

## **Multi-proxy evidence for compositional change of organic matter in the largest tropical (peninsular) river basin of India**

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### **Abstract**

The distribution and compositional changes of organic matter (OM) within the Godavari river system is increasingly influenced by reduced monsoon rainfall and an increased number of damming. To track these changes, stable isotopes of organic carbon and concentrations of lignin phenols were analyzed in total suspended matter (TSM), sediments, agriculture soils and plants from Godavari basin. The results indicated that the upper tributaries drained heavier carbon ( $\delta^{13}\text{C}_{\text{org}} = -20.4 \pm 2.2\text{‰}$ ) than the lower tributaries ( $\delta^{13}\text{C}_{\text{org}} = -25.4 \pm 1.5\text{‰}$ ) owing to the regional vegetation in the upper to lower basins. OM originating from algae near dam impoundments was incorporated into TSM and sediment due to extreme drought condition. The organic carbon (OC) content was higher in TSM and in the sediment of the region after the middle reach dam (Sriram Sagar) than before ( $2.2 \pm 1.6$  vs.  $1.0 \pm 0.1$  % OC and  $2.1 \pm 2.3$  vs.  $0.6 \pm 0.2$  % OC, respectively). The lignin yield ( $\Lambda_8$ ) was lower in TSM and in the sediment after the dam impoundment than before ( $0.37$  vs.  $1.94$  mg/100 mg OC and  $2.9 \pm 1.1$  vs.  $5.4 \pm 2.3$  mg/100 mg OC, respectively) due to an increased contribution of lignin free OC from algae and degraded soil. Less rainfall and dam impoundments enhanced the fraction of labile OM from freshwater algae and an estuarine phytoplankton bloom in the study year. Our study is the first to document lignin fluxes from an Indian monsoonal river (Godavari). The flux of lignin phenols of  $7.26 \times 10^9$  g yr<sup>-1</sup> is much lower than those of most world rivers except the rivers from polar arctic.

**Key Words:** Organic carbon; carbon isotopes; lignin phenols; Godavari River; composition; South West Monsoon

## 1. Introduction

OM in rivers is an integrator of terrestrial processes related to the lithology of river basins (Longworth et al. 2007) and its landscape (Bianchi et al. 2007a; Eckard et al. 2007). Terrestrial OM originates from sources such as vascular plants, soil, and riverine phytoplankton. OM in plants and soil undergo primary degradation processes driven by bacterial and/or fungal action, which alters their molecular composition before their input into riverine environment (Hedges et al. 1986). Riverine OM incorporated into coastal marine sediments is an important component of the marine biogeochemical cycle (Keil et al. 1994). The nature of riverine OM is broadly responsive to processes of the terrestrial carbon cycle such as continental and chemical weathering (Galy and France-Lanord 1999; Sempere et al. 2000; Barth et al. 2003). In addition, anthropogenic processes such as agricultural activities and damming greatly impact OM transport, processing and deposition within river system (Ellis et al. 2012).

Rivers from tropical regions are important for carbon transport, and deliver >60% terrigenous OC to the world oceans (Meybeck, 1982; Ittekkot, 1988; Ludwig et al. 1996; Dagg et al. 2004). Studies highlighting the variability of OM compositions in tropical river systems are limited. Except the studies on large rivers such as Amazon (Hedges et al. 1986; Aufdenkampe et al. 2007), Kapus (Loh et al. 2012), Mekong (Ellis et al. 2012) and Congo (Spencer et al. 2012). OM studies in Indian rivers have been documented by Ittekkot and Zhang (1989) and Ittekkot and Laane (1991). In recent years compositional changes of OM in tropical rivers of India have become an important issue in view of increasing human pressure (damming and over agriculture) and the variability in the South West Monsoon (SWM). Monsoon rain feeding the Godavari river system in peninsular India is the second most important source after Himalayan Rivers (Ganges and Brahmaputra) of the annual freshwater discharge to the Bay of Bengal (BOB) from Indian subcontinent. Reduced monsoon rainfall and increased damming in the Godavari basin have not only enhance the rate of reduction in sediment load ( $1.4 \times 10^6$  ton yr<sup>-1</sup>; Panda et al. 2011) but also cause biogeochemical changes within the river and estuarine systems (Sarma et al. 2009). The OM composition in the Godavari river basin depends on water chemistry, microbial population and natural sedimentation processes (Gupta et al. 1997).

In this study we report on the change in OM composition within the Godavari river basin under extreme climatic variability (i.e. reduced SWM) and various anthropogenic activities (excessive agricultural land use and damming). Organic geochemical tools such as elemental and, isotopic ratios,

and biomarker approach were used to identify the nature of OM and their sources in total suspended matter (TSM) and sediments from the Godavari river basin during the SWM period of 2009.

## **2. Materials and methods**

### **2.1 Study area**

The Godavari River has the largest monsoon fed river basin of India with its source at an elevation of 1065 m in the Western Ghat (Sahyadris). It travels 1465 km in SE direction before entering the BOB. The total catchment area is  $0.3 \times 10^6 \text{ km}^2$  (~ 9.5% of the geographical area of India) populated by 75.3 million people (~ 6.5% population of India). The tributaries Pravara, Manjira and Maner in the right bank occupy 16% of the catchment area whereas the tributaries Purna, Panhita, Indravati and Sabri in left bank occupy 60% of the catchment area. The basin experiences a semi-arid to monsoonal climate with average rainfall of  $0.003 \text{ mm km}^{-2} \text{ yr}^{-1}$ . Major part of the annual rainfall (84%) occurs during the SWM period (June-September) and periodic cyclonic storms often cause high rainfall (~88%) in the lower catchment of the Godavari River (CPCB, 1995). The whole basin is mainly covered with agriculture land ( $0.2 \times 10^6 \text{ km}^2$ ) followed by forest land ( $0.09 \times 10^6 \text{ km}^2$ ). A patch of coal belt is spread over the lower part of basin ( $0.01 \times 10^6 \text{ km}^2$ ) covering the lower mainstream and a major part of the lower tributaries.

Construction of dams over Godavari basin have increased in numbers since 1965 and at present 300 hydrologic projects (various sizes) are operated regulating the total fluvial load to the BOB. The average surface runoff potential of the basin is  $110.5 \text{ km}^3 \text{ yr}^{-1}$  from which  $31.3 \text{ km}^3 \text{ yr}^{-1}$  is stored in the dam basins. Based on the water utilization the whole basin is classified into four parts, the upper reaches (from the source to the Manjira tributary), the middle reaches (from Manjira to the Pranahita and Indravati tributaries), the lower reaches (from Indravati up to the Rajahmundry) and the deltaic region (from Rajahmundry to the sea; Figure 1).

### **2.2 Data source and sampling**

Monthly rainfall data from selected gauge stations in the Godavari basin were obtained from the Indian Meteorological Department (IMD). Water runoff at the terminal site (Polavaram) was obtained from the long term dataset (1965-2010) of the Central Water Commission, India (CWC). Annual water

runoff and sediment load at selected gauge stations were calculated from the 20 year (1990-2010) dataset (CWC, 2005, 2007, 2009, 2010 and 2012).

Fifty six samples (35 sediments and 21 TSM samples) were collected from the Godavari mainstream and tributaries during the SWM of 2009. Agricultural land soils representing the major vegetation in the catchment were sampled along the mainstream. Agricultural and forest plant samples were collected according to their area of dominance along the river basin. Nearly 5–10 L of running water was collected in acid cleaned jars for TSM. The TSM was obtained through settling technique as described in Gupta et al. 1997. Relatively turbid water samples were kept undisturbed for 48 hrs and apparently low turbid ones kept for 72 hrs for particle settling. The supernatant (i.e. TSM free clean water) was siphoned off and remaining 50-150 ml was centrifuged at 1000 rpm (rotations per minute) for 5 minutes and dried, in order to get the TSM. Sediment samples were collected using a van Veen grab (15×15cm) and stored at  $\sim 4^{\circ}\text{C}$  until analysis. TSM and sediments were freeze dried and homogeneously grinded prior to isotopic analysis.

## 2.3 Chemical analysis

### 2.3.1 Bulk properties

Sediment grain size analysis was performed using a Coulter laser granular meter (LS-100Q) after the removal of organic matter by adding  $\text{H}_2\text{O}_2$  (10%) as described in Liu et al. 2009. Grain size is expressed as proportion of clay ( $<4\ \mu\text{m}$ ), silt ( $4\ \mu\text{m}$ – $63\ \mu\text{m}$ ) and sand ( $>63\ \mu\text{m}$ ) with a measurement error of  $\leq 1\%$  in the entire dataset.

Sediment and soil samples were treated with 1 M HCl to remove inorganic carbon prior to the stable isotopic composition ( $\delta^{13}\text{C}_{\text{org}}$ ) and organic carbon (OC) analysis. Weight percentages of total nitrogen (TN) and OC, TN in plant samples were measured directly without acid treatment. The concentration of OC and TN (relative precision,  $\pm 5\%$ ) were determined using a CHNOS Elemental analyzer (Model: Vario EL III) before the isotopic analysis. The  $\delta^{13}\text{C}_{\text{org}}$  was measured in total OM fraction of the samples (TSM and sediment) using an elemental analyzer interfaced with an isotope ratio mass spectrometer (EA-IRMS Delta plus/XP, Finnigan MAT co.) as described in Wu et al. 2007. The analytical precision for  $\delta^{13}\text{C}_{\text{org}}$  was  $\pm 0.1\%$ . Results are expressed as per mill (‰) deviations

relative to the Vienna–Pee Dee Belemnite (V-PDB) standard and the  $\delta^{13}\text{C}_{\text{org}}$  was calculated using the following calculation:

$$\delta^{13}\text{C}_{\text{org}} (\text{‰}) = \left[ \left\{ \frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{PDB}}} \right\} - 1 \right] \times 1000$$

### 2.3.2 Lignin phenols

Lignin phenols were characterized using the method described by Hedges and Ertel (1982) and modified by Goñi and Hedges (1992) and Miltner and Emeis (2000). Cupric oxide (CuO) and ferrous ammonium sulphate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ ) were added to the samples in PTFE bombs along with 8M NaOH in a glove box under nitrogen spurge. Samples were digested at  $165^\circ\text{C}$  for 3.5 hrs. After digestion, the supernatant was collected by centrifugation ( $\sim 3000$  rpm for 5 min.) and acidified with concentrated HCl to  $\text{pH} < 2$  prior to extraction with ethyl acetate (Yu et al. 2011). Quantitative separation of lignin phenols was performed using gas chromatography (Agilent 6890 N GC with a flame ionization detector (GC-FID) and a DB-1 capillary column of 30 m length, 0.25 mm inner diameter and 0.25  $\mu\text{m}$  film thicknesses; J&W Scientific).  $\text{N}_2$  was used as carrier gas during the separation of lignin molecules measured as trimethylsilyl derivatives of BSTFA+TMCS (99:1; Supelco). The average precision was  $\sim 5\%$  or 15–24% when the lignin phenol concentration was  $> 0.05$  or  $< 0.05$  mg/100mgOC, respectively (Yu et al. 2011). The concentration of lignin phenols V (vanillyl), S (syringyl), and C (cinnamyl), also other phenols such as P (p-hydroxybenzenes) is representative of only a fraction of OM in TSM and sediment samples. The ratio S/V and C/V are used to distinguish between angiosperm vs. gymnosperm derived and between woody vs. non-woody tissue derived OM respectively (Hedges et al. 1984). The lignin degradation due to brown/white rot fungi, causes alterations in acid to aldehyde ratios of V phenols (i.e. (Ad/Al)<sub>v</sub>). The ratio such as P/(V+S) (i.e. the ratio of total P phenols divided by the sum of V and S phenols) is used as an indicator of lignin diagenesis due to demethylation by brown rot fungi (Dittmar and Lara, 2001). The ratio between p-hydroxyacetophenone and total P phenol (Pn/P) is used to distinguish between OM originating from terrestrial plants and plankton (Teisserenc et al. 2010).

### 2.4 Statistical treatment

Multivariate statistical analyses, Pearson's 2-tier correlation, were performed on the normalized data using SPSS 10.0 with confidence levels  $p \leq 0.05$  (95%) and  $p \leq 0.01$  (99.9%). The results are illustrated using Grapher 4.0 (Golden Software Inc., USA) and SPSS 10.0 (SPSS Inc., USA).

### 3. Results

#### 3.1 Variability of SWM and sediment load in the Godavari basin

Rainfall data from more than 40 rain gauge stations throughout the Godavari basin shows that normal SWM prevails from June to September and that lower precipitation occurred during our study period in 2009 (Figure 2a). The total fresh water storage have been increased from 4.5 km<sup>3</sup> yr<sup>-1</sup> during 1970 to 25.1 km<sup>3</sup> yr<sup>-1</sup> during 2007 and is expected to rise in future up to 31.5 km<sup>3</sup> yr<sup>-1</sup> (CWC, 2012). Compared with the previous study periods of Gupta et al. (1997) and Balakrishna et al. (2005), the freshwater storage volume of dams is much higher observed during our study period (Figure 2b). Due to damming the fresh water discharge (mean of 20 years) of the upper basin contributes only 5±3% to the annual fresh water discharge followed by the middle basin (8±6%), and the highest contribution is from the lower basin (87±8%). The water discharge and sediment load from the lower tributaries are higher compared to the upper tributaries (Table 1) due to higher precipitation in the lower basin (CWC, 2009).

The annual sediment load from the Godavari basin has declined from ~170 × 10<sup>6</sup> t yr<sup>-1</sup> (in 1988) to ~25 × 10<sup>6</sup> t yr<sup>-1</sup> during our study year (2009) and ~15 × 10<sup>6</sup> t yr<sup>-1</sup> (in 2010). The decrease is significant (R<sup>2</sup>=0.98; p ≤0.01; Figure 2c) during last half decade due to decreasing SWM rainfall and damming along the mainstream. The rate of siltation in the two major dams, Jayakwadi (22 × 10<sup>3</sup> km<sup>2</sup>) and Sriram Sagar (92 × 10<sup>3</sup> km<sup>2</sup>) of Godavari basin, is 4.8 ha-m 100 km<sup>-2</sup> yr<sup>-1</sup> and 2.8 ha-m 100 km<sup>-2</sup> yr<sup>-1</sup>, respectively (Jothiprakash and Garg, 2009).

#### 3.2 Bulk properties

Bulk chemical properties, %OC, [C/N]<sub>atom</sub> ratio and δ<sup>13</sup>C<sub>org</sub> (‰) in plants, soils, TSM and sediments are shown in Table 2. The C4 plants, sorghum (*Sorghum vulgare*), sugarcane (*Saccharum officinarum*) and sweet corn (*Zea mays var. rugosa*), largely spread over the upper and few parts of the middle basins had a higher OC content in their leaves compared to the C3 plants, rice (*Oryza sativa Indica*), cotton (*Gossypium sp.*), jackfruit (*Artocarpus heterophyllus*) and teak (*Tectona grandis*) spreads over the middle and lower basins (Table 2). Agricultural soils showed OC content between 0.81% and 2.26% increasing along the mainstream and tributaries from the upper to the lower reaches (Table 2). The average value of POC (in TSM) was higher at the stations after the middle reach dam (Sriram Sagar) than before (2.2±1.6% vs.1.0±0.1%). POC of deltaic regions (Gautami and Vaistha) was about 1%

comparable with previous studies (Balakrishna et al. 2005). The TOC (%) content of sediments closely followed the distribution of POC in the Godavari basin (Table 2).

The  $[C/N]_{\text{atom}}$  ratios in the C3 plants were lower than in the C4 plants. Rice is the main crop in this basin and the agricultural soil samples from rice field in the middle and lower reaches exhibited the lowest  $[C/N]_{\text{atom}}$  ratio (Table 2). The  $[C/N]_{\text{atom}}$  ratio of TSM of the mainstream and the tributaries gradually decreased from the upper to lower reaches (Table 2). The  $[C/N]_{\text{atom}}$  ratio in the sediment samples along the mainstream increased from the upper to the lower reaches with lowest values in the middle reaches. Tributary sediments showed decreasing  $[C/N]_{\text{atom}}$  ratios from the upper to the lower tributaries except for the Pranahita sediments (Table 2).

The C4 plants exhibited an average  $\delta^{13}C_{\text{org}}$  value of  $-11.8 \pm 0.56$  ‰, C3 plants  $-29.1 \pm 0.53$  ‰ (Table 2) and soils from the agriculture land ranged from  $-19.2$ ‰ to  $-23.9$ ‰ depending on the type of crops (Table 2). The  $\delta^{13}C_{\text{org}}$  of TSM of the mainstream varied between  $-22.2$ ‰ and  $-24.7$ ‰, the lighter values were found in the middle reaches and heavier ones in the upper reaches. More light values (i.e.  $-25.6$ ‰ and  $-26$ ‰) found in the vicinity of dam with heavy algae in the water. The upper tributaries drained heavier carbon (ca.  $\delta^{13}C_{\text{org}} = -20.9 \pm 2.3$ ‰) than the middle and lower tributaries (ca.  $\delta^{13}C_{\text{org}} = -23.2 \pm 0.2$ ‰). Sedimentary  $\delta^{13}C_{\text{org}}$  values varied between  $-22.4 \pm 2.0$ ‰ in the upper reaches to  $-24.4 \pm 0.8$ ‰ in the lower reaches with slightly depleted values in the middle reaches. Deltaic sediments exhibited a narrow range of  $\delta^{13}C_{\text{org}}$  of  $-23.6 \pm 1.8$ ‰ and  $-24.8 \pm 1.1$ ‰ (Table 2). Sediments from Godavari River are mainly composed of silt and clay, among which the clay fraction dominated in the upper reaches (65%), silt in the lower reaches (65%) and sand remains near to dam impounded region (20%). The deltaic region sediment is composed of silt (~60%) and clay (~40%).

### 3.3 Lignin phenols

The compositions of lignin phenols and ratios are presented in Table 3. C4 plant leaves showed higher  $\Lambda 8$  ( $13 \pm 3.4$  mg/100 mg OC) than C3 leaves ( $\Lambda 8 = 5.6 \pm 3.2$  mg/100 mg OC; Table 3). The average S/V and C/V ratios in plants were  $0.9 \pm 0.4$  and  $0.7 \pm 0.4$ , respectively. The means of  $\Lambda 8$  and  $\Sigma 8$  in the soils were  $2.2 \pm 1.1$  mg/100 mg OC and  $0.2 \pm 0.1$  mg/10g dry wt, respectively. The S/V and C/V ratios of soils were  $0.4 \pm 0.1$  and  $1.0 \pm 0.2$ , respectively and the average  $(Ad/Al)_V$  of soil was  $0.6 \pm 0.1$ .

$\Lambda 8$  and  $\Sigma 8$  of TSM increased from the upper to lower reaches (Table 3). The lowest value was found in the middle reaches at the confluence point of Manjira and the highest value in deltaic region (Vasistha branch). In the middle reaches lower  $\Lambda 8$  of TSM was observed in the region after the dam (Sriram Sagar) than before (0.37 vs. 1.94), however, both  $\Lambda 8$  and  $\Sigma 8$  of TSM were higher in the lower reaches and increased towards the deltaic region (Table 3). This indicates input of fresh plant material from agriculture and dense forest along the lower Godavari basin. The relative abundance of CuO oxidation products (S + V + C) in TSM varied from ~40% to 87% with higher values in the lower reaches and lower values in the tributary confluence region. The average C/V ratio of TSM is  $0.3 \pm 0.1$  which is almost similar to the C/V ratio of agriculture soils but lower than that of plants (Table 3). The average S/V ratio of TSM was  $1.0 \pm 0.2$  being similar to the S/V ratio of agriculture soils but higher than that of plants (Table 3). The  $(Ad/Al)_v$  in TSM indicated higher values along the mainstream (ca.  $0.5 \pm 0.2$ ) compared to the tributaries and deltaic samples [ $(Ad/Al)_v = 0.3 \pm 0.1$ ; Table 3]. P/ (V+S) of TSM (ca.  $2.2 \pm 1.0$ ) was higher than in soils, and TSM in the mainstream had higher P/ (V+S) than TSM of tributaries (Table 3). P/ (V+S) of TSM was higher at the tributary confluence (station G-13) and the deltaic region (Vasistha branch). Higher P/ (V+S) in these regions were associated with lower Pn/P (0.04 and 0.06, respectively) during the study period. The average  $\Lambda 8$  in sediments decreased from the upper reaches to the deltaic region (Table 3). Higher  $\Lambda 8$  were found in the upper and middle tributary sediment compared to the lower tributary (Sabri). The spatial distribution of  $\Lambda 8$  in the sediment along with the sediment yield of the tributaries indicated increased  $\Lambda 8$  in the region between the dam impoundments due to contributions from the tributaries (Figure 3a). Decreasing  $\Lambda 8$  in the middle reaches before the Sriram Sagar dam than after ( $2.9 \pm 1.1$  vs.  $5.4 \pm 2.3$ ) was observed during the study period. The distribution of  $\Sigma 8$  closely followed the distribution of  $\Lambda 8$  in the sediment (Table 3; Figure 3b) except higher  $\Sigma 8$  (>5 mg/10g dry wt.) observed at Bhadrachalam (middle reaches). The relative abundance of CuO oxidation products is 70–78% in the mainstream sediment except in the lower tributary (~40%; Sabri) (Table 3). This lower abundance together with lower  $\Lambda 8$  and  $\Sigma 8$  indicated non-lignin products in the lower reaches derived from the Sabri tributary. The C/V ratios in sediments were higher (>0.4) in the upper and middle reaches compared to the lower reaches (0.25 to 0.32). The average S/V ratio of sediments was  $\geq 1$  and remained constant along the entire basin (Table 3). Figure 3c shows elevated levels of sedimentary  $(Ad/Al)_v$  at the stations after each dam than the before. Sediments from the lower reaches showed higher  $(Ad/Al)_v$  values ( $0.7 \pm 0.4$ ) and lower C/V ratio ( $0.3 \pm 0.1$ ; Table 3).



The distribution of P/ (V+S) in the sediment was similar along the mainstream except higher values in the lower reaches and the lower tributary (Table 3). Higher P/ (V+S) was found in between the dam site and the plain region (Figure 3d). Sediments of the upper and lower mainstream exhibited lower Pn/P ratios and compares to that of the middle and deltaic region (Table 3; Figure 3e).

### 3.4 Statistical results

The interrelationship among the bulk properties and lignin phenols are calculated using Pearson's 2-tier correlations. Both silt (%) and sand (%) in sediments were significantly correlated with OC ( $R^2= 0.62$ ;  $p \leq 0.01$ ). This could be due to the OC of coarser particles was derived from soil or plant debris and in finer particles OC derived from algal detritus or microbial degraded products of the soils. This was further confirmed by a significant correlation between OC vs.  $\Sigma 8$  ( $R^2=0.65$ ;  $p \leq 0.01$ ), a negative correlation ( $p \geq 0.05$ ) between all grain size parameters vs.  $\Sigma 8$  and a significant correlation between C/V and silt content ( $R^2= -0.71$ ;  $p \leq 0.01$ ).

## 4. Discussion

Reduced SWM rainfall and increased damming in the Godavari catchment caused a non-linear reduction in annual sediment load (~ ten fold) in the last two decades; however, the reduction is highly significant in last half decade. Water storage capacities of the dams in this basin have been increased substantially in the end of 20<sup>th</sup> and begin of 21<sup>st</sup> century, which is responsible for the lower water levels across the river streams. The apparently clean and stagnant water helped in production of algae and contributed to the riverine OM composition. This is consistent with the lower  $\Lambda 8$  and  $\Sigma 8$  after the dam than before. The variability in rainfall within the tropical rivers such as Amazon exhibited OM compositional change owing to OM enhancement from previously deposited sediments in flood plains (Hedges et al. 1986; Dunne et al. 1998). The Godavari system is comparatively small and the developments of floodplains are mostly sandbars. These sandbars presumably responsible for the sediment sorting processes in the mainstream, and therefore the mixture of autochthonous and degraded material from the catchment significantly contributed to the riverine OM composition.

#### 4.1 Composition and sources of organic carbon in the Godavari River system

Agriculture soil samples from the rice fields of the Godavari basin exhibited low  $[C/N]_{\text{atom}}$  ratios compared to other fields and are due to higher nitrogen assimilation during fertilizer usage. Fertilizer usage in the deltaic plain of the Godavari basin is double than the national average ( $\sim 49.34 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) (Acharyya et al. 2012). Low  $[C/N]_{\text{atom}}$  of agricultural plants compared to the higher plants in this study appears to have higher potential for further decomposition in soil (Milroy et al. 2001; Li et al. 2009). The still lower  $[C/N]_{\text{atom}}$  ratios in TSM than in soils indicated a mixture of phytoplankton and soils (Balakrishna et al. 2005). The  $[C/N]_{\text{atom}}$  ratios of up to 28 in the sediments of up to 28 indicated the contribution of OC from fresh plant remains ( $C/N > 12$ ; Goñi et al. 2003) such as tree leaves, grass and herbaceous plants (Hedges et al. 1986).

Stable isotopic ratios of organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) have been used widely for identifying potential source of OM in different aquatic regimes (Hedges et al. 1986; Goñi et al. 2003; Zhang et al. 2007; Wu et al. 2007 and references therein).  $\delta^{13}\text{C}_{\text{org}}$  in terrestrial plants are conjectured as per their photosynthetic pathways, for example, C3 plants follow the Calvin-Benson cycle and exhibit lighter values ( $-22\text{‰}$  to  $-33\text{‰}$ ) than C4 plants using the Hatch-Slack pathways ( $-10\text{‰}$  to  $-20\text{‰}$ ) (Hatch and Slack, 1970; Bender, 1971). Compared with the other tropical river basins of the world, soils from the Godavari basin exhibited a narrower range of  $\delta^{13}\text{C}_{\text{org}}$  ( $-19.1\text{‰}$  to  $-23.9\text{‰}$ ) than Amazon soils ( $-14\text{‰}$  to  $-27\text{‰}$ ; Freitas et al. 2001) indicating a mixed signatures of savanna, tropical grassland, and tropical forest (Asouti and Fuller, 2008). TSM shows a wide range of  $\delta^{13}\text{C}_{\text{org}}$  ( $-19.3\text{‰}$  to  $-25.4\text{‰}$ ) compared to Amazon ( $-24.5\text{‰}$  to  $-30.1\text{‰}$ ; Hedges et al. 1986), Congo ( $-26.3\text{‰}$  to  $-27.8\text{‰}$ ; Mariotti et al. 1991), Orinoco ( $-24.4\text{‰}$  to  $-29.5\text{‰}$ ; Tan and Edmond, 1993) and Mekong ( $-29\text{‰}$ ; Ellis et al. 2012). Unlike the diagenetic and metabolic fractionation of OM sources occurring in Amazon and Orinoco (Hedges et al. 1986; Tan and Edmond, 1993), in Godavari basin the OM from algae and agriculture soil are responsible for the variability of  $\delta^{13}\text{C}_{\text{org}}$ . The heavier values of  $\delta^{13}\text{C}_{\text{org}}$  of the sediments in the upper reaches and the depleted values in the lower reaches correspond to the distinct vegetation pattern (C4 to C3). Low  $[C/N]_{\text{atom}}$  ratios ( $>8-13$ ) and depleted  $\delta^{13}\text{C}_{\text{org}}$  ( $-26\text{‰}$  to  $-27\text{‰}$ ) observed in sediments along the middle and lower reaches were due to contributions of freshwater algae. OC content of  $\sim 6\%$  found in the sediment in the middle reaches (one place) could be enhanced from the coal mining remnants.

Lignin, a macromolecule synthesized only by vascular plants, is used as sensitive biomarker to identify terrestrial OM (plant OC) in TSM and sediments from different aquatic systems (Hedges et al. 1984; Cotrim da Cunha et al. 2001; Goñi et al. 2003; Yu et al. 2011). Carbon-normalized lignin yield ( $\Lambda 8$ ) and mass normalized lignin yield ( $\Sigma 8$ ) have been used in this study to estimate the lignin contribution to the OC and to the total sample. Compositional ranges of the S/V and C/V ratios of soils from the Godavari basin suggest that soils are a potential mixture of angiosperm woody and non-woody tissues (Hedges and Mann, 1979). Higher  $(Ad/Al)_v$  of soils ( $>0.4$ ) in our study suggests microbial degradation of lignin molecules in the soil (Hedge et al. 1988; Goñi et al. 1993; Opsahl and Benner, 1995). Sediment and TSM samples correspond to the mixing between non-woody angiosperm leaves/grasses and angiosperm woody materials (Figure 4a). Lower C/V ratio in TSM attributed to degraded lignin products derived from agriculture soils (Hedge et al. 1988). High  $\Lambda 8$  associated with low C/V ratios and depleted  $\delta^{13}C_{org}$  in the lower reaches sediments indicated OM sources from decayed woods or degraded soil. In addition, the significant correlation between OC and  $\Sigma 8$  (see section 3.4) indicated an enhancement of plant OM present in the agriculture soils. Shift agriculture practice predominantly carried out in this basin causes higher agriculture soil erosion ( $40 \text{ t ha}^{-1} \text{ yr}^{-1}$ ) compared to forest soil erosion ( $< 5 \text{ t ha}^{-1} \text{ yr}^{-1}$ ; Singh et al. 1992). Apparently no correlation exists between the grain size parameters and  $\Sigma 8$  in the sediment suggesting that OM in sediments is partially mixed of detritus (from the algal growth region) or microbial degraded land soils. This is evident from a significant negative correlation between C/V and silt content (see section 3.4) of the sediment as cinnamyl phenols are prone to microbial degradation in plant detritus (Hedges et al. 1988). Higher  $(Ad/Al)_v$  ( $>0.4$ ) and lower C/V ratios in the lower reaches sediments attribute to a mixture of degraded soil OM composed of decayed wood affected by soft or white-rot fungi (Figure 4b; Hedges et al. 1988; Goñi et al. 1993). Low water level along the mainstream due to damming favors decay of plant tissues under aerobic conditions and causes degradation of lignin molecules exhibiting higher  $(Ad/Al)_v$  to the sediment (Hedges et al. 1988; Opsahl and Benner, 1995). Higher P/ (V+S) together with lower Pn/P ratios in the lower reaches sediment including the lower tributary (Sabri) corresponded more to a mixture of autogenic OM rather than lignin degradation due to demethylation (Dittmar and Lara, 2001). Furthermore, mean Pn/P of above regions are between 0.07 and 0.08, which is lesser comparatively Pn/P value obtained when obtained from terrestrial plants (Teisserenc et al., 2010). Therefore algal OM seems only the secondary source after terrestrial plants. Apart from  $[C/N]_{atom}$  ratios we made another approach to characterize the lignin poor (algae) vs. lignin rich (plant) OM sources. Figure 4c shows the significant positive

correlation ( $R^2 = 0.68$ ;  $p \leq 0.05$ ) between  $\Lambda 8$  and  $[C/N]_{\text{atom}}$  of the different samples (plants, plankton, TSM and surface sediments) which has a positive intercept (10.4) of  $[C/N]_{\text{atom}}$  at  $\Lambda 8 = 0$ . This indicates that the lignin free OM is more carbon rich than plankton ( $[C/N]_{\text{atom}} \sim 6.6$ ; Redfield et al. 1963). Therefore it is possible that a preferential degradation of nitrogen in plankton remains and the degradation of lignin in vascular plant material are two important processes for changes of the OM composition (Hedges et al. 1984). The correlation between  $\Lambda 8$  and  $[C/N]_{\text{atom}}$  ratio of soil samples is negative ( $R^2 = 0.67$ ;  $p \leq 0.05$ ) which suggests that lignin in agriculture soils exhibit a lower  $[C/N]_{\text{atom}}$  ratio probably due to more nitrogen rich molecules acquired from fertilizer application.

#### 4.2 Assessment of organic matter sources

To evaluate the contribution of different OM sources we used a three end member mixing model. The plot between  $[N/C]_{\text{atom}}$  and  $\delta^{13}\text{C}_{\text{org}}$  indicated that the three end members, C3 plants, C4 plants and freshwater algae, potentially contributed to TSM and sediments (Figure 4d). The contribution of the OM sources is calculated based on the equations

$$1 = f_{\text{C3}} + f_{\text{C4}} + f_{\text{Alg}} \quad (1)$$

$$[N/C]_{\text{S}} = f_{\text{C3}} [N/C]_{\text{C3}} + f_{\text{C4}} [N/C]_{\text{C4}} + f_{\text{CAlg}} [N/C]_{\text{CAlg}} \quad (2)$$

$$\delta^{13}\text{C}_{\text{S}} = f_{\text{C3}} \delta^{13}\text{C}_{\text{C3}} + f_{\text{C4}} \delta^{13}\text{C}_{\text{C4}} + f_{\text{CAlg}} \delta^{13}\text{C}_{\text{CAlg}} \quad (3)$$

where “f” indicates the fraction of OM from the different end members.  $[N/C]_{\text{atom}}$  is the ratio of atomic nitrogen and OC in sediment (S), C3 plant (C3), C4 plant (C4) and river algae (Alg). Similarly  $\delta^{13}\text{C}_{\text{org}}$  is their isotopic compositions. Absolute errors for the end members  $[N/C]_{\text{atom}}$  and  $\delta^{13}\text{C}_{\text{org}}$  is estimated as  $\sim 14\%$  for C3 plants,  $6\%$  for C4 plants and  $18\%$  for river algae. The average limits of  $[N/C]_{\text{atom}}$  and  $\delta^{13}\text{C}_{\text{org}}$  for C3 plants ( $0.04 \pm 0.02$ ;  $-29.1 \pm 0.6\text{‰}$ ), C4 plants ( $0.03 \pm 0.01$ ;  $-11.5 \pm 0.7\text{‰}$ ) and river algae ( $0.12 \pm 0.01$ ;  $-25.6 \pm 0.5\text{‰}$ ) was used as end members. The variation in the contributions was calculated using the simple standard deviations of  $[N/C]_{\text{atom}}$  and  $\delta^{13}\text{C}_{\text{org}}$  of end member. The average limits of  $[N/C]_{\text{atom}}$  and  $\delta^{13}\text{C}_{\text{org}}$  for C3 as well as C4 plants were chosen from the observed values for plant samples collected from Godavari basin (Table 1). The isotopic limits for plants found here is consistent with previous studies in other tropical region (Hedges et al., 1986; Hamilton and Lewis JR, 1992). The TSM samples from algae growth water (i.e. close to the dam) in Godavari basin showed  $\delta^{13}\text{C}_{\text{org}}$  between -

25.1‰ and -26.1‰ whereas the N/C varied between 0.11 and 0.13. These values were within close proximity of  $\delta^{13}\text{C}_{\text{org}}$  of tropical river algae, therefore chosen as the limit of algal end member in Godavari system. The limits of  $\delta^{13}\text{C}_{\text{org}}$  of algae (-23.4‰ to -33‰; Hamilton and Lewis JR, 1992) and (-25.6 ± 1‰; Yu et al., 2010) were previously reported for tropical river systems. Based on the model, river algae contributed 50 to 65% to the OM in TSM; the contribution is higher than that from C4 and C3 plants near the dam impoundment (Sriram Sagar) due to higher algal growth. Higher contributions from algae to the TSM presumably dilute the fraction of  $\Delta 8$  near the dam impoundment whereas higher rainfall in the lower reaches would enhance lignin input from lower reaches and delivered into the estuary. Increased contributions from C3 plant OM in the lower reaches was due to higher water delivery from the lower tributaries (Indravati and Sabri) flowing through dense forest. In the deltaic region both fresh water and estuarine algae contributed OM to TSM minimizing the contribution from plants. Reduced river discharge caused water column stabilization and increased estuarine phytoplankton growth in recent years (Acharyya et al. 2012). The sedimentary OM in the upper reaches was dominated by C4 plants and river algae (40-45%) due to algal growth in the river and arid conditions which favor growth of C4 vegetation in the region. The OM source from C3 plants increased towards the lower reaches (~54%) minimizing the contribution from C4 plants (20%). The sedimentary OM in the lower reaches was characterized by C3 plants and river algae (~45%) indicating higher contributions from forests and estuarine mangrove vegetation.

#### *4.3 Terrestrial organic carbon flux of the Godavari system*

Reduced monsoon rainfall and increased damming make it difficult to determine the carbon flux from the Godavari basin to the BOB. Based on recent sediment load data obtained from the CWC, the POC flux estimated from our study is  $0.22 \times 10^{12} \text{ g yr}^{-1}$  which is three fold less than reported in Balakrishna et al. (2005) and ten fold less than reported in Gupta et al. (1997). The higher POC flux in the past was due to a higher sediment load ( $170 \times 10^{12} \text{ g yr}^{-1}$ ) and sporadic mass transports (Balakrishna et al. 2005). POC and lignin fluxes in the Godavari river basin are depicted in Figure 5. A significant portion of POC is lost in the middle and lower reaches behind the dam either caused by rapid burial and/or oxidation of labile OM. The POC flux is reduced more than 50% in the mainstream between the Pranahita and Indravati tributaries despite the higher POC flux ( $0.1 \times 10^{12} \text{ g yr}^{-1}$ ) from Pranahita (Figure 5). The significant increase of the POC flux in the region between Pranahita and Indravati is probably

due to the Indravati tributary (not sampled) contributing significantly to the annual carbon flux from Godavari basin.

Our study constitutes the first report of lignin fluxes in the particulate phase from any monsoon fed Indian River. The lignin flux was calculated as the product of mass normalized lignin yield ( $\Sigma 8$ ) of TSM and the average annual sediment load at the different sites in the Godavari basin. The lignin flux decreased from the upper to the middle reaches (~14 fold) suggesting an entrapment or loss of plant OM in the middle reaches behind the dam. The sediment trapping efficiency of the Sriram Sagar dam is about 72%, the highest among all. However, the low lignin flux from the middle reaches ( $0.001 \times 10^9 \text{ g yr}^{-1}$ ) could also be caused by the presence of lignin free compounds such as algae or soil OM with less lignin concentrations. The lignin flux from Godavari basin shows a direct linear relationship with the annual sediment load [lignin flux ( $\times 10^9 \text{ g yr}^{-1}$ ) =  $0.602 \times$  sediment load ( $\times 10^{12} \text{ g yr}^{-1}$ ) - 0.02;  $R^2=0.99$ ]. The lignin flux at the terminal site (Rajahmundry) was  $7.26 \times 10^9 \text{ g yr}^{-1}$  which is ~1.7 fold higher than at the previous site (Bhadrachalam) indicating a clear input of plant tissues from the lower tributaries.

The annual lignin flux from the Godavari basin is  $7.26 \times 10^9 \text{ g}$ , which is nearly half of the same from Yangtze River ( $14.8 \times 10^9 \text{ g yr}^{-1}$ ; Yu et al. 2011) and much lower than from the major world rivers such as Mississippi River ( $17 \times 10^9 \text{ g yr}^{-1}$ ; Bianchi et al. 2007b) and Amazon River ( $250 \times 10^9 \text{ g yr}^{-1}$ ; Hedges et al. 1986). However, compared to the lignin fluxes from large arctic rivers it is much higher (Lobbés et al. 2000). The ratio of POC/lignin flux is controlled by factors such as weathering or erosion in the drainage basin, vegetation cover and climate setting. The plot between POC/lignin flux and annual sediment yield of world rivers (Figure 6) indicates that tropical rivers such as Godavari, Amazon and Mekong shows lower POC/lignin compared to the northern most rivers (Yana, Yenisey and Lena). Higher sediment yield and lower POC/lignin in tropical rivers indicate that the lignin contribution to POC in these basins is enhanced through soil OM or fresh plant OM during high flow conditions. However, reduced SWM rainfall and damming in peninsular Indian rivers such as the Godavari basin enhance OM from mixture of degraded land soils and river algae in its catchment with an input of C3 plant OM in the lower reaches.

## 5. Summery & Conclusion

Bulk isotopic compositions and lignin phenols were measured in the Godavari basin to understand the sources of OM and their composition. The bulk parameters in TSM and sediments were

determined by a mixture of agriculture soils and freshwater algae as well as C3 and C4 vegetation in the catchment. The upper and lower tributaries are responsive to distinct vegetation and agriculture cover in the upper to lower basins. The OM in TSM samples was dominated 50-65% by freshwater algae. Sedimentary OM was characterized by C3 plants and their contribution increased from the upper to the lower reaches with decreasing contributions from C4 plants. Deltaic sediments were dominated by OM from C3 plants with a minimal contribution from C4 and river algae. When compared to the OC source in Himalayan Rivers, such as Ganges, as a mixture of fossils from Himalayan rock and natural vegetation (Galy et al. 2008), the sources of OC in the Godavari sediment is mostly plant derived (C3 or C4) depending on their relative distribution in the catchment. Reduced SWM rainfall and increased water storage in the dams caused enhancement of algal OM in the riverine TSM and sediments and might not resistant to OM oxidation during fluvial transport. The OC concentration in sediments from peninsular Godavari basin is higher compared to that in Himalayan Rivers (Subramanian and Ittekkot, 1991; Aucour et al. 2006; Galy et al. 2007).

The composition of lignin phenols indicated that the TSM of the Godavari basin is characterized by fresh plant tissues in the lower reaches and degraded plant materials in the upper reaches. The sediments were composed of non-woody angiosperm leaves and grasses, except in the lower reaches and deltaic region which shows angiosperm woody material. The annual lignin export from the Godavari basin is much lower compared to some world large rivers (e.g. Amazon, Mekong and Yangtze). Extreme drought condition due to mutual impact of lower SWM and increased water storage in the dams on peninsular rivers (Godavari) generated significant fraction of labile OM from river algae during study year.

Although the non-linear distribution of the declining sediment load is consistent with the SWM rainfall variability the increased damming in the Godavari basin substantially reduced its annual sediment load in the last half decade. Such conditions significantly controlled the characteristics and amount of terrestrial OM delivered from the peninsular Godavari basin. In view of this information on seasonal variability of OM composition and their relationship with the inter-annual variability of SWM events (dry and wet years) might obscure the exact patterns of OM enhancement in this basin. Understanding the impact of excess fertilizer usage and biomass burning together with controlled river runoff condition will be an asset towards the knowledge of functioning of anthropogenic processes on compositional OM change in monsoonal river basins of India. In view of reducing terrestrial OM flux

policy measures on soil and water conservation in the peninsular rivers (such as Godavari basin) are required also towards further constructions of dams.

## **Acknowledgements**

The authors would like to thank Director NIO for constant support for this study. The sampling campaign was organized by PVS group and Dr. P.Babu (National Institute of Oceanography). Technical help from Mr. R. Wu in grain size measurement is deeply appreciated. Analytical measurements done at the State Key laboratory of Estuarine and Coastal Research and expenses were met under Natural Science Foundation of China grants (Nos.41021064, 41076052), SKLEC (2010RCDW04, 2012RCDW05), 111 project (B08022). UKP sincerely thank to Ministry of Human Resource Development, Department of Higher Education, Government of India and Chinese Scholarship Council, PR China for providing visiting fellowship. WY thanks for AvH Foundation's support. Finally the authors express their sincere thanks to anonymous reviewers.

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## Figure captions

**Figure 1** (a) Location of Godavari River basin in the tropical (central-peninsular) India (b) location of sampling sites along the river basin during. Solid circles represent riverine samples (sediment and TSM) and triangles indicated the agriculture soil samples. Black circles with numeric inside indicate the position of the dams and their respective water volumes have been mentioned below. The directions of the SW and NE monsoon have been indicated by arrow marks (source: [www.imd.gov.in](http://www.imd.gov.in)). A Solid double line indicated the proposed canal (175 km) joining the Godavari and Krishna River. (c) Enlarged view of the deltaic region.

**Figure 2** (a) Inter annual variability of south west monsoon (SWM) and mean monthly values of rainfall during last half decades across Godavari basin (data sourced from IMD), (b) Total fresh water storage capacity of dams over Godavari basin (data sourced from National register of large dams, NRLD). (c) Long term inter annual variability of sediment load at the terminal site of Godavari river system (data sourced from CWC).

**Figure 3** Plot of spatial distribution of CuO oxidation products and their ratios in sediment samples together with the sediment yield of different tributaries draining into the mainstream. Solid circles represent the sediment samples and grey bars represents average sediment yield of tributaries. Vertical dotted lines represented the dam positions along the mainstream.

**Figure 4** (a) Property–property plot of C/V and S/V ratio; (b) oxidative degradation of V and S phenols and (c) interrelationship between elemental ratio and lignin phenols in environmental samples from Godavari. (d) Elemental and stable isotopic compositional limits samples (TSM, sediment) and end members (agriculture soil and C3 and C4 plants) from Godavari river basin. Tributary sediments are presented as plus sign in the graph and their names as T1: Pravara, T2: Purna, T3: Pranahita, T4: Manjira, T5: Sabri. End member compositional ranges are plotted as average  $\pm$  standard deviation. The highlighted grey boxes are the published ranges of different ratios, adapted from Hedges and Mann, (1979); Hedges et al. 1986; Goñi and Hedges, (1992).

**Figure 5** Schematic diagram of mean annual water discharge and sediment load at different locations along the mainstream of Godavari River. Histograms represent the mean annual water discharge from different tributaries draining into the mainstream during the study period. Values inside the transparent and solid arrow symbol represents POC and lignin flux at specific sites respectively. Vertical dotted lines represent positions of dams along the mainstream.

**Figure 6** Ratio between POC and lignin flux vs. sediment yield from World Rivers. (Data source: Bianchi et al. 2007b; Ellis et al. 2012; Hedges et al. 1986; Lobbes et al. 2000; Wu et al. 2007; Yu et al. 2011).

## Table captions

**Table 1** Hydro-geological data of major tributaries of Godavari basin.

**Table 2** Bulk compositional parameters in different samples from Godavari basin.

TSM: Total suspended matter; OC: organic carbon (wt. %);  $[C/N]_{\text{atom}}$ : atomic ratio of organic carbon and total nitrogen;  $\delta^{13}C_{\text{org}}$ : stable isotope ratio of organic carbon.

**Table 3** CuO oxidation product ratios in different samples from Godavari river system.

$\square 8$ : Carbon normalized lignin yield ; CuO: Relative abundance of lignin (S+V+C) oxidation products;  
 $\square 8$ : Mass normalized yield of lignin phenols; P/(V+S): Ratio between total P and sum of vanillyl (V) and Syringyl (S) phenols; Pn/P: Ratio between p-hydroxyacetophenone and total P phenols; C/V: Ratio between cinnamyl (C) and vanillyl (V) phenols; S/V: Ratio between syringyl (S) and vanillyl (V) phenols; (Ad/Al)<sub>v</sub>: acid to aldehyde ratios of V phenols.

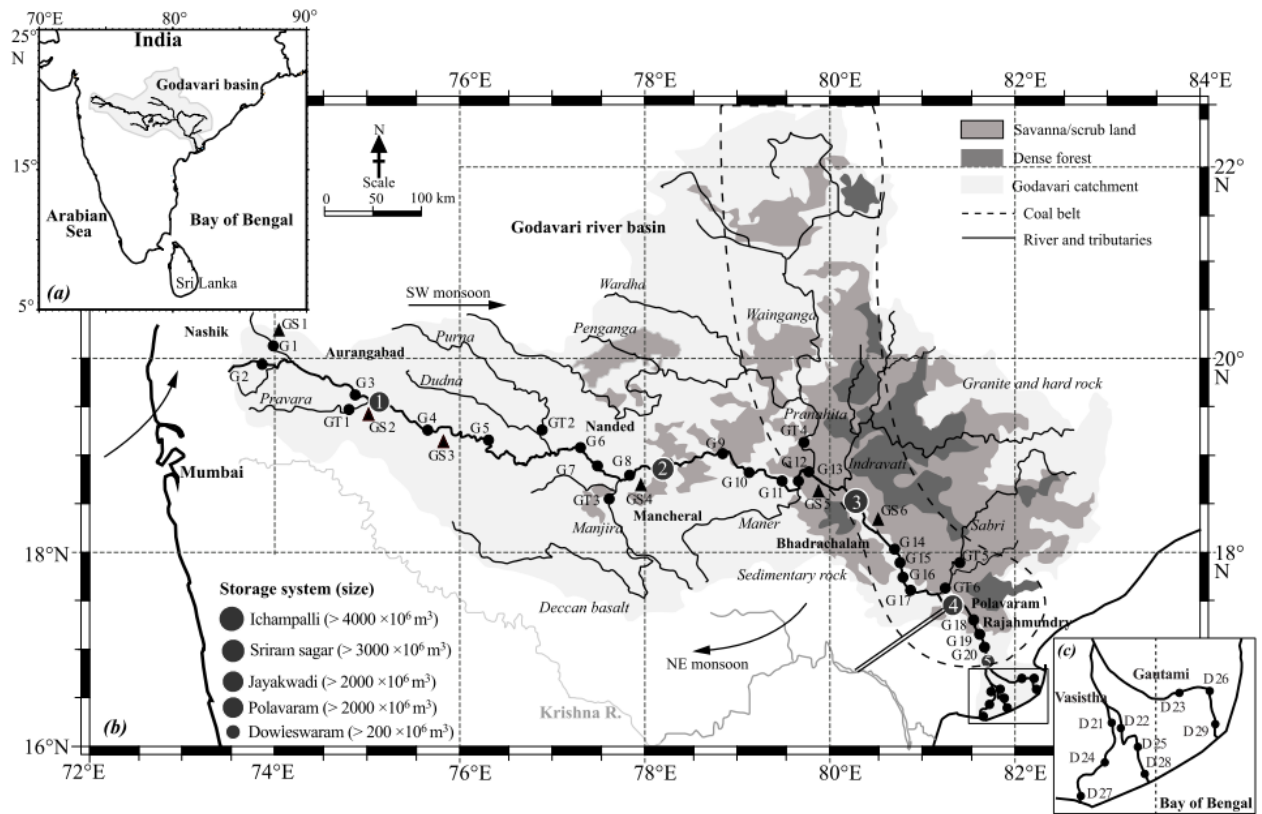


Figure 1

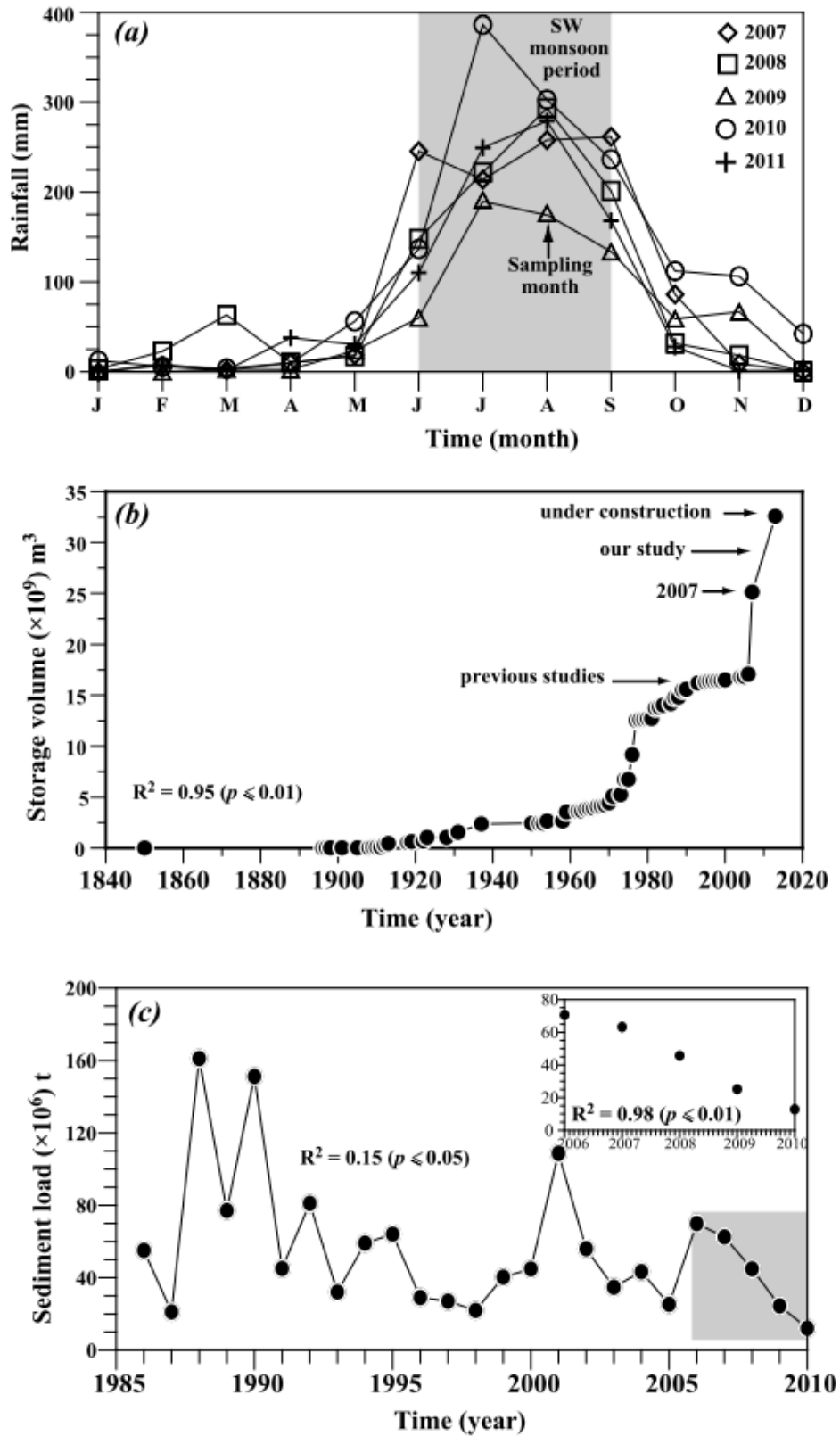


Figure 2



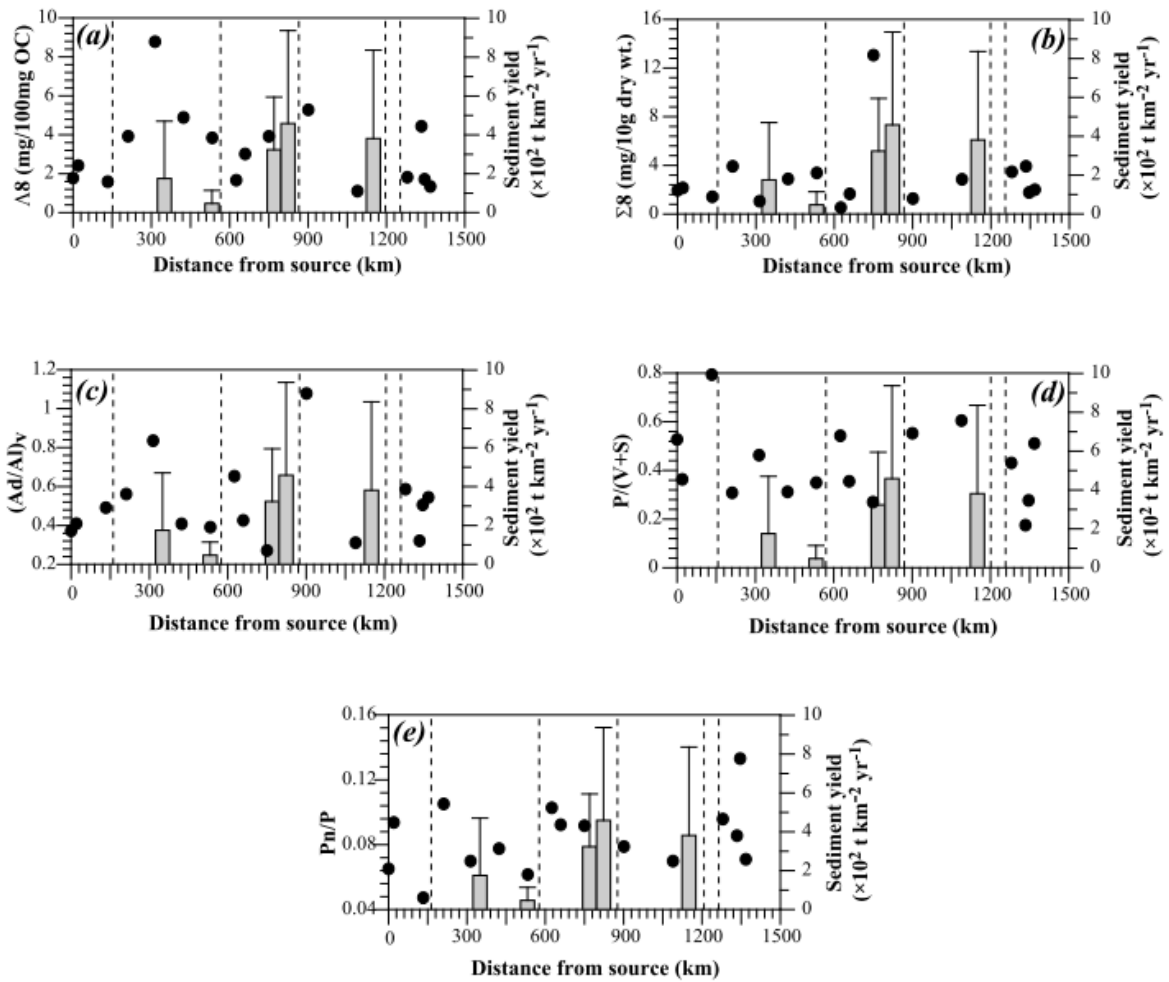


Figure 3

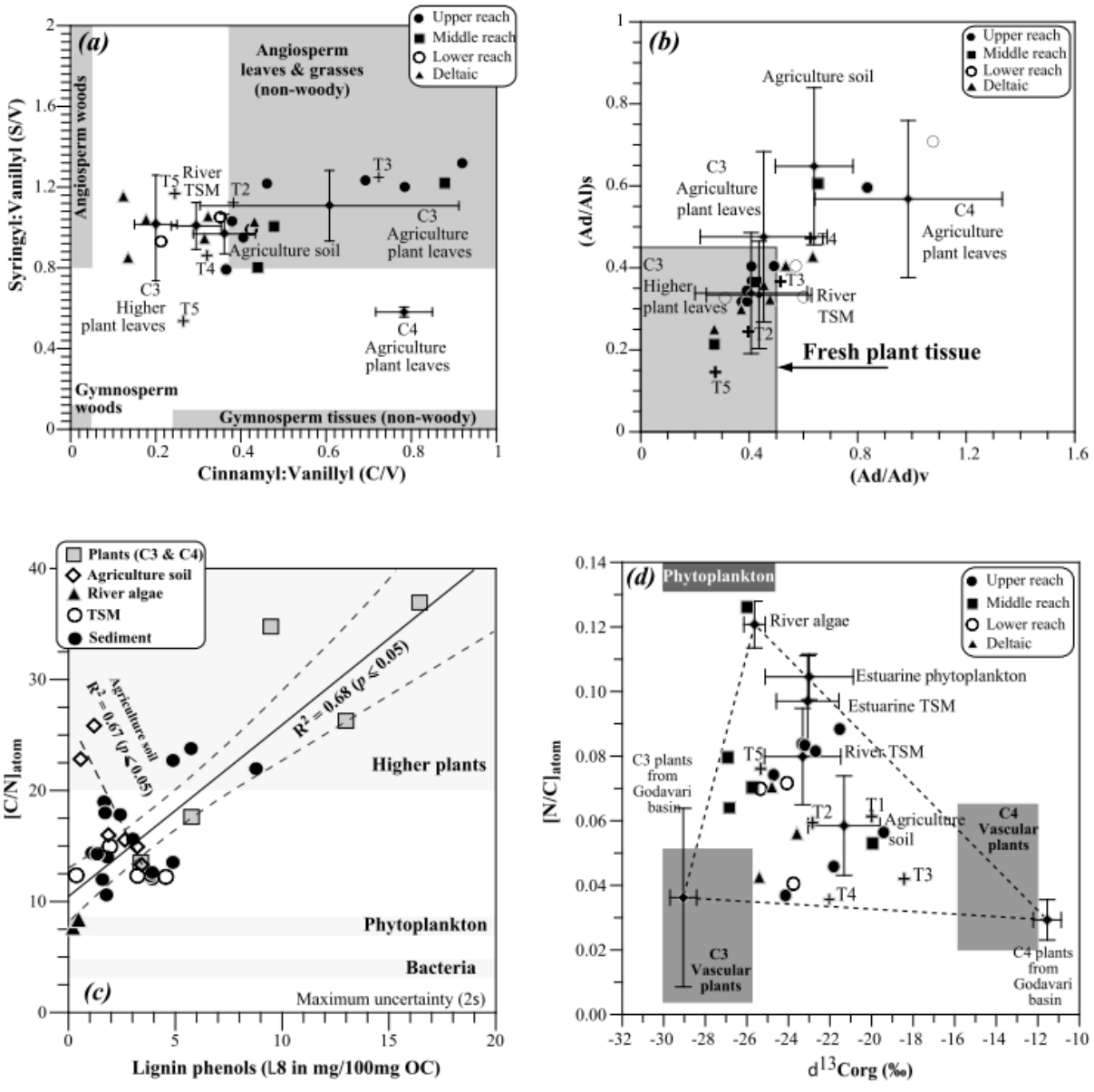


Figure 4

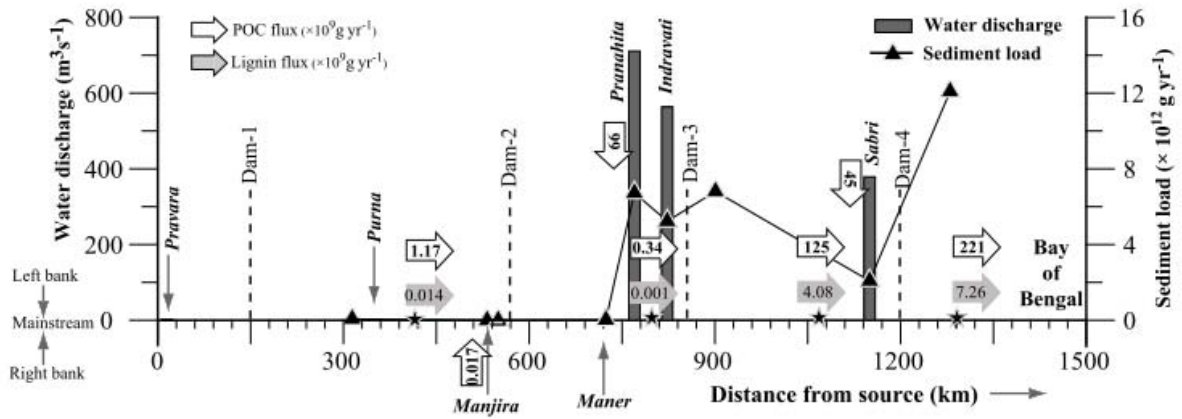


Figure 5

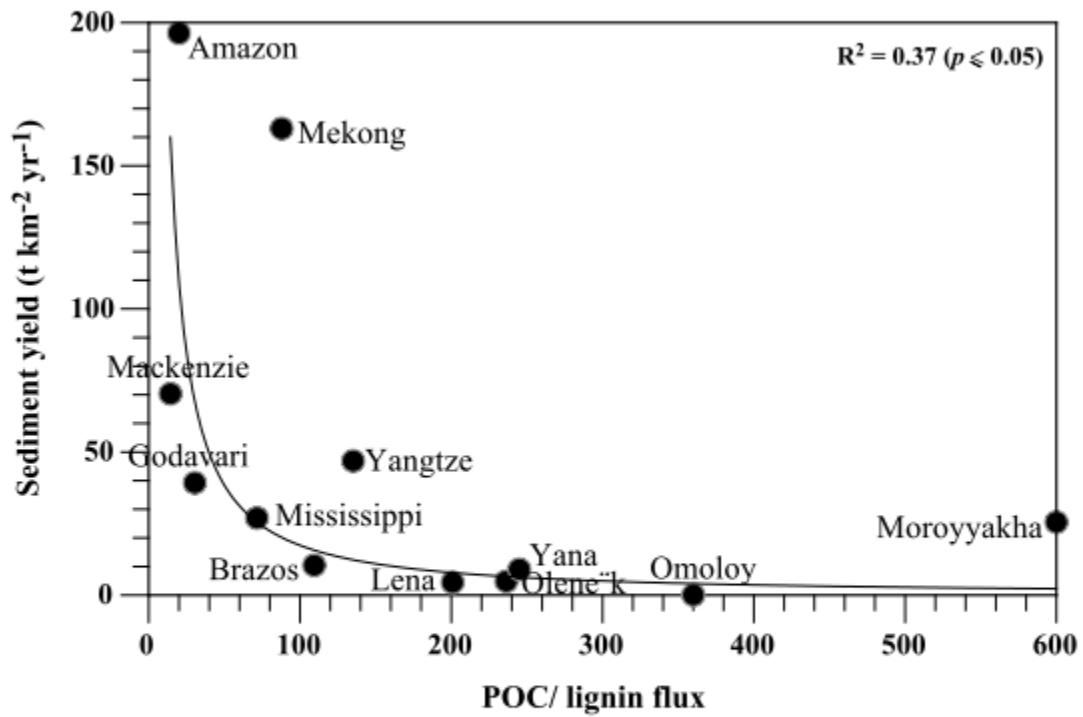


Figure 6

**Table 1**

<b>Name of the tributary (region in Godavari basin)</b>	<b>Catchment area <math>\times 10^3 \text{ km}^2</math></b>	<b>Water discharge <math>\times 10^9 \text{ m}^3 \text{ yr}^{-1}</math></b>	<b>Sediment load <math>\times 10^6 \text{ t yr}^{-1}</math></b>	<b>Sediment yield <math>\text{t km}^{-2} \text{ yr}^{-1}</math></b>
Pravara (upper)	5.8	$0.5 \pm 0.6^{\text{d}}$	na	na
Purna (upper)	15.0	$1.5 \pm 1.6^{\text{d}}$	$2.6 \pm 4.4^{\text{b}}$	$175.3 \pm 295.1$
Manjira (upper)	9.9	$0.8 \pm 1.2^{\text{d}}$	$0.5 \pm 0.7^{\text{a}}$	$47.1 \pm 67.2$
Maner (middle)	2.1	$0.2 \pm 0.2^{\text{d}}$	na	na
Pranahita (middle)	108.7	$26.8 \pm 20.4^{\text{d}}$	$35.2 \pm 29.5^{\text{a}}$	$323.7 \pm 271.1$
Indravati (lower)	40.0	$23.5 \pm 9.9^{\text{c}}$	$18.3 \pm 19.1^{\text{a}}$	$458.7 \pm 478.1$
Sabri (lower)	19.5	$15.3 \pm 4.7^{\text{d}}$	$7.5 \pm 8.9^{\text{a}}$	$381.4 \pm 455.2$

<sup>a</sup> average values for the period 1992-2009; <sup>b</sup> average values for the period 1992-2005; <sup>c</sup> average values for the period 1990-2005; <sup>d</sup> average values for the period 1990-2009; <sup>na</sup> data not available.

Table 2

Samples	OC (%)	TN (%)	[C/N] <sub>atom</sub>	$\delta^{13}\text{C}_{\text{org}}$ (‰)
<b>TSM</b>				
Upper mainstream (n=8)	1.10 ± 0.1	0.08 ± 0.07	13.3 ± 1.4	-22.2 ± 1.9
Middle mainstream (n=5)	2.19 ± 1.6	0.17 ± 0.15	12.6 ± 3.1	-24.7 ± 0.9
Lower mainstream (n=7)	1.96 ± 0.1	0.16 ± 0.13	12.0 ± 0.3	-24.5 ± 0.3
Upper tributaries (n=3; Pravara, Purna & Manjira)	1.29 ± 0.6	0.08 ± 0.03	15.7 ± 7.7	-20.9 ± 2.3
Middle tributary (n=1; Pranahita)	1.48	0.12	12.2	-23
Lower tributary (n=1; Sabri)	2.16	0.19	11.5	-23.3
Deltaic (Gautami branch; n=3)	1.00	0.11	9.1	-21.5
Deltaic (Vasishta branch; n=3)	1.15	0.09	12.2	-23.2
<b>Sediment</b>				
Upper mainstream (n=5)	0.68 ± 0.2	0.04 ± 0.03	15.9 ± 6.0	-22.4 ± 2.0
Middle mainstream (n=5)	2.08 ± 2.3	0.15 ± 0.12	13.9 ± 4.1	-25.1 ± 2.9
Lower mainstream (n=3)	1.57 ± 1.1	0.09 ± 0.05	17.7 ± 6.2	-24.4 ± 0.8
Upper tributaries (n=3; Pravara, Purna & Manjira)	0.84 ± 0.3	0.04 ± 0.02	19.1 ± 4.2	-20.4 ± 2.2
Middle tributary (n=1; Pranahita)	0.76	0.03	28.0	-22
Lower tributary (n=1; Sabri)	1.71	0.12	14.1	-24.4
Deltaic (n=3; Gautami branch)	1.31 ± 0.2	0.07 ± 0.03	18.0 ± 2.0	-23.6 ± 1.8
Deltaic (n=3; Vasishta branch)	1.70 ± 1.0	0.12 ± 0.04	14.3 ± 2.1	-24.8 ± 1.1
<b>Agriculture soil (Godavari basin)</b>				
Grape field (upper)	2.26	0.09	26.3	-21.3
Sugarcane field (upper)	1.10 ± 0.1	0.07 ± 0.03	15.5 ± 0.8	-17.9 ± 1.8
Rice field (middle & lower)	0.89	0.07	13.3	-21.8
Vegetable field (middle & lower)	0.81	0.05	15.5	-23.9
Pulses field (middle & lower)	0.97	0.04	22.8	-20.5
<b>Plant (type)</b>				
<i>Sorghum vulgare</i> leaf (C4)	35.1	1.01	34.8	-11.5
<i>Zea mays</i> var. <i>rugosa</i> leaf (C4)	32.0	1.22	26.3	-11.5
<i>Saccharum officinarum</i> leaf (C4)	33.8	0.92	36.9	-12.4
<i>Sorghum vulgare</i> fruit (C4)	36.7	0.86	42.8	-10.8
<i>Gossypium sp.</i> leaf (C3)	31.6	2.34	13.5	-28.5
<i>Artocarpus heterophyllus</i> leaf (C3)	38.9	0.42	91.6	-29.8
<i>Tectona grandis</i> leaf (C3)	32.5	0.52	62.7	-28.3
<i>Oryza sativa Indica</i> leaf (C3)	31.0	1.76	17.6	-29.6
<i>Oryza sativa Indica</i> fruit (C3)	32.7	0.77	42.6	-29.1

Table 3

Samples	CuO oxidation product ratios							
	$\Delta 8$ mg/100mg OC	CuO %	$\Sigma 8$ mg/10 g dry wt.	P/(V+S)	Pn/P	C/V	S/V	(Ad/Al) <sub>v</sub>
<b>TSM</b>								
Upper mainstream (at Nanded)	1.94	72.4	2.08	1.91	0.06	0.43	1.23	0.31
Middle mainstream (at Kandakurti)	0.37	38.1	0.55	3.86	0.04	0.37	0.91	0.77
Lower mainstream (at Parnasala)	3.24	86.4	5.99	1.84	0.19	0.36	1.10	0.50
Upper tributary (at Purna)	1.45	76.9	1.20	1.01	0.08	0.18	0.59	0.39
Lower tributary (at Konta)	1.15	70.4	2.49	1.50	0.11	0.30	1.05	0.44
Deltaic region (Vasistha branch)	4.56	79.4	5.24	2.92	0.06	0.13	1.17	0.21
<b>Sediment</b>								
Upper mainstream (n=5)	3.89 ± 2.5	72.9 ± 7.6	2.41 ± 1.0	0.45 ± 0.2	0.07 ± 0.01	0.57 ± 0.2	1.09 ± 0.2	0.47 ± 0.2
Middle mainstream (n=5)	2.87 ± 1.1	75.5 ± 6.6	5.08 ± 6.9	0.39 ± 0.1	0.11 ± 0.03	0.58 ± 0.2	1.01 ± 0.2	0.45 ± 0.2
Lower mainstream (n=3)	2.74 ± 2.2	70.3 ± 12.4	2.53 ± 1.1	0.53 ± 0.1	0.08 ± 0.01	0.31 ± 0.1	0.92 ± 0.1	0.66 ± 0.4
Upper tributaries (n=2; Purna & Manjira)	1.79 ± 0.3	78.9 ± 5.8	0.96 ± 0.4	0.29 ± 0.1	0.12 ± 0.03	0.55 ± 0.2	1.18 ± 0.1	0.46 ± 0.1
Middle tributary (n=1; Pranahita)	2.34	77.2	1.34	0.25	0.13	0.32	0.86	0.63
Lower tributary (n=1; Sabri)	0.48	34.3	0.82	1.95	0.07	0.25	1.17	0.28
Deltaic region (n=3; Gautami branch)	1.72 ± 0.4	80.5 ± 2.4	1.77 ± 0.7	1.31 ± 0.1	0.13 ± 0.02	0.32 ± 0.01	0.99 ± 0.1	0.51 ± 0.04
Deltaic region (n=3; Vasistha branch)	1.3 ± 0.7	66 ± 15.9	1.56 ± 0.6	1.92 ± 0.7	0.11 ± 0.01	0.31 ± 0.2	0.91 ± 0.1	0.48 ± 0.1
<b>Agriculture soil (Godavari basin)</b>								
Grape field (upper)	1.46	75.9	0.33	1.44	0.05	0.36	1.12	0.57
Sugarcane field (upper)	2.54 ± 1.0	80.9 ± 0.05	0.31 ± 0.1	1.62 ± 0.3	0.11 ± 0.08	0.42 ± 0.1	1.08 ± 0.1	0.72 ± 0.03
Rice field (middle & lower)	2.64	79.1	0.21	1.77	0.08	0.49	1.06	0.70
Vegetable field (middle & lower)	3.43	84.3	0.31	1.83	0.07	0.39	0.95	0.41
Pulses field (middle & lower)	0.57	68.5	0.06	0.98	0.03	0.09	0.61	0.85
<b>Plant (type)</b>								
<i>Sorghum vulgare</i> leaf (C4)	9.47	65.0	33.3	3.42	0.72	0.85	0.54	1.13
<i>Zea mays var. rugosa</i> leaf (C4)	13.0	93.9	41.6	3.78	0.18	0.63	0.63	1.24
<i>Saccharum officinarum</i> leaf (C4)	16.4	93.8	55.6	4.01	0.19	0.87	0.57	0.59
<i>Gossypium sp.</i> leaf (C3)	3.39	77.4	10.7	2.01	0.04	0.56	0.95	0.62
<i>Artocarpus heterophyllus</i> leaf (C3)	10.1	91.6	39.2	5.80	0.45	0.24	1.51	0.26
<i>Tectona grandis</i> leaf (C3)	3.18	71.9	10.3	1.94	0.29	0.16	0.71	0.55
<i>Oryza sativa Indica</i> leaf (C3)	5.76	85.7	17.9	2.56	0.20	1.48	1.25	0.29