# Biogeochemistry of particulate organic matter transported by the Godavari River, India

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**Abstract.** The Godavari River, the third largest river of India, has been sampled for Particulate Inorganic and Organic Carbon (PIC, POC), Particulate Nitrogen (PN), and Particulate Amino Acids (PAA, including 2 hexosamines (HA)). During the dry season Particulate Organic Matter (POM) in the upper reaches is relatively fresh and autochthonous, in the lower reaches it is degraded and inorganic suspended matter content is higher here. In the wet season (wet monsoon) heavy rains cause a basin-wide flushing of humus from entire catchment area consequently POM in the river is mainly degraded and allochthonous. Annual transport of the Godavari River amounts to  $2.81 \times 10^6$  ton POC,  $0.29 \times 10^6$  ton PN and  $0.10 \times 10^6$  ton Particulate Amino Acid Nitrogen. These amounts rank the Godavari River to one of the most important organic carbon transporting rivers in the world.

#### Introduction

River input into the ocean is an important link in the biogeochemical cycling of carbon between its two major pools viz. land and ocean. The carbon compounds in these pools may be in the form of biologically inert metal complexed humic materials, polyphenols and polysaccharides and rather unstable compounds such as polypeptides, fatty acids and carbohydrates, which get easily decomposed in the riverine environment (Degens 1982). The total amount of organic matter transported by rivers annually is extremely low (ca.  $0.5 \times 10^{15} \, \mathrm{g C \ a^{-1}}$ ) in comparison to the two carbon pools linked by the rivers. The amount of carbon held within the soils of the earth is about 1 515  $\times 10^{15} \, \mathrm{g C}$  (Schlesinger 1984) and in the ocean (dissolved and particulate together)  $40.600 \times 10^{15} \, \mathrm{g C}$  (JGOFS 1992).

Total organic carbon (TOC) transported by the rivers to the oceans has been estimated to range from  $0.03 \times 10^{15}$  g C a<sup>-1</sup> (Williams 1971) to  $1.0 \times 10^{15}$  g C a<sup>-1</sup> (Richey et al. 1980). Intermediate values have been proposed,

for instance, by Garrels and Mackenzie (1971)  $0.32 \times 10^{15}$  g C a<sup>-1</sup>, Duce and Duursma (1977) 0.1– $0.15 \times 10^{15}$  g C a<sup>-1</sup>, Schlesinger and Melack (1981)  $0.4 \times 10^{15}$  g C a<sup>-1</sup> and Sarmiento and Sundquist (1992) 0.3– $0.5 \times 10^{15}$  g C a<sup>-1</sup>. On a world average ca.  $0.5 \times 10^{15}$  g C a<sup>-1</sup> organic carbon is being transported by the rivers annually to the ocean. This transport is, in general, equally distributed between dissolved and particulate fraction of the riverine load (Spitzy & Ittekkot 1991). Particulate organic carbon (POC) transport is in the range of 0.19– $0.23 \times 10^{15}$  g C a<sup>-1</sup>, ca. 35% of which ( $0.081 \times 10^{15}$  g C a<sup>-1</sup>) belongs to the labile fraction (Ittekkot & Laane 1991). Though river input is only 7.5% of the primary production, because of its stable nature its contribution to total carbon burial in the coastal areas may be significant (Degens & Ittekkot 1985).

The global particulate nitrogen (PN) transport by rivers amounts to  $33 \times 10^{12}$  g N a<sup>-1</sup>, more than 80% of which occurs in rivers having high suspended matter concentrations, e.g. the Ganges, Brahmaputra, Mekong and Huanghe (Ittekkot & Zhang 1989). Particulate amino acids (PAA) account for about 20% of the PN transport. Deforestation in the drainage basin has been found to increase loss of elements from the soils and their transport via rivers (Vitousek 1983). In addition to this, wide application of fertilisers in catchment area and waste disposals directly into the river channel have led together to a five fold increase in riverine input of nitrogen (Van Bennekom & Salomons 1981). Converse to this apparent increase in riverine transport of nitrogen, retention of nutrients in reservoirs behind large dams has led to reduction of nitrogen input by rivers to the sea (Ittekkot & Arain 1986).

With reference to global carbon cycle modelling, riverine fluxes of carbon need not be further investigated as it makes only about 10% of the annual anthropogenic carbon release. But on regional scale, river carbon flux studies may give important insight into the biogeochemical cycle operating in coastal environments, which are under the direct influence of mass transport by rivers. Other than the direct input of POM, rivers induce high phytoplankton growth in the estuary by supplying nutrients. Climatic and hydrologic extreme events may bring rapid change in mass transport of rivers (Spitzy & Ittekkot 1991). The organic matter in sediments can give valuable information about the organisms and environment at the time of deposition. To make the most efficient use of this information, the nature, distribution, source and fate of the organic matter in contemporary aquatic environments must be studied (Goldberg 1978). Besides the erosion of bed rocks effected by river water, part of weathered material is flushed into the rivers from their catchment areas. Many authors have pointed out the strong influence of continental weathering in the geologic carbon cycle (Walker et al. 1981; Berner et al. 1983; Berner 1991, 1992).

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The major objective of this study is to obtain information on the nature and quantity of POM transported by the Godavari River. In terms of catchment area, water and sediment discharges the Godavari River is the third largest river in India. For the other two rivers, the Ganges and the Brahmaputra, some biogeochemical information is available (e.g. Ittekkot et al. 1985, 1986, 1991; Ramesh et al. 1995), but similar information on the Godavari river is lacking. The present study is an effort to fill in this gap.

## **Biogeochemical indicators**

Amino acids (AA) and carbohydrates make 40-80% of the organic matter associated with plants and animals, and consequently constitute a considerably large fraction of the initial organic input into the aquatic sedimentary environment (Degens & Mopper 1976). They and hexosamines (HA) are among the more easily degradable constituents of POM and are preferentially degraded during settling of organic particles in the water column (e.g. Handa & Tominaga 1969; Lee & Cronin 1984). According to Wakeham et al. (1984), the decrease in bulk protein AAs relative to bulk non-protein AAs in a sample may result from the preferential decomposition of protein AAs. which are easily digestible. For instance, non-protein AAs  $\beta$ -alanine ( $\beta$ -ala) and  $\gamma$ -aminobutyric acid ( $\gamma$ -aba) in sediments may be enzymatically decomposed products of aspartic and glutamic acid (Lee & Cronin 1982). Ratios of these AAs, i.e. Asp/ $\beta$ -ala and Glu/ $\gamma$ -aba, have been used as indicators of the degree of microbial degradation of POM, whereby low ratios indicate a relatively more microbially degraded nature of POM (Degens & Mopper 1976: Ittekkot et al. 1984).

Arg is known to be hydrolysed to Orn and urea by the action of enzyme araginase (Lehninger 1982). The ratio between Total Hydrolysable Amino Acid (THAA) and Total Hydrolysable Hexoseamine (THHA) indicates the nature of POM in terms of their relative degree of microbial reworking and their phyto- and zooplankton sources. The low THAA/THHA ratios, with HA being mostly Glucoseamine (Gluam), are a clear indication of large amounts of chitinous materials (Degens & Mopper 1976; Degens & Ittekkot 1984). Chitinous zooplankton and bacterial biomass may be distinguished by their Gluam/Galam ratios. Gluam is the major constituent of chitin whereas Galam (Galactoseamine) is present only in trace amounts in zooplankton (Müller et al. 1986). In many bacterial cell walls both HA are present (Wolla et al. 1984) and Gluam/Galam ratio <4 was measured within various bacterial species (Reistad 1975; Kandler 1979). Humus contains Gluam primarily from fungal and bacterial cell walls (Parsons 1981; Stevenson 1994). In various soils the Gluam/Galam ratio has been found to vary from 2–6 (Stevenson 1994).

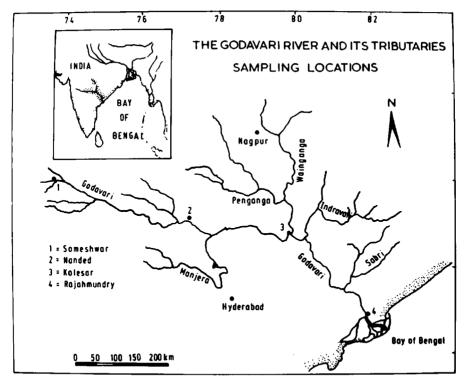
The utility of AAs and HAs as biogeochemical indicators for source and decompositional pathways of organic matter has been reported for sediments (e.g. Degens et al. 1964; Henrich et al. 1984; Montani et al. 1982; Steinberg et al. 1987; Seifert et al. 1990a, b). Individual AAs in sediment trap material and sediments have been used as indicators for intensity of decomposition; and HA distribution has been used to determine organic matter sources (e.g. Cowie & Hedges 1984; Izdar et al. 1987; Liebezeit & Bodungen 1987; Seifert et al. 1990a, b; Haake et al. 1992).

Another parameter, which is being used as indicator, is the weight ratio of POC to PN (C/N) – a bulk parameter. Since proteins have a C/N ratio of about 3, organisms rich in protein show low C/N ratios (Müller 1977). On an average phytoplankton has a C/N ratio of about 6 and terrestrial organic matter upto 36 (Redfield et al. 1963; Walsh et al. 1981; Ertel & Hedges 1983). Higher plants are main contributors of organic matter in the terrestrial environment. They contain <20% proteins and therefore show high C/N ratios (Müller 1977). A wide range of C/N ratio is also indicative of the extent to which organic matter has been degraded, and of depletion of its protein compounds. Humus compounds account for the greater part of the organic matter of river waters, and are chemically typified by high biological stability (Bordovskiy 1965).

## Study area

In central India, the Deccan Plateau is drained eastward by the Godavari River, which has a catchment area of  $3.1 \times 10^5$  km² (ca. 9.5% of the total geographical area of India). The river basin lies between  $73^{\circ}26'$  and  $83^{\circ}07'$  E and  $16^{\circ}16'$  and  $22^{\circ}36'$  N (Figure 1). Principal tributaries of the river are the Pravara, Purna, Manjera, Pranhita, Indravati and Sabari. Of these, the Pranhita with its major tributaries the Penganga, Wardha and Wainganga, is the most important tributary of the Godavari River. The mean annual water discharge of the Godavari River is  $1.1 \times 10^{14}$  L (Anonymous 1995) of which 93-96% occurs during the wet monsoon season. Sediment discharge (170  $\times$  106 tons a<sup>-1</sup>) is also predominantly wet monsoon influenced, because 95% of the total annual load is transported in the wet season (July–September) (Biksham & Subramanian 1980, 1988).

Heavy wet monsoon rains over the basin and consequent water discharge by the river cause drastic seasonal changes in the salinity gradient in the estuarine region (Ramana et al. 1989). The distributaries (the Gautami and Vashishtha Godavari) are fresh water in the peak season of the wet monsoon (July); towards the end of the wet monsoon (September) they are brackish partly mixed estuaries, and in the dry season (February) they are fully mixed estuaries (Ramana et al. 1989).



Source: Der Grosse Bertelsmann Weltatlas.196

Figure 1. Sampling locations in the Godavari River basin.

The climate over this basin is semi-arid to monsoonal. Temperature (mean 24 °C) ranges from 10 °C (minimum) in December–January to 47 °C (maximum) in April–May. The delta region of the basin experiences periodic cyclones (Biksham & Subramanian 1980). The Godavari basin receives its maximum rainfall during the wet monsoon, which accounts for more than 80% of the annual rainfall (mean 1 062 mm). However, temporal and spatial variations in rainfall over the basin do occur (Anonymous 1995). The rainfall data compiled from satellite based observations (Finch 1994) show that the wet monsoon rains are prevalent from mid June till the end of October, with sporadic rains during winter months (Figure 2). The individual sections in this diagram depict a rather short period of rainfall in the upstream region of the river and longer period of rainfall in the downstream and estuarine region. The diagrammatic presentation of the monthly discharge data provided by Central Water Commission, India, corroborates the above mentioned observation by showing a pattern (Figure 3) peaking in the month of August.

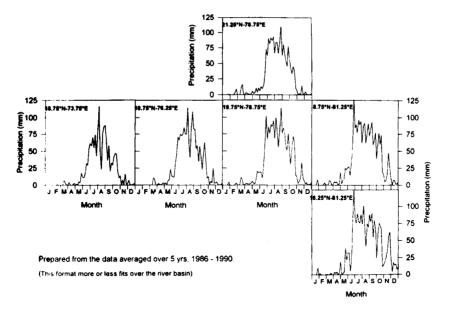


Figure 2. Rainfall pattern over the Godavari River basin.

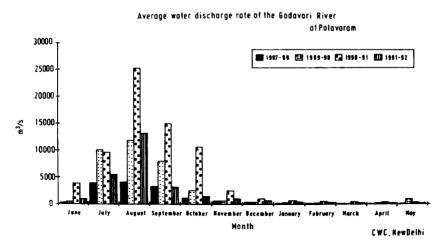


Figure 3. Average water discharge rate of the Godavari River.

## Geology

Sediment and solute transport by a river depend primarily on the rock formations in the catchment area. Based on their erodibility, rock types in the Godavari basin are categorised as follows (Biksham & Subramanian 1988): (a) Granites, Charnokites and similar hard rocks account for 39% of the basin geology. The river tributaries draining through these relatively stable and

low erodibility rock formations carry low sediment loads. (b) Deccan traps are volcanic in origin and belong to the Tertiary age. They are known for their distinct spheroidal weathering and high fluvial erosion. The whole area (48% of the basin area) is covered by 10–40 cm thick black clay loam, which may be released to the river as suspended sediments. (c) Sedimentary rocks located in the central and lower part of the catchment area (11% of the total basin area) are of Precambrian and Gondwana age and are known for their high degree of erodibility. They consist of sandstones and quartzite with a few slate bands. The sediments are mostly argillaceous in nature.

## Pedology

Aqualfs, Aquepts, Fluvents, Ochrepts, Orthents, Tropepts, Udalfs, Ustalfs, Usterts, Ustolls and rock outcrops are reported in the basin (Census of India 1981). Orthents are largely confined in the western half and in a small zone on eastern boundary of the river basin. Usterts are prevalent in the central part, with considerable extensions towards western part, of the basin. Eastern part of the basin is dominated by Ustalfs. In the lower reaches, close to and in the estuarine region, soil type varies within relatively short distances.

#### Human activities

The Godavari River basin has  $1.9 \times 10^5$  km²cultivable area. Exploitation of ground water for irrigation and other uses is ca. 13% of the estimated utilisable potential of the basin. The utilisable surface waters have been estimated to be  $0.76 \times 10^{14}$  L a $^{-1}$ , which has led to formulation of a number of large and small water resource development projects, which are of special interest in river basin studies as they create localised imbalances in sedimentation and erosion processes. Industries in this basin are based on agricultural products, e.g. rice milling, cotton spinning, weaving, sugar and oil extraction. Some industries on cement, fertilisers, paper and engineering goods also exist (Anonymous 1989). Mining of coal, limestones, slates, manganese and iron ore is among important human activities in the basin.

#### Material and methods

## Sample collection

Sampling started in May 1993. 10 litre running water was collected in polythene bottles from 4 locations (Figure 1) in the river basin. This water was kept undisturbed for 72 hours; then supernatant was siphoned off. The remaining water (<250 mL) was evaporated at 40  $^{\circ}$ C, and the dried suspended matter

was scrapped out from the watch glass and weighed for total suspended matter (TSM). A second set of suspended matter samples was collected from 5 equally spaced points across the river at Rajahmundry (site 4) in August 1994. 5 litre water was collected with a Niskin bottle (Hydrobios, Kiel) from approximately 1 meter below the water surface at each point. Water was filtered in the field through 4–5 preweighed  $0.45\mu$  polycarbonate membrane filters (Schleicher & Schuell), and the suspended matter on filter was poisoned by a few drops of 3.3 g/L mercuric chloride solution and then air dried. Later in the laboratory the filters were dried at 40 °C. These filters were weighed again for TSM estimation. The sediments were powdered with the help of pestle and mortar and homogenised for (before performing any) chemical analyses. The suspended matter on filters was analysed seperately for all five points, and then these data were averaged to give wet monsoon season data.

## Sample analyses

Samples were analysed at the Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Germany.

#### Carbonate carbon

Carbonate carbon was determined with a *Carmhograph* 6 from Wösthoff. About 5 mg dried and homogenised sediment was weighed in 50 mL Erlenmeyer flask. As a standard approximately 10 mg CaCO<sub>3</sub> was also weighed in 4 flasks. About 10 mL 2N H<sub>3</sub>PO<sub>4</sub> was added, and the mixture was heated to boiling temperature. The CO<sub>2</sub> generated from this mixture was passed through 18 mL 0.05 N NaOH solution. The change in conductivity of this solution was compared with that generated by CaCO<sub>3</sub> standard. Standard deviation in this technique was 1%.

## Total carbon and nitrogen

Total C and N were determined with a Carlo-Erba*Nitrogen Analyser NA1500*. Samples (1–5 mg) were weighed in tin capsules and placed in the autosampler of this instrument. The sample is flash combusted at 1 020 °C in an oxidation column under oxygen current for 40 sec. The combustion products (CO<sub>2</sub>, N<sub>2</sub>, NOx, SO<sub>2</sub>, H<sub>2</sub>O) are transported by a constant flow of the carrier gas (He). The oxidation column contains chromium (III) oxide and silver coated cobaltous cobaltic oxide granules. In this column, formation of NOx is inhibited and interfering halogenated and sulphur compounds are removed. The reduction column contains cupric-copper metal in the form of coarse powder at 650 °C. In this column, O<sub>2</sub> is removed and NOx are reduced to elemental N. Then the

gas mixture is directed through water filter (magnesium perchlorate) followed by separation column. A thermal conductivity detector (TCD) measures the difference between thermal conductivity of the carrier gas and that of the reference gas (He). Sulphanilamide ( $C_6H_8N_2O_2S$ ) was used to calibrate the instrument. After every 10 samples, 1 standard was measured. Reproducibility of results in this method was  $\pm 1\%$  of the absolute value.

The *Particulate organic carbon* (POC) content was calculated as a difference between total carbon and carbonate carbon.

#### Amino acids

Amino acids were determined with *LKB Amino Acid Analyser* (4151 Alpha *Plus*) from Pharmacia Biotech. Details of the methodology have been given by Michaelis & Ittekkot (1982). In brief, acid hydrolysed amino acids elute in accordance with their molecular structure and charge under the influence of sodium citrate buffers with ascending pH. The eluted amino acids form o-Phthaldialdehyde (OPA)/mercaptoethanol complex, which is quantified by a fluorescence detector.

5-10 mg sample was hydrolysed under argon gas atmosphere with 3 mL 6 N HCl (suprapure) for 22 hrs. at  $110\,^{\circ}$ C. 2 mL supernatant was pipetted out and evaporated to dryness 3–4 times (each time the residue was dissolved into ca. 5 mL DDW) with a rotary evaporator until free of acid. The residue was then dissolved into 1 mL dilution buffer.  $20-60~\mu$ L of this solution was injected in the sample loading capsule, which transferred the sample to a gas liquid chromatography (GLC) column of the analyser. Total hydrolysable amino acids (THAAs) were calculated as the sum of individual amino acids (AA) detected and quantified. Total hydrolysable hexosamines (THHAs) concentrations were multiplied by 1.4 (Müller et al. 1986) in order to compensate for the partial loss during hydrolysis. The analytical error in this method was less than 10%.

#### Results and discussion

## Suspended matter

Suspended matter transported by the river shows seasonal and spatial variation (Table 1). During the dry period the amount of TSM is low in the upstream and middle course of the river, but considerably high just above the estuarine region. Site 1 is characterised by rocky terrain and the possibility of high sediment transport by the river is low. Water scarcity in downstream area leads to temporary construction of small barrages across the river, which

Site	TSM mg/L	PC %	PIC %	POC % (a–b)	PN %	C/N (a-b)/c
1	16.2	3.95	0.00	3.95	0.49	8.03
2	18.9	6.51	2.66	3.85	0.57	6.80
3	4.8	4.30	1.26	3.04	0.35	8.79
4	176.2	0.39	0.23	0.16	0.02	8.42
4*	500.2	1.85	0.20	1.65	0.17	9.66

Table 1. TSM, carbon and nitrogen distribution in the suspended matter.

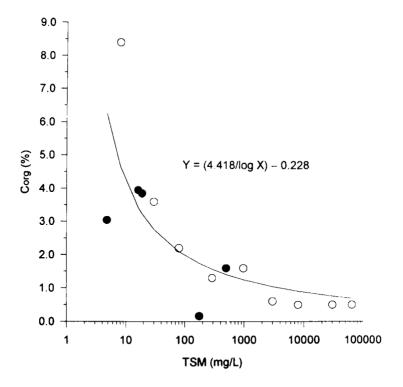
hinders free river flow reducing its sediment transport capacity. Retention of large quantity of river sediments in a reservoir lake behind Sriramsagar dam, further reduces TSM content downstream (site 3). The lower reaches of the river consist of recent sediments. This and water and sediment inputs from tributaries viz. the Penganga, Wainganga and Indravati increase the sediment transport resulting in relatively high TSM just above the estuarine region (site 4).

During the wet-monsoon, the TSM load, as estimated at site 4, increases by ca. 3 times. Heavy rains during the wet monsoon throughout the river basin contribute to proportionately large amount of sediments in the main channel. Owing to excessive availability of water in the basin, dam and barrages are no longer an obstacle in this season, therefore rapidly flowing water has a high capacity to transport TSM.

## Carbon and nitrogen

Particulate inorganic carbon (PIC) content of the suspended matter varies, with decreasing concentration in downstream, from zero to 2.66% and makes upto 59% of the particulate carbon (PC). At site 4, the compositional change in suspended matter during the wet monsoon season brings drastic reduction in contribution of PIC to PC – a change from 59% to 11%. Suspended matter is rich in POC in the upstream region (3.95%) but poor in the downstream region close to the estuary (0.16%). However, during the wet monsoon, relatively high POC content (1.65%) has been recorded at the same location (site 4). Fine texture of the particulate matter plays an important role in adsorbing POM (Jha 1986). 95–99% suspended sediments in the upper reaches are less than 75 $\mu$  in size whereas in the lower reaches this percentage drops down to 67% (Biksham & Subramanian 1988). Close to the estuarine region the river is turbid, which hinders phytoplankton growth and dilutes the amount of already present POM with suspended sediments. Figure 4 shows good inverse correlation between TSM and POC. It has been inferred from the studies on

<sup>\*</sup> wet monsoon season



Data (0) from Ittekkot (1988) and present work (1988)

Figure 4. Correlation between TSM and POC in some major rivers.

major world rivers that, rivers with low TSM have high POC content and vice versa (Ittekkot 1988). The reasons attributed to this tendency are: 1. dilution of riverine POM by mineral matter, 2. reduction in autochthonous input due to lack of light (turbidity), and 3. differences in the sources and biogeochemical processes affecting the nature of POM at various stages of the hydrographic regime.

From the Indian stretch of the Brahmaputra River, Mahanta (1995) estimated POC in the range of 0.88–1.34% (av. 1.16% of suspended matter); the Hooghly River transports suspended matter having ca. 1.0% POC (P.G. Jose, pers. comm.), and the Yamuna River in a range of 0.12–0.74% (Jha 1986). These estimates of POC in other rivers are comparable with that (1.65%) in the Godayari River.

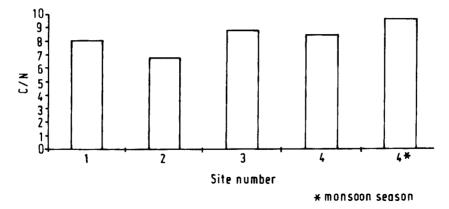


Figure 5. Downstream and seasonal variations in C/N ratio.

#### C/N ratio

Irrespective of diverse climatic conditions over their catchment area, large rivers have been found to transport POM having a C/N ratio in the range of 8.1–12.9 (Ittekkot & Zhang 1989). C/N ratio in suspended matter of the Godavari River varies from 6.80 to 9.66 (av. 8.34) (Figure 5). During low water and sediment discharge period, the phytoplankton growth increases POM concentration in the river water (Ittekkot et al. 1985). This phenomenon may account for the low C/N ratios observed in the suspended matter samples from the upper reaches of the river. The lowest C/N ratio recorded at site 2 may be largely due to fresh phytoplankton POM, because on average phytoplankton has a C/N ratio of about 6. During the wet monsoon, however, the C/N ratio increases to 9.66. This increase is attributable to a basin-wide input of terrestrial POM, which introduces large amounts of relatively stable POM with a higher C/N ratio.

#### Amino acids

Spectral distribution of individual AAs shows almost uniform relative concentration of all protein AAs except Met, Tyr and Arg (Table 2). Non-protein AAs ( $\beta$ -ala,  $\gamma$ -aba and Orn) show a rapid increase in their relative concentrations in downstream areas. The wet monsoon season sample shows a spectral distribution of AAs, which has close similarity with those of the dry season samples. THAA content shows a distinct decrease from 21 900 to 510  $\mu$ g/g sediment downstream. THAA consists mostly (>95%) of protein AAs, which along with non-protein AAs decrease downstream (Table 3). Contribution of amino acid carbon (THAA-C) to POC in the suspended matter varies from 11.4 to 24.7% and that of amino acid nitrogen (THAA-N) to PN varies

from 36.2 to 55.0%. Both of these characteristics decrease downstream. The suspended matter has almost uniform composition of POM in terms of the molar concentrations of individual AAs spatially and seasonally. Consistency in the distribution of AAs has also been noticed after grouping them into acidic, basic, neutral, aromatic and non-protein AAs. Neutral AAs are the most abundant followed by acidic, basic and aromatic AAs. The absolute quantity of THAAs and related parameters shows downstream variation, which depends to some extent on the nature of POM.

Among biogeochemical indicators, Asp/ $\beta$ -ala and Glu/ $\gamma$ -aba increase initially and then gradually decrease downstream. Gluam/Galam shows a downstream increase from 1.4 to 2.7. The THAA/THHA ratio gradually decreases downstream from 19.5 to 13.4. The C/N ratio is low (6.80) at site 2, elsewhere it varies from 8.03 to 9.66. These indicators for the sample collected during the wet monsoon show close similarity with that of the dry season sample from the same location (site 4). Ratios, Asp/ $\beta$ -ala, Glu/ $\gamma$ -aba and THAA/THHA, are all high and decrease downstream by about 50%. Increase in non-protein AAs downstream is a direct indication of the extent of microbial degradation of POM in suspension. In this respect, the wet monsoon season sample does not differ from the dry season sample collected from the same location. During the dry season, upper reaches of the river have largely autochthonous production of POM. The site 4 had turbid water conditions (relatively high TSM value of 176.2 mg/L), which reduced the in situ production of POM. The POM at this location is perhaps of mixed origin. This is comparable with the wet monsoon situation when enormous amount of water and sediment discharge restricts phytoplankton growth, and large quantity of degraded matter from the catchment is transported in suspension.

THAA-C and POC both show an increase in their absolute concentration in the wet monsoon season sample, but the contribution of THAA-C to POC is less than that observed at the same location in the dry season sample. During the wet monsoon, the river transports large quantities of terrestrial POM, which is known to be highly degraded and therefore low in THAA-C content. Same parameters for the upstream samples represent a relatively large fraction of POC, indicating relative freshness of the POM. THAA-C makes upto 25% of the POC in the suspended matter. A similar pattern of distribution for these two parameters exists in samples collected from downstream of the river. Similar tendencies occur also in the case of THAA-N and PN distribution.

Spatial and seasonal distribution of PAA vary from river to river and within rivers, depending upon the prevailing TSM concentrations (Ittekkot et al. 1985; Ittekkot & Arain 1986; Ittekkot & Zhang 1989; Paolini & Ittekkot 1990). Concentration of PAAs in the Godavari (90–2 166  $\mu$ g/L) (Table 3) are comparable with that of the other major rivers in the Indian subcontinent,

Table 2. Amino acid characteristics in particulate organic matter transported by the Godavari River.

Amino acids			Sites		
(mol %)	1	2	3	4	4*
ASP	12.8	14.8	13.7	12.7	12.9
GLU	11.7	11.1	11.3	11.2	11.0
$\Sigma$ Acidic	24.4	25.9	25.0	23.9	23.8
HIS	1.5	1.4	1.6	1.3	1.7
ORN	0.2	0.2	0.3	0.6	0.6
LYS	5.1	4.3	4.3	5.0	5.6
ARG	5.1	5.6	4.4	3.9	4.4
$\Sigma$ Basic	11.9	11.5	10.9	10.7	12.3
THR	7.1	7.1	6.9	7.1	7.0
SER	6.6	7.0	6.7	7.1	7.5
$\Sigma$ Hydroxy	13.7	13.9	13.5	14.2	14.5
GLY	14.0	13.5	14.2	14.0	14.4
ALA	10.5	11.4	11.9	12.6	10.6
$\Sigma$ Straight	24.4	24.9	26.1	26.6	25.0
VAL	9.1	7.0	7.5	7.1	7.9
ILE	4.1	3.9	4.2	4.2	4.0
LEU	6.4	6.8	6.7	6.4	6.0
$\Sigma$ Branched	19.5	17.6	18.4	17.7	17.9
$\Sigma$ Neutral	57.6	56.4	58.1	58.6	57.4
TYR	1.1	1.1	1.2	1.7	1.3
PHE	3.7	3.8	3.7	3.7	3.1
$\Sigma$ Aromatic	4.8	4.9	4.9	5.4	4.4
$\beta$ -ALA	0.7	0.5	0.9	0.9	1.1
$\gamma ext{-ABA}$	0.3	0.2	0.3	0.6	0.6
ORN	0.2	0.2	0.5	0.5	0.6
$\Sigma$ Non-protein	1.2	0.9	1.7	2.0	2.3
MET	0.3	0.6	_	-	0.4

<sup>\*</sup> sample collected at site 4 during wet monsoon

e.g. the Ganges (24–2 395  $\mu$ g/L), Indus (178–2 009  $\mu$ g/L) and Brahmaputra (91–1 163  $\mu$ g/L) rivers (Ittekkot & Zhang 1989). Contribution of particulate amino acid nitrogen (PAAN) to PN has been recorded to vary from 3–97% in rivers. The largest differences between the minimum and maximum PAAN contribution to PN were found in the Asian rivers: e.g. the Ganges (16–82%), Brahmaputra (9–86%) and Indus (3–63%). A higher contribution of

Table 3.	Biogeochemical	indicators	and	other	parameters	observed	in the	Godavari
River susp	ended matter.							

Amino acid	Sites						
characteristics	1	2	3	4	4*		
THAA μg/g	17 567.1	21 921.4	9 147.7	510.6	4 330.9		
Prot.AA $\mu$ g/g	17 392.8	21 743.6	9 013.4	501.8	4 245.1		
Non-prot.AA $\mu$ g/g	174.3	177.8	134.2	8.8	85.7		
THHA $\mu$ g/g	1 323.4	1 668.1	929.1	56.5	558.7		
THAA-N $\mu$ g/g	2 494.0	3 115.5	1 284.4	71.0	615.3		
THAA-C $\mu$ g/g	7 679.9	9 508.5	3 985.9	223.2	1 880.3		
$ASP/\beta$ -ALA	17.8	28.6	15.9	13.8	11.5		
$GLU/\gamma$ -ABA	45.0	47.5	39.6	20.4	20.9		
THAA/THHA	19.5	19.3	14.6	13.4	11.5		
GLUAM/GALAM	1.4	1.7	1.7	2.7	2.1		
THAA-C% (of POC)	19.4	24.7	13.1	13.9	11.4		
THAA-N% (of PN)	50.7	55.0	37.1	37.0	36.2		
THAA μg/L	284.6	414.3	43.9	90.0	2 166.1		

<sup>\*</sup> sample collected at site 4 during wet monsoon

AAs to PN was observed mostly during low sediment discharge periods and lower during high sediment discharge periods (Ittekkot & Zhang 1989). Spatial distribution of THAA in the Godavari River suspended matter shows a similar trend (Table 3). THAA-N makes upto 55% of the PN and lowest value, 36.2% THAA-N, has been recorded in the sample collected during high sediment discharge period.

In comparison with THAA-C%, THAA-N% shows less decrease in the wet monsoon season sample, which is partly attributable to abundance of low C/N ratio AAs like Gly, Ser, His, Arg, and Lys, and a deficiency in high C/N ratio AAs like Ile, Leu, Tyr and Phe (Table 2). Absolute concentration of THHA shows a decrease downstream, but in comparison with THAA, THHA concentration increases from 7.5 to 11.1% of THAA, which is higher than that recorded in some of the major world rivers (3–5% of the THAA, Ittekkot & Zhang 1989). The wet monsoon season sample shows the highest relative concentration of 12.9%. This pattern of distribution of HAs in suspended matter in the Godavari River is attributable to a contribution from soils, where these HAs are common (Parsons 1981).

High correlations among THAA/THHA and  $Glu/\gamma$ -aba and THAA/THHA and Arg/Orn further substantiate the inference that the observed high concentration of POM in the upstream of river is largely from autochthonous production of organic matter (Figure 6). The inference from these two characteristics

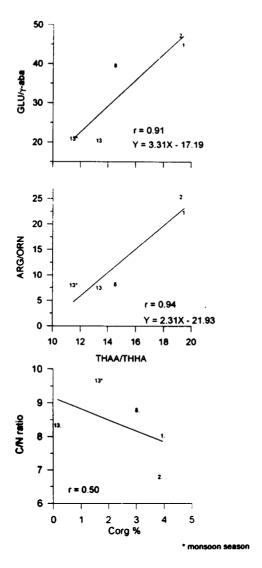


Figure 6. Important ratios indicating freshness of organic matter (data points correspond to sampling location 8 = 3, 13 = 4 and  $13^* = 4^*$ ).

is further supported by POC – C/N diagram, which shows a gradual decrease in C/N ratio with increasing POC content in suspended matter.

Considering the wet monsoon season sample as representative of the maximum sediment discharge period and using  $170 \times 10^6$  ton  $a^{-1}$  sediment flux (Biksham & Subramanian 1988), we estimate that the river Godavari transports about  $3.14 \times 10^6$  ton PC per year, 89% of which is accounted for by POC ( $2.81 \times 10^6$  ton). PN transport by the river is ca.  $0.29 \times 10^6$  ton  $a^{-1}$ ,

## DISTANCE METRIC IS EUCLIDEAN DISTANCE SINGLE LINKAGE METHOD (NEAREST NEIGHBOR)

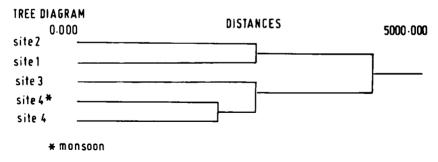


Figure 7. Tree diagram correlating organic matter at various sites.

36.2% of which is accounted for by THAA-N (0.10  $\times$   $10^6$  ton  $a^{-1}$ ). THAA-C (0.32  $\times$   $10^6$  ton  $a^{-1}$ ) makes 11.4% of the POC transport by the river. Annual transport of AAs is about 0.74  $\times$   $10^6$  ton. About 98% of this transport is accounted for by protein AAs.

Raw data in terms of PIC (%), POC (%), PN (%), C/N ratio and individual AA (nmol/g) have been used to perform cluster analysis, which involves single linkage method based on nearest neighbour and Euclidean distance. The results (Tree diagram) show that the nature of POM in upstream areas is quite different from that in downstream areas (Figure 7). Large Euclidean distances among these groups signify that the nature of POM at each location has very low similarity.

## Comparison of Godavari River with some major rivers in the world

POC fluxes of various rivers in the world are compiled in Table 4. It is obvious from the table that the amount of POC transported by the river Godavari places it among some of the largest POC transporting rivers in the world. Compared to the listed major rivers, the Godavari has smallest basin area and third lowest annual water discharge even then the Total Suspended Solid (TSS) flux of the Godavari is quite high. Low TSS flux in the case of some rivers, e.g. the Nile and Indus, is attributable to terrain geology and dams.

The distribution pattern of PAAs in some of the tropical rivers and in the Godavari River (Figure 8) shows that neutral AAs are the most dominant AAs. Except in the Magdalena River, acidic AAs are the next most abundant AAs followed by basic AAs. Although the Godavari River originates from and drains through quite different geological settings as compared to that of Himalayan rivers, the bulk composition of AAs in this river is more or less same as in other major rivers of the Indian subcontinent. The catchment

Table 4. Comparison of Godavari River characteristics with that of some major world rivers.

River	Basin area 10 <sup>3</sup> km <sup>2</sup>	Water discharge km <sup>3</sup> /a	TSS flux 10 <sup>6</sup> t/a	POC flux 10 <sup>3</sup> t/a
Amazon	6 300	5 520	900.0	13 000
Ganges	970	412	573.0	
Indus	1 170	224	100.0	18 000*1
Brahmaputra	700	560	597.0 /	
Huanghe <sup>§</sup>	752	44	681.0	6 100
Zaire	3 750	1 267	48.0	2 800
Orinoco	1 000	1 135	121.0	1 990
Mackenzie	1 810	249	_	1 820
Parana	2 800	473	80.0	1 270
Mississippi	3 220	410	296.0	850
Niger	1 162	154	25.4	660
Yukon	840	210	_	320
St Lawrence	1 150	413	5.1	310
Nile	3 000	38	2.0	190
Godavari#	313	92	170.0	2 805*

Data compiled from Degens et al. 1991

areas of rivers Mekong, Amazon, and Magdalena are under direct influence of tropical vegetation as compared to that of the rivers of Indian subcontinent. This difference in vegetation might be responsible for relatively high basic AA content in suspended matter of the Mekong, Amazon and Magdalena River. Compared to the South American rivers, the nature of POM entering the Godavari River, water chemistry and kind of microbial population control the composition of degraded POM and more specifically of PAAs.

## Deposition in the Bay of Bengal

Despite the retention of POM in the estuarine region, considerable amount of river derived material may be deposited on the continental shelf and even in distant offshore regions. This is likely to take place during the wet monsoon, when the river discharge and sediment load are maximal and the brackish water has been replaced by fresh water in the estuary. The data (Shaefer & Ittekkot, and Ahrens-Sobanski, pers. comm.) based on samples collected during the wet monsoon in 1990 from a location in the Bay of Bengal, ca. 350

<sup>§</sup> Zhang et al. 1992

<sup>\*</sup> Biksham and Subramanian 1988

<sup>\*</sup> Present study

<sup>\*1</sup> Ganges, Indus and Brahmaputra together

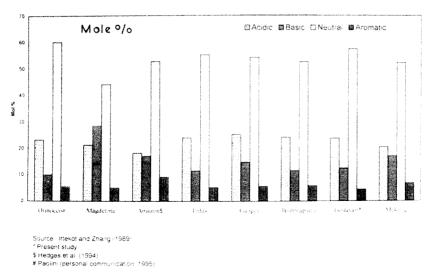


Figure 8. Distribution of particulate amino acids in tropical rivers compared with that in the Godavari River.

km south east of the river mouth, provide a unique opportunity to examine this deposition.

The bulk parameters and important ratios listed in Table 5 show considerable difference among suspended matter transported by the river Godavari and plankton, sinking particles and surface sediments from the Bay of Bengal. Sinking particles and surface sediments are rich in inorganic carbon. Sinking particles have higher POC concentration and correspondingly high AA, THAA-C and THAA-N concentrations as compared to that in suspended matter and surface sediments. Asp/ $\beta$ -ala ratio in plankton is 48.0, which is quite high as compared to that in all other categories. However, there are some similarities among them. For instance, PN in suspended matter is comparable with that in surface sediments.

Relative concentration of AAs in sinking particles from two different depths is quite similar (Table 6). There is a little increase in the relative concentration of  $\beta$ -ala and  $\gamma$ -aba with depth. These AAs have lowest relative concentration in plankton and highest in surface sediments. Asp concentration is comparable in suspended matter and sinking particles. Arg concentration is almost same in all five category of the samples. Contribution of PAAN to PN (THAA-N%) and to certain extent THAA/THHA and Gluam/Galam ratios are quite similar in the suspended and sinking particles. Asp/ $\beta$ -ala ratio in suspended matter is comparable with that in sinking particles collected at 2 327 m depth.

Table 5. Characteristics of particulate organic matter in the Godavari River and Bay of Bengal.

			Bay of Bengal			
	Godavari River	Plankton	Sinking particles#		Surface sed.	
Parameter	suspended matter*		Shallow (988 m)	Deep (2 327 m)	3 290 m	
TIC%	0.20	0.78	4.54	3.91	2.27	
POC%	1.65	33.70	6.95	4.98	1.00	
PN%	0.17	1.92	0.87	0.60	0.13	
C/N	9.70	17.55	7.98	8.30	7.69	
POC/PIC	8.25	43.19	1.53	1.28	0.44	
THAA mg/g	4.3	105.2	23.6	15.1	2.2	
THAA-C mg/g	1.9	47.4	10.2	6.6	0.9	
THAA-N mg/g	0.6	14.6	3.4	2.2	0.3	
THAA-C%	11.4	14.1	14.7	13.2	9.1	
THAA-N%	36.2	76.1	38.9	36.4	25.0	
HA mg/g	0.6	11.9	3.2	2.3	0.2	
THAA/THHA	11.5	12.7	10.6	10.0	18.4	
$Asp/\beta$ -ala	11.5	48.0	14.2	11.9	3.4	
Glu/ $\gamma$ -aba	20.9	117.2	13.4	8.9	2.2	
Gluam/Galam	2.1	16.8	2.7	2.6	1.2	
Tyr/Phe	0.4	1.2	1.1	1.1	0.03	

<sup>\*</sup> south west wet monsoon, 1994

Data: Plankton and sinking particles – Schäfer and Ittekkot, unpublished Surface sediments – Ahrens-sobanski, unpublished

The ratios involving individual AAs are uniformly high in plankton and quite low in all other samples. This difference is attributed to fresh POM in plankton and degraded (to various degrees) POM in the other samples. The Tyr/Phe ratio in plankton is 1.2. This ratio is almost the same (1.1) in sinking particles. Suspended matter and surface sediments have fairly low ratios. This pattern of Tyr/Phe ratio sets the POM at all five locations in an order of degradation. Fresh planktonic organic matter gets degraded while sinking. At the water – sediment interface degradation of organic matter takes place at the fastest rate (Emerson et al. 1985), which results in the lowest Tyr/Phe ratios. Relative concentrations of aromatic and non-protein AAs prove that the organic matter in surface sediments is more degraded than that in suspended matter.

Cluster analysis performed on suspended matter, sinking particles, surface sediments and plankton, selecting AAs (mmol/g), PIC (%), POC (%) and PN (%) as variables, signifies close similarities between the POM of suspended matter and surface sediments (Figure 9). The nature of POM in sinking particles collected at two different depths is almost the same. The level of

<sup>\*</sup> south west wet monsoon, 1990

*Table 6.* Amino acid distribution in particulate organic matter in the Godavari River and Bay of Bengal.

		Bay of Bengal				
Amino acids	Godavari River	Plankton	Sinking p	Surface sed.		
(mol %)	suspended matter*		Shallow (988 m)	Deep (2 327 m)	3 290 m	
ASP	12.9	9.7	11.9	12.5	14.1	
GLU	11.0	11.2	10.5	10.1	8.0	
$\Sigma$ Acidic	23.9	20.9	22.4	22.6	22.1	
HIS	1.7	3.4	2.5	2.1	6.1	
ORN	0.6	0.1	0.5	0.5	1.9	
LYS	5.6	4.8	5.5	5.7	2.2	
ARG	4.4	4.0	4.3	4.1	4.2	
$\Sigma$ Basic	12.3	12.3	12.8	12.4	14.4	
THR	7.0	6.0	5.5	6.5	6.3	
SER	7.5	5.6	8.4	7.9	6.9	
$\Sigma \ {\rm Hydroxy}$	14.5	11.6	13.9	14.4	13.2	
GLY	14.4	13.7	17.7	17.7	19.7	
ALA	10.6	11.0	9.6	9.6	8.0	
$\Sigma$ Straight	25.0	24.7	27.3	27.3	27.7	
VAL	7.9	6.9	5.6	6.1	5.2	
ILE	4.0	5.2	3.5	3.2	2.8	
LEU	6.0	8.0	5.1	4.6	4.3	
$\Sigma$ Branched	17.9	20.1	14.2	13.9	12.3	
$\Sigma$ Neutral	57.4	56.4	55.4	55.6	53.2	
TYR	1.3	4.5	3.5	3.3	0.1	
PHE	3.1	3.8	3.1	3.0	1.8	
$\Sigma$ Aromatic	4.4	8.3	6.6	6.3	1.9	
$\beta$ -ALA	1.1	0.2	0.8	1.1	4.2	
$\gamma$ -ABA	0.6	0.1	0.8	1.1	3.6	
ORN	0.6	0.1	0.5	0.5	1.9	
$\Sigma$ Non-protein	2.3	0.4	2.1	2.7	9.7	
MET	0.4	1.8	1.2	1.0	0.8	

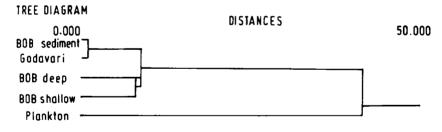
<sup>\*</sup> south west wet monsoon, 1994

Data: Plankton and sinking particles – Schäfer and Ittekkot, unpublished Surface sediments – Ahrens-sobanski, unpublished

uniformity in POM in sinking particles is comparable with that in suspended matter and surface sediments put together. Plankton, being fresh in organic content, does not show a close association with any other of the four groups,

<sup>#</sup> south west wet monsoon, 1990





raw data: A A m mol/g , TIC % , Corg. % and TN % BOB - Bay of Benaal

Figure 9. Tree diagram showing association among particulate organic matter in the Godavari River and Bay of Bengal.

but a general and rather distant association (large Euclidean distance) among them has been noted.

The close grouping due to certain characteristics of POM in suspended matter of the river and that in the samples from the Bay of Bengal, however, should not be mistaken for source and sink relationship due to two reasons. Firstly, the samples collected from river do not belong to the same time period when the Bay of Bengal samples were collected, and secondly, part of riverine transported material may be getting deposited in the estuary and associated coastal region and thus not reaching to open ocean at all.

#### Conclusions

The Godavari River transports ca.  $3.14 \times 10^6$  ton PC per year. 89% of this transport (2.81  $\times$  10<sup>6</sup> ton) is in the form of POC. The river transports ca. 0.29  $\times$  10<sup>6</sup> ton PN annually, 36% of this transport (0.10  $\times$  10<sup>6</sup> ton) is accounted for by PAAN. 98% of the total estimated AA transport is protein AAs.

During the dry period the POC level in suspended matter is high in the upper reaches of the river and drops drastically before entering the estuarine region. Most probable reason for this reduction is dilution with easily erodible recent sediments carrying turbid water at this sampling location.

C/N ratio shows spatial variation in the main channel of the river. High C/N ratio in the wet monsoon season sample has a bearing on terrestrial POM washed away from the catchment area.

The combined use of the biogeochemical indicators like POC, C/N, Asp/ $\beta$ -ala, Glu/ $\gamma$ -aba, Tyr/Phe, Gluam/Galam, THAA/THHA, THAA-C% and THAA-N% in interpreting the nature of POM transported by rivers may give important clues on the origin of POM and thus also on eutrophic condition in river water and/or on soil erosion taking place in the river basin.

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