Environmental Monitoring and Assessment (2006) **122:** 355–364
DOI: 10.1007/s10661-006-9188-7

NATURAL AND ANTHROPOGENIC FACTORS CONTROLLING THE DISSOLVED ORGANIC CARBON CONCENTRATIONS AND FLUXES IN A LARGE TROPICAL RIVER, INDIA

K. BALAKRISHNA[1,*], ITTA ARUN KUMAR[1,2], G. SRINIKETHAN[1] and GOPAL MUGERAYA[1]

[1]*Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore-575025, INDIA;* [2]*Present address: Department of Environmental Engineering, National Chung-Hsing University, TAIWAN (Republic of China)*

*(*author for correspondence, e-mail: kbalak@gmail.com)*

(Received 9 July 2005; accepted 16 January 2006)

Abstract. Carbon studies in tropical rivers have gained significance since it was realized that a significant chunk of anthropogenic CO_2 emitted into the atmosphere returns to the biosphere, that is eventually transported by the river and locked up in coastal sediments for a few thousand years. Carbon studies are also significant because dissolved organic carbon (DOC) is known to complex the toxic trace metals in the river and carry them in the dissolved form. For the first time, this work has made an attempt to study the variations in DOC concentrations in space and time for a period of 19 months, and estimate their fluxes in the largest peninsular Indian river, the Godavari at Rajahmundry. Anthropogenic influence on DOC concentrations possibly from the number of bathing ghats along the banks and domestic sewage discharge into the river are evident during the pre-monsoon of 2004 and 2005. The rise in DOC concentrations at the onset of monsoon could be due to the contributions from flood plains and soils from the river catchment. Spatial variations highlighted that the DOC concentrations in the river are affected more by the anthropogenic discharges in the downstream than in the upstream. The discharge weighted DOC concentrations in the Godavari river is 3–12 times lower than Ganga-Brahmaputra, Indus and major Chinese rivers. The total carbon fluxes from the Godavari into the Bay of Bengal is insignificant (0.5%) compared to the total carbon discharges by major rivers of the world into oceans.

Keywords: anthropogenic, carbon flux, DOC, Godavari river, Rajahmundry, temporal and spatial variations

1. Introduction

Carbon is transported in the river in four forms as dissolved organic carbon (DOC), particulate organic carbon (POC), dissolved inorganic carbon (DIC) and particulate inorganic carbon (PIC). Particulate inorganic carbon concentrations in tropical rivers are negligible because of the dissolution of PIC into DIC during the weathering of carbonate rocks. The following equations represent the natural sources of carbon (Sarin, 2001).

Carbonate weathering of rocks:

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3 \quad (1)$$

Silicate weathering of rocks:

$$CaSiO_3 + 2CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^- + SiO_2 \quad (2)$$

Photosynthesis:

$$CO_2 + H_2O \longrightarrow CH_2O + O_2 \quad (3)$$

Weathering of rocks transports the carbon in inorganic form as bicarbonate, whereas photosynthesis produces foliage, which decay in the soils as humus and are transported as organic carbon. Discharge of domestic sewage and industrial effluents into the river and usage of river-banks for washing and bathing contributes to the anthropogenic sources of carbon. In the recent decades, with the advent of green revolution, contribution of organic carbon into the world rivers from anthropogenic sources has multiplied (Degens and Kempe, 1982). The biomass generated from food production eventually gets disintegrated in the soil as soil organic carbon that is transported into the rivers during monsoon as DOC and POC. The DOC and POC originating from the soils are allochthonous, which are more stable and refractory and reach the oceans, while those originating *in-situ* in the river, such as phytoplanktons, are termed as autochthonous which are labile and disintegrate quickly.

Fluxes of carbon from the river to the global oceans are being measured in all the major rivers of the world to estimate the amount of carbon disposed into the coastal sediments annually. This is important in the backdrop of rising anthropogenic CO_2 concentrations in the atmosphere and the resulting global warming. It is estimated that an average of 7×10^{15} g yr^{-1} of CO_2 is emitted into the atmosphere from anthropogenic activities, of which 5×10^{15} g yr^{-1} are from the burning of fossil fuels and 2×10^{15} g yr^{-1} are from forest fires (Degens and Kempe, 1982; Sarmiento and Sundquist, 1992). About 2.5×10^{15} g yr^{-1} is absorbed by the ocean while an equal amount remains in the atmosphere leading to the rise in CO_2 and global warming (Sarmiento and Sundquist, 1992). It is suspected that the remaining anthropogenic CO_2 might be used by the biomass generated for food production and the abundant phytoplanktons in the river resulting from the increased flow of nutrients (Degens and Kempe, 1982).

Gaps exist in the understanding of spatial and temporal variations of organic carbon and their fluxes from the tropical rivers, which are less studied because of their location in the developing countries. This is in spite of their high water discharge ($>$60%) and 34% of total suspended load supply into the global oceans (Martin and Meybeck, 1979; Meybeck, 1988; Ludwig *et al.*, 1996; Ludwig and Probst, 1998; Balakrishna and Probst, 2005). Scattered studies are made on the organic carbon in Godavari, the largest peninsular Indian tropical river. Sarin *et al.*, 2002 studied the DOC, POC and DIC concentrations in this river but they restricted to one station at Rajahmundry and only four samples were collected at different periods. Balakrishna and Probst, 2005 studied the POC concentrations in the Godavari river; this study was complementary to the study made by Sarin *et al.* (2002) and their objectives did not match with the objectives of this study. Gupta *et al.* (1997) studied the POC concentrations in the Godavari river, but with only two samples in different periods at Rajahmundry. For the first time, this study has reported the temporal and spatial variations in DOC concentrations in the river Godavari at Rajahmundry spread over19 months with the following objectives:

i) Dissolved organic carbon is known to complex toxic trace metals and pesticides/insecticides, which are transported in the dissolved form (Degens *et al.*, 1991). Thus, instead of the toxic substances getting precipitated after sorption to suspended particulates, they continue to travel in the dissolved mode with the DOC. There could be deleterious impacts on the river biota because DOC serves as a primary nutrient or micronutrient for a number of organisms. Therefore, this is an attempt to generate a baseline data by monitoring the changing levels of DOC between September 2003 and March 2005.
ii) To study the temporal variations in DOC concentrations to track the dominance of natural and anthropogenic sources of organic carbon entering the river at different periods of time.
iii) To study the spatial variations in DOC concentrations along a stretch of 5 km in the Godavari river at Rajahmundry, to pinpoint the local sources that may influence the DOC concentrations along the downstream.
iv) To estimate the flux of DOC in the Godavari river and compare with the DIC and POC fluxes reported for the same river by Balakrishna and Probst, 2005.

1.1. Study area

Godavari ranks 34th and 32nd in terms of catchment area and water discharge respectively, amongst the 60 largest rivers of the world (Balakrishna and Probst, 2005; Gaillardet *et al.*, 1999). The Godavari basin (16–18°N and 75–83.3°E) covers an area of 313,147 km^2 in the central and southern part of Indian sub continent and discharges an average of 105 km^3 of water annually to the Bay of Bengal (Rao, 1975). Godavari originates in the Western Ghats near Nashik in Maharashtra and extends for 1465 km before emptying into the Bay of Bengal. Around 50% of the Godavari basin is under agricultural cover, which uses abundant fertilizers and pesticides. The climate over the basin is primarily semi arid (10–45 °C) with annual rainfall of 1185 mm.

Rajahmundry, one of the largest cities of coastal Andhra Pradesh is situated in the left bank of Godavari, about 75 km upstream of the confluence of the river into the Bay of Bengal. The entire population of Rajahmundry is dependent on Godavari for drinking water. There are many industries located in Rajahmundry, of which Andhra Pradesh Paper Mills is prominent (Figure 1). The treated effluents from this

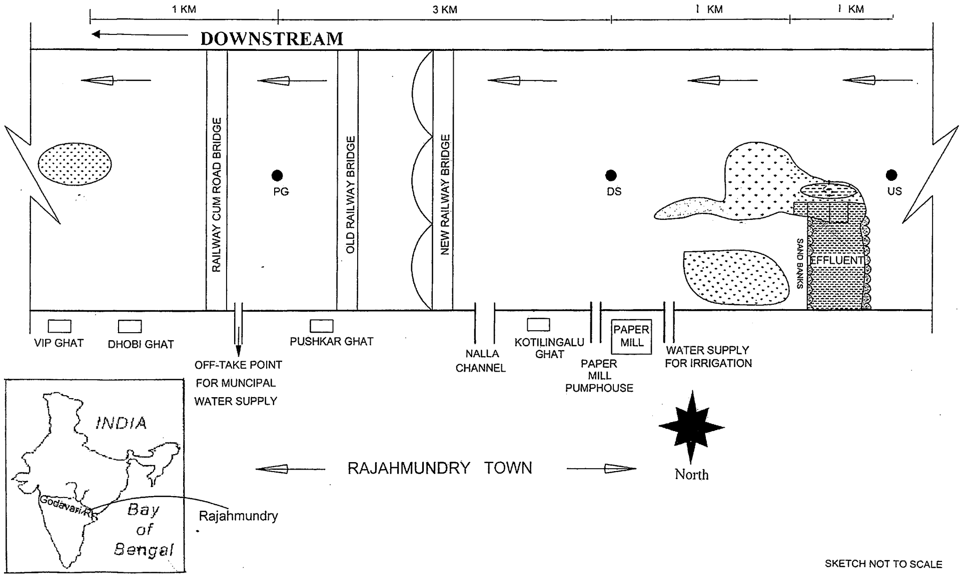

Figure 1. Location map of sampling stations at Godavari river, Rajahmundry.

industry are discharged into the river. The sewage from the municipal corporation of Rajahmundry was being let into Godavari through a canal (Nalla channel) until recently (Figure 1). The off-take point for pumping of Godavari waters for municipal supply is located just downstream of the confluence of Nalla channel. The Godavari waters are utilized for irrigating about 10 lakh acres in East Godavari and West Godavari districts of Andhra Pradesh, by means of Sir Arthur Cotton barrage located at Dowlaiswaram, about 10 km downstream of Rajahmundry. In addition, there is widespread cultivation of aquaculture in this area, using Godavari waters (Rao, 2003; Deepa *et al.*, 2004).

2. Methodology

Water samples are collected from three stations in the Godavari at Rajahmundry as shown in the Figure 1. The sampling points from the upstream to downstream are:

1. Upstream of the paper mills (US)
2. Downstream of the paper mills (DS)
3. Pushkar Ghat (Place for holy dip and recreation; PG)

Sampling is done every alternative month from September 2003 to March 2005 and a total of 25 samples are collected. A motorboat is employed to collect surface water samples from the centre of the river. Water samples are collected in pre-

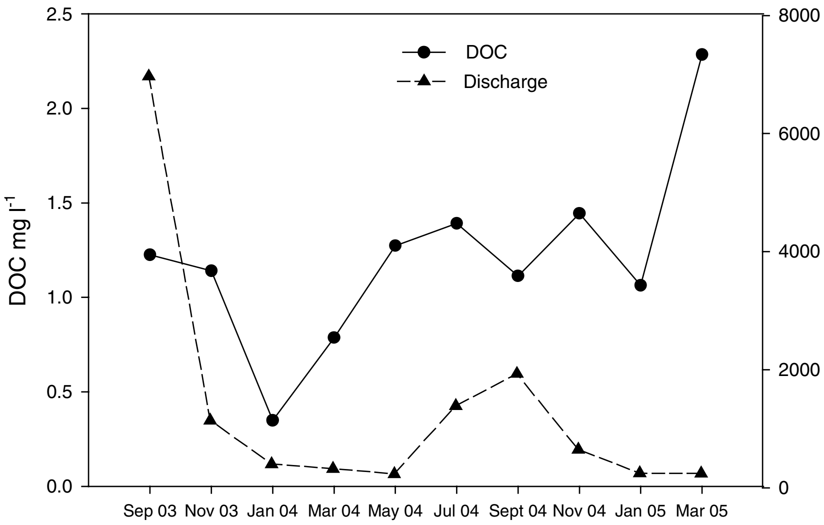

Figure 2. Temporal variations in the DOC concentrations at River Godavari, Rajahmundry.

cleaned polypropylene (PP) bottles (rinsed in ultra-pure water). While sampling, the bottles are rinsed with the sample to avoid dilution. Samples are processed within few hours of collection by filtering through 47 mm dia, 0.45 μm pore size cellulose acetate membrane filters (Millipore make), using a Millipore filtration apparatus and a hand vacuum pump (Nalgene make). Since the filters are made up of cellulose acetate, it is rinsed several times with the sample and about 500 ml of the sample is filtered out such that no trace amount of carbon is leached into the filtrate collected for DOC. Studies made by J.L.Probst (personal communication) indicate that no leaching of carbon from the cellulose acetate filter takes place after it is rinsed thoroughly with the sample. Filtered water samples are collected in 60-ml volume pre-combusted (500 °C) Pyrex grade glass bottles for DOC analysis. Filtered sample is immediately acidified with phosphoric acid to prevent any biological growth and wrapped in aluminum foils. Samples are analysed using the Shimadzu 5000A TOC analyzer available at the biochemical engineering laboratory of National Institute of Technology Karnataka (NITK). All the measurements had a precision of within$\pm$5%.

3. Results and Discussion

3.1. Temporal variations in DOC concentrations

Figure 2 represent the temporal variations in DOC concentration at station PG. There is an increase in DOC concentrations observed at the onset of monsoons

(July 2004) when a high discharge is observed. Higher DOC during this period could be due to the monsoon rains draining the flood plains and the catchment soils and its transportation to the river. Dissolved organic carbon concentration are observed to decrease in September 04 at station PG with decreasing influence of monsoons and thus decreasing input from the catchment and flood plains (Figure 2). Increase in DOC concentrations is observed in the pre-monsoon seasons (March 2004, May 2004 and March 2005), when the river discharge is minimal. The DOC concentrations in these periods are higher by 1.6–2.3 times the DOC concentrations observed in the previous sampling period, with the discharge either being low or constant. This is a clear indication of anthropogenic impact on these samples during the hot and dry period, when the effects of sewage discharge, and washing and bathing activities on the banks of the river could be magnified. In the rest of the periods, DOC concentrations at PG are controlled by discharge (Figure 2).

3.2. Spatial variations in DOC concentrations

Figures 3a–i represent the spatial variations in DOC concentrations across three stations, from the upstream end (station US) to the downstream end (station PG), via station DS (Figure 1), from November 2003 to March 2005. There is an increase in concentration in station PG as compared to station US between May 04 and March 05. It is possible that PG receives DOC from additional sources because there are several washing and bathing ghats, crematorium, domestic sewage and industrial effluent discharges and small channels from agricultural fields entering the river (Figure 1). However, in post-monsoon periods and pre-monsoon of 2003–2004 (November 03, January 04 and March 04), there is a decrease in DOC concentrations in PG as compared to US. This could be due to local impacts like excessive draw down of water for irrigation purposes in US leading to decrease in discharge and magnification of DOC concentrations in dry periods. Another such local impact at US could be due to the contamination of water by remains of cow-dung. The authors observed during their sampling expeditions in and around station US, that, several buffaloes were swimming in the river at shallow depth leading to possible contamination of samples from the dung.

Station DS is sampled between May 04 and March 05 (six samples) wherein, DOC concentrations are observed to be lowest in July 04, November 04 and January 05 as compared to US and PG samples (Figure 3). More detailed sampling is necessary to understand the process.

3.3. Carbon fluxes

Discharge data of the Godavari river measured at Dowlaiswaram (10 km downstream of Rajahmundry), is obtained from Andhra Pradesh irrigation department and from Rao, 1975. Discharge weighted concentrations (*Cw*) of DOC in the

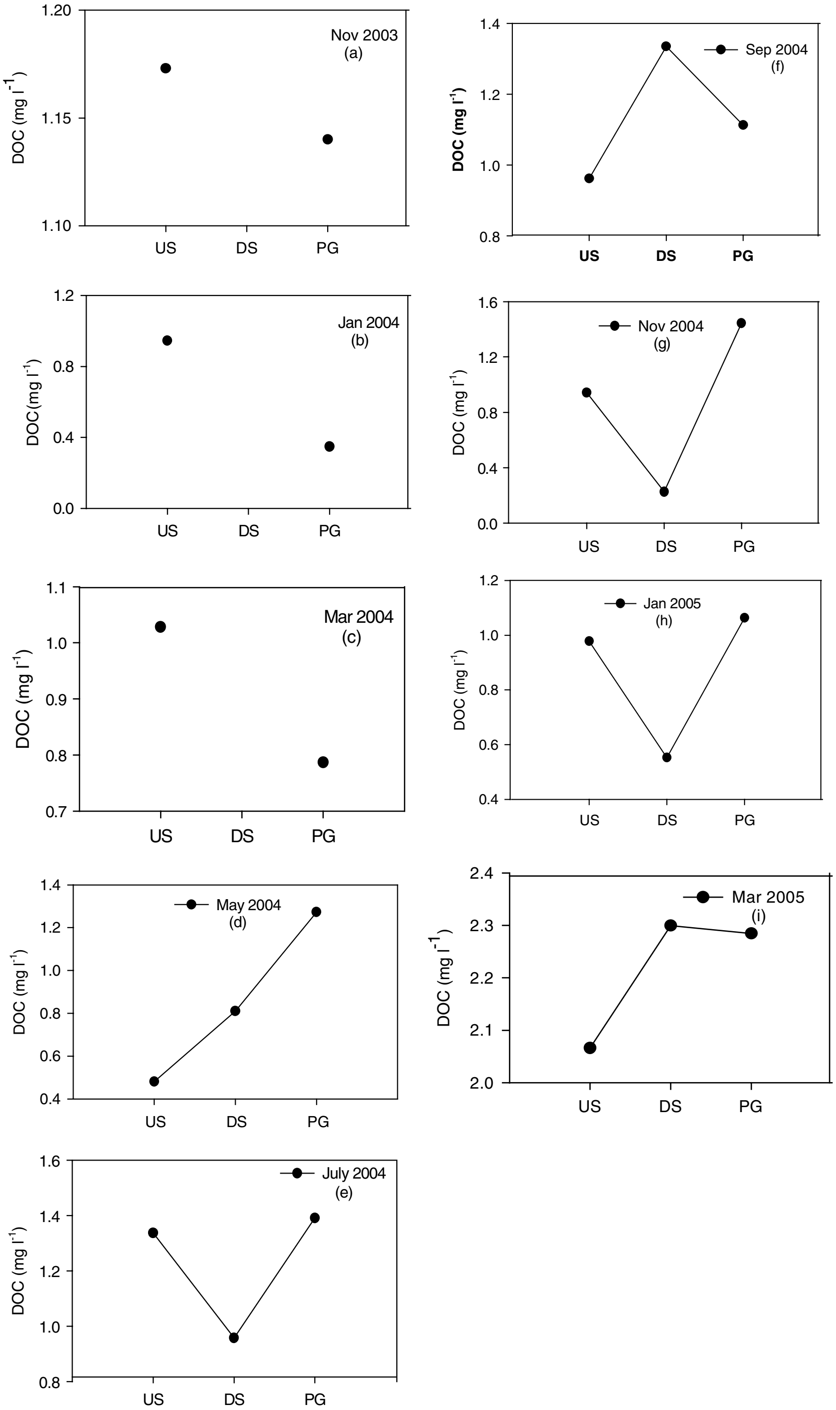

Figure 3. Spatial variations in the DOC concentrations at River Godavari, Rajahmundry.

Godavari river are calculated as follows:

$$Cw = 0.88C1 + 0.06C2 + 0.06C3 \quad (4)$$

C1, C2 and *C3* are the average concentrations of DOC measured during monsoon (June-Sept) , post-monsoon (Oct-Jan) and pre-monsoon (Feb-May) seasons respectively and the factor prefixed to it are the percent discharge during those periods. The discharge-weighted average for the Godavari river at Rajahmundry is calculated as $1.24\,\mathrm{mg\,l^{-1}}$, which is ~4 times lower than the DOC concentration calculated for the world average river (5.37 mg $\mathrm{l^{-1}}$; Ludwig *et al.*, 1996). The average concentrations of rivers, Ganga-Brahmaputra and Huanghe (Yellow river) is $3.9\,\mathrm{mg\,l^{-1}}$ and $6.2\,\mathrm{mg\,l^{-1}}$ (Ludwig *et al.*, 1996) which is ~3 times and ~5 times higher respectively than the Godavari river. Rivers, Indus and Changjiang contains highest DOC concentrations amongst the major world rivers ($14.4\,\mathrm{mg\,l^{-1}}$ and $12.3\,\mathrm{mg\,l^{-1}}$; Ludwig *et al.*, 1996), which is ~12 and 10 times higher than the DOC concentrations of the Godavari river. However, high concentrations in Indus and Changjiang could be due to anthropogenic influence, high organic carbon content in the soils distributed in the catchment and extreme seasonal variability in the discharge leading to strong flushing effect (Ludwig *et al.*, 1996). Lower DOC concentrations in the Godavari river could be due to relatively poor contribution from soil organic C source and less photosynthetic activity in the river due to high turbidity during monsoons. Similar low concentrations were reported for the European rivers, the Rioni and Rhone (1.1 and $1.7\,\mathrm{mg\,l^{-1}}$), which was attributed to low to moderate soil carbon and steep basin morphologies (Ludwig *et al.*, 1996).

Annual flux for the DOC from the Godavari river to the Bay of Bengal is calculated by the following equation

$$\text{Annual flux} = Cw \times \text{Annual water discharge}\,(105\,\mathrm{km^3}) \quad (5)$$

The DOC flux in the Godavari river is estimated as $130 \times 10^9\,\mathrm{g\,yr^{-1}}$. Particulate organic carbon flux ($756 \times 10^9\,\mathrm{g\,yr^{-1}}$) and DIC flux ($2520 \times 10^9\,\mathrm{g\,yr^{-1}}$) data from an earlier study done by Balakrishna and Probst, 2005 is used in the total carbon flux calculations from the Godavari river. The earlier study extrapolated the DOC concentrations with the assumption that the ratio of POC/DOC is ~1 for tropical rivers (Ludwig *et al.*, 1996). But this study has pointed out that the assumption does not hold good for the Godavari river, where the POC/DOC ratio is 5.8. Therefore, the mean annual flux of carbon (DOC + POC + DIC) is estimated as $3406 \times 10^9\,\mathrm{g\,yr^{-1}}$ which is ~15% lower than the flux calculated by Balakrishna and Probst, 2005. The flux constitutes 0.5% of the total C flux exported to the ocean by global rivers. Out of the total C flux of the Godavari river, the organic carbon contributes 26%. However, a clear picture of the C balance in the Godavari river system could emerge when the estimates are made for the net evasion of CO_2 from the DIC in the river surface and the quantity of CO_2 evolved due to respiration/oxidation of POC and DOC.

4. Conclusions

1. Increase in DOC concentrations is observed at the onset of monsoons, on account of draining of flood plains and the forest catchment soils of the river.
2. Anthropogenic influence on the DOC concentrations are observed in pre-monsoon sampling, possibly due to the effects of domestic sewage discharge in the river, bathing activities coupled with a low discharge during the period.
3. The station PG has higher DOC concentrations compared to the upstream stations US and DS in most of the sampling periods. It is observed that there are several "anthropogenic" inputs to the Godavari river between station US and PG, which could be influencing the DOC concentrations.
4. The mean annual flux of carbon is estimated as 3406×10^9 g yr^{-1}, which is 0.5% of the total carbon flux exported to the ocean by the global rivers.

Acknowledgements

The Department of Science and Technology (DST) is thanked for the financial support extended to KB under DST Young Scientist Research Project. Prof D.V.R.Murthy, NITK and an anonymous referee are thanked for giving valuable suggestions in improving the quality of the manuscript. Thanks to Ms V J Deepa, NITK, for help in the field trip and processing of samples. NITK's TIFAC-CORE is thanked for providing laboratory facilities. Thanks to Mr. Dinesh (Drawing and Maintenance), NITK, for neatly drawing the Figure 1.

References

Balakrishna, K. and Probst, J. L.: 2005, 'Organic carbon transport and C/N ratio variations in a large tropical river: Godavari as a case study, India', *Biogeochemistry* **73**, 457–473.

Deepa, V. J., Balakrishna, K., Gopal Mugeraya, Srinikethan, G. and Krishnakumar, P. K.: 2004, 'Preliminary findings on the water quality and trace metal variations in the river Godavari at Rajahmundry', *NITK Res. Bull.* **13**, 9–16.

Degens, E. T. and Kempe, S.: 1982, 'Riverine carbon – an overview, In: Degens ET (ed), Transport of Carbon and Minerals in Major World Rivers', Mitt. Geol.-Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderbd. pp. 757–764.

Degens, E. T., Kempe, S. and Richey, J.E.: 1991 'Summary: Biogeochemistry of major world rivers', In: E. T., Degens, S., Kempe. and J. E., Richey (eds) *Biogeochemistry of Major World Rivers SCOPE, John Wiley and Sons*, London. pp. 323–347.

Gaillardet, J., Dupre, B., Louvat, P. and Allegre, C.J.: 1999, 'Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers', *Chem. Geol.* **159**, 3–30.

Gupta, L. P., Subramanian, V. and Ittekkot, V.: 1997, 'Biogeochemistry of particulate organic mater transported by the Godavari river, India', *Biogeochemistry* **38**, 103–128.

Ludwig, W. and Probst, J. L.: 1998, 'River sediment discharge to the oceans: Present-day controls and global budgets', *American Journal of Science* **298**, 265–295.

Ludwig, W., Probst, J. L. and Kempe, S.: 1996, 'Predicting the oceanic input of organic carbon by continental erosion', *Global Biogeochem. Cycles*, **10**, 23–41.

Martin, J. M. and Meybeck, M.: 1979, 'Elemental mass-balance of material carried by world major rivers', *Mar. Chem*. **7**, 173–206.

Meybeck, M.: 1988, 'How to establish and use world budgets of riverine materials', In: A., Lerman, and M., Meybeck: (Eds) *Physical and Chemical Weathering in Geochemical Cycles,* Kluwer Academic. 247–272.

Rao K. L.: 1975, *India's Water Wealth, its Assessment, Uses and Projections.* Orient Longman, New Delhi, 255p.

Rao, P. A. A. N.: 2003, 'Water quality monitoring of river Godavari near Rajahmundry – A case study', *A report submitted to the Govt. of Andhra Pradesh*, India.

Sarin, M. M.: 2001, 'Biogeochemistry of Himalayan rivers as an agent of climate change', *Curr. Sci*. **81**, 1446–1450.

Sarin, M. M., Sudheer, A. K. and Balakrishna, K.: 2002, 'Significance of riverine carbon transport: A case study of a large tropical river', Godavari (India). *Science in China* (Series C). **45**, 97–108.

Sarmiento, J. L. and Sundquist, E. T.: 1992, 'Revised budget for the oceanic uptake of anthropogenic carbon dioxide', *Nature* **356**, 589–593.