography (NIO), Goa, and the Scientist-In-Charge, NIO-Regional Centre, Visakhapatnam for their support and encouragement. This work is part of the Institutional Project funded by the Council of Scientific and Industrial Research (CSIR), Government of India.

Author contributions
MSK and NPCR conceptualized the work and planned for field campaign. SAN, MHKP and ChV S were participated in the field campaign for sample collection and analysis of samples. Original draft of the manuscript was prepared by MSK and, NSR provided land use change and soil OC maps of Godavari basin. All authors read and approved the final manuscript.

Funding
The work is part of the Council of Scientific and Industrial Research (CSIR), Government of India, funded research project (OLP 2011). It is already mentioned in the acknowledgement section.

Declarations

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-025-99286-0.

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