Significance of riverine carbon transport: A case study of a large tropical river, Godavari (India)

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Abstract Although riverine carbon fluxes are a minor component of the global carbon cycle, the transfer of organic carbon from land to ocean represents a flux of potential carbon storage, irreversible over 10³ to 10⁴ a. Future carbon transfers through river basins are expected to accelerate, with respect to both sources and sinks, because of the large-scale human driven land-use and land-cover changes. Thus, the increased amounts of carbon transported to and sequestered in marine sediments (through fertilization by river-borne inorganic nutrients) may be an important net sink for anthropogenic CO₂. Particularly, the humid tropics of South Asia are regions very sensitive to this lateral C transport because of high precipitation and high rates of land use and cover change. In this paper we report on the role of upland tributaries in the transport processes influencing the lateral carbon and nitrogen fluxes of the Godavari, a large tropical river of India. By far, dissolved inorganic carbon (DIC) is the dominant form of carbon transport in the river basin. It constitutes as much as 75% to the total carbon load. Particulate and dissolved organic carbon (POC and DOC) fluxes account for 21% and 4%, respectively. In the upper basin, DOC fluxes exceed that of POC due to large-scale anthropogenic activities. In contrast, tributaries in the central basin are characterized by comparable fluxes of POC and DOC. However, downriver POC export is 35% less than the import from upriver and tributaries due to the entrainment of sediments in river channels and dam sites. We argue that for highly disturbed watersheds in tropical regions, downstream transport of sediments and carbon requires long-term sampling programmes.

Keywords: riverine carbon flux, Godavari, case study.

Global carbon fluxes transported via rivers, although small compared with the fluxes at atmosphere-biosphere (120 Pg C a^{-1}) and atmosphere-ocean (90 Pg C a^{-1}) interfaces, often play important roles in regional budgets of carbon entering the continent-ocean interface (estuaries, deltas and coastal zone). In fact, lateral carbon flows and storage in dams and coastal zones could well account for part of the missing C sink. To date we are far from knowing the current contribution of lateral transport and storage in the global carbon cycle, and even less is known about its future contribution given the expected changes on land use and cover due to human activities.

Large rivers tend to integrate the biogeochemical activities within the drainage basin and the total carbon observed in river water is a mixed component that originates from different sources. In a pristine environment, the basic nature of riverine carbon consists of three categories: a) Dissolved inorganic carbon (DIC) derived from chemical weathering of rocks which is largely transported as HCO_3^- ion, b) particulate organic carbon (POC) derived from soil organics, litterfall

and autochthonous production; and c) dissolved organic carbon (DOC) arising from leaching of top-soil, peat and regulated by *in situ* pH. Superimposed on these natural forms, the present-day increased amounts of industrial effluents, fertilizers, sewage and other human wastes are modulating the riverine concentrations of carbon. Anthropogenic changes and river eutrophication is an important factor in future for algal POC, which can create near-anoxic conditions when reaching coastal waters.

Critical issues on river carbon transport include: a) How much carbon is oxidized and stored within the basin; b) What is the best estimate of organic carbon flux from rivers to ocean; c) Has the lateral flux or resulting storage changed with time? Worldwide, the amount of terrigenous carbon that enters the river systems is on the order of 1.5 Pg C a⁻¹ (range: 0.8 to 2 Pg C a^{-1[1]}). Of this carbon, roughly 25%—30% is oxidized within the river system and nearly equal amount is represented by temporary storage in the lowland areas. It is estimated that net global natural carbon (organic and inorganic transport) from rivers to oceans is about 0.8 Pg C a⁻¹ (range: 0.4 to 1.2); half of which is organic and the other half is inorganic^[2–5]. Additional fluxes due to human activity have been estimated to be about 0.1 Pg C a⁻¹ (mainly organic carbon)^[3]. Storage of organic carbon in coastal zones may account for 10% to 15% of the annual atmospheric increase in CO₂ over the past two decades^[6]. The natural DIC transport via rivers, however, is part of a large-scale cycling of carbon between the open ocean and land associated with dissolution and precipitation of carbonate minerals. Globally, this natural cycle drives net outgassing from the ocean of the order of 0.6 Pg C a^{-1[5]}.

1 Carbon transport via rivers

Data on water discharge and total suspended sediments are generally available for a number of watersheds worldwide, but studies on the concentrations of DOC and POC are much fewer.



Fig. 1. Past estimates of organic carbon fluxes to the ocean via rivers; data derived from Richey^[7] and references cited therein. A: Garrels & Meckenzi(1971); B: Garrels et al. (1975); C: Duce & Duursma (1977); D: Richey et al. (1980); E: Meybeck (1981). The differences and uncertainties in the estimates are largely due to the assumption involved in methods of extrapolation. The annual organic carbon flux of 0.4 Pg is considered to be most representative of the world rivers^[2].

Thus, several methods of extrapolation have been used in the past to arrive at carbon budgets based on assumed average concentrations of total organic carbon (2—10 mg C L⁻¹, DOC plus POC) and global water discharge. Data from Richey^[7] are summarized in fig. 1 and shows limited case studies for Asian rivers. These estimates assume that the ratio of fine particulate organic carbon to total suspended solids (TSS) equals that in the average shale (POC/TSS~1%)(fig. 1). However, 1% to 8% ratios of POC/TSS are possible within the range of values observed in temperate regions. Since several regions of Asia are densely populated and heavily disturbed (and are thus capable of high organic outputs), the higher riverine transport fluxes of carbon are possible. Net transport of organic carbon via rivers is 0.4 Pg C a⁻¹, and the tropical zone accounts for 60% of the estimated flux^[2] (fig. 2). Fivefold change in POC values within a single year has been reported for the Ganga in Bangladesh^[8], and almost 15-fold change within a year and 3—4 fold change from year to year for the Indus^[9]. The total organic carbon transpo



Fig. 2. River transport of total organic carbon (POC+DOC) from different climatic regimes clearly demonstrate the importance of carbon fluxes (0.24 Pg a^{-1}) from the tropical zone that constitute nearly 60% of the global flux^[2].

for the Indus^[9]. The total organic carbon transport in these rivers amounts to 30×10^{12} g C a⁻¹.

The global average export of carbon from land to the marine environment (0.8 Pg C $a^{-1[2,3]}$) is a result of the complex balance between storage, release and respiration (oxidation) of organic carbon in terrestrial and aquatic environments. In additon, processes such as extensive use of phosphorous and nitrogen fertilizers, cultivation of nitrogen-fixing crops, discharge of municipal wastes, and extensive deforestation contribute to the final loads of DOC and POC in river system^[10,11] and to carbon sink strength.

Model results show that N, P and S resulting from land use enhance the CO₂ fertilization effect^[12,13], and that larger flux of river-borne nutrients could also increase the carbon sink capacity of the coastal ocean. The humid tropics of Asia are potential among the highest contributors to this increased carbon storage. About half of the suspended sediments entering the ocean today come from Asian countries^[12,14], and this is likely to increase in the future in ways that will impact the global biogeochemical cycles of C-N-P-S. Asia's large and expanding population coupled with economic growth have the potential to dominate the global perturbation of the carbon cycle^[12].

2 Biogeochemistry of large rivers

Carbon and nutrient fluxes in large rivers are considered to be reflections of their watersheds and floodplains and processes occurring in the tributaries^[15]. The physical size and logistical problems posed by large rivers present challenges in the efforts to determine carbon dynamics. Over the past two decades, some of the major rivers in the temperate and tropical regions have been studied: The Amazon^[16]; Major North American, Russian Arctic and Siberian rivers^[17]; The Parana and Orinoco^[18]; Major African rivers^[19]. However, long-term studies of the major world rivers are lacking and it is the only way to understand their nature as non-steady-state systems governed by episodic events.

2.1 Case study of a large tropical river, Godavari (India)

Motivated by the perspective of understanding the carbon transport fluxes through the study of large tropical rivers in South Asia, a comprehensive project has been conducted in the Godavari

mainstream and its tributaries to understand the spatial and temporal distribution and composition of POC, DOC, and DIC. The actual distributions of particulate and dissolved organic and inorganic carbon may be unique to the Godavari, but the mass balance approach used to determine the relative magnitude of fluxes provides a template applicable to the other large river systems in South Asia (e.g. The Ganga, Brahmaputra, Indus). Godavari is the third largest river in India, after the Ganga and the Brahmaputra. The river originates in the Western Ghats near Nasik, at an elevation of 1065 m above sea level. The river basin lies between 22°35', 16°05'N and 73°25', 83°08'E, occupying an area of 3×10^5 kms, with a mean-annual water discharge of 2830 m³ s⁻¹. The river flows east-south (fig. 3) for a distance of 1465 km before it debouches into the Bay of Bengal through three main distributaries (Gautami, Vashishtha and Vainatayam). The principal tributaries of the Godavari are Purna, Pranhita, Indravati and Sabari draining the northern basin and joining from the left bank; Pravara, Manjara and Maneri drain the southern basin and join the mainstream from the right bank (fig. 3). Of these tributaries, the Pranhita and Indravati transport nearly 80% of the annual water discharge. The climate of the river basin is semi-arid to monsoonal, with minimum temperature of ~8 to 9°C in winter months (Dec.—Jan.) and maximum of ~45 to 46℃ in summer months (April—May). The precipitation over the basin and water discharge is dominated by south-west monsoon, July to October, when almost 85% of the annual discharge takes place.



Fig. 3. Godavari basin and sampling location map. The river mouth sampling site at Rajahmundry is marked as location #20. The Pranhita and Indravati are the principal tributaries sampled from the sites # 5 and 6, respectively.

Deccan basalts dominate the geology of the upstream catchment; while granites, gneisses and sedimentary rocks (sandstones, quartzites and shales) are predominant in the lower catchment. The

central river basin is characterized by large area of coal deposits. The cultivable land is 1.85×10^5 km², accounting for almost 60% of the basin area; while the land under forest is 0.9×10^5 km². As regards irrigation practices, different chemical inputs comprising of fertilizers, pesticides and insecticides are abundantly added to the soil over the last two decades of green revolution. The application of fertilizers is reportedly high in the basin, ~50 kg per hectare^[20] in comparison to 25 kg per hectare at country level.

2.2 Material and methods

Godavari mainstream was sampled at several locations, from its source (at Nasik) to the river mouth at Rajahmundry (fig. 3), during Nov. 1998, March, August 1999 and August 2000, so representing the seasonal and annual variations in river flow. Sampling of the tributaries was carried out near to their confluence point with the main stem. Samples were collected from the midchannel, filtered at site, through glass fibre filters (for POC. and DOC); while the decanted water samples were stored for DIC. In the laboratory, C and N composition of the particulate matter was analysed with an Elemental Analyser (Fisons NA-1500 model). The HCO_3^- content, as a measure of DIC, was analysed by acid titration on an auto-titration system using glass pH electrode. DOC concentrations were measured on TOC Analyser (Shimadzu CA 5000 model). The relevant details of samples collection, field processing and laboratory based analyses will be described elsewhere. Nearly 15 to 18 samples were collected and analysed from different sites (fig. 3) per sampling period.

2.3 Results and discussion: seasonal and spatial distributions

2.3.1 Dissolved inorganic carbon. The total dissolved inorganic constituents (conventionally referred to as TDS) along the Godavari main stem ranged from 142 to 622 mg L^{-1} . The upriver TDS concentrations, within a few hundred meters of the source region, were lowest and increased downstream. The concentration near the river mouth (at Rajahmundry, fig. 3) varied from 182 to 240 mg L^{-1} , directly in relation to the mixing proportions of the tributaries with the main channel. The dissolved constituents in the tributaries also varied significantly (54 to 460 mg L^{-1}) over the annual cycle of water discharge. In general, the lower TDS concentrations occurring during high river stages and higher values during lean flow conditions. The lowest TDS concentrations were characteristic feature of the two tributaries, Indravati and Sabari (fig. 3), with values ranging from 54 to 115 mg L^{-1} . The HCO₃⁻ ion, used as an index of DIC (carbonate alkalinity was virtually zero in the tributaries and main channel) was the dominant component of the TDS. Its contribution to the dissolved inorganic constituents ranged from 55% to 65%. However, contribution of HCO_3^- in the upriver main stem is relatively low, accounting for only 35%—50% of the TDS. The spatial and temporal variations of DIC content in the tributaries and along the main stem are significantly pronounced; the concentration in the tributaries ranged from 7 to 53 mg C L^{-1} and

that along the main stem ranged from 22 to 53 mg C L^{-1} (fig. 4). A distinct inverse relationship with discharge was found, relatively high DIC observed at lean discharge. With the exception of Indravati and Sabari, DIC concentrations in the tributaries were comparable to those in the main stem during different stages of river flow. The discharge-weighted concentrations in the tributaries ranged from 7.4 to 47 mg C L^{-1} (fig. 5), with relatively high concentrations in the three tributaries:



Fig. 4. Concentrations of DIC, POC, DOC and C : N ratio in the tributaries exhibit significant variations in space and time. In general POC concentrations are higher during high flow, while DIC and DOC concentrations increase during lean flow conditions.

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The Purna, Penganga and Wardha. The annual-mean DIC in the main channel also varied in space, with highest concentration occurring upriver, $\simeq 43 \text{ mg C L}^{-1}$ (at sampling sites marked as 7 and 13, fig. 3) and decreased downriver (fig. 5).



Fig. 5. Annual-discharge-weighted concentrations and fluxes of DIC $(2270 \times 10^9 \text{ g})$, POC $(650 \times 10^9 \text{ g})$ and DOC $(130 \times 10^9 \text{ g})$ are summarized for the Godavari main stream. By far, DIC flux is the dominant form of carbon transported in Godavari river. In the upriver tributaries (Purna and Penganga), the DOC flux exceeds that of POC. In the tributaries of central basin (Pranhita, Indravati), POC fluxes are comparable to DIC transport. However, POC fluxes exhibit non-conservative trend suggestive of sediments entrainment in river channels and dam sites.

2.3.2 Particulate and dissolved organic carbon. The particulate organic carbon concentration in the Godavari basin closely tracks the sediment distribution in the respective river channels; with highest concentration during high river stage and the lowest during lean stage. The concentrations of total suspended sediments (TSS) in the main channel increased downstream; the upriver catchment largely dominated by Deccan basalts, granite and gneissic rocks while relatively sediment-rich tributaries characterize the lower basin. Most of the suspended fraction, during high river stage, is carried as fine sediments. Thus, POC concentrations were highest (10–20 mg C L⁻¹, fig. 4) in the principal tributaries: Wardha, Pranhita and Indravati during the monsoon flow (high river stage), suggesting basin-wide flushing with dominant allochthonous POC from soils and litter. POC levels in the tributaries varied considerably over time and space (range: 0.3 to 20 mg C L^{-1} , fig. 4) with lower concentrations occurring during lean flow but higher than those in the main stem (range: 0.16 to 9.3 mg C L^{-1}). The discharge-weighted POC concentrations in the tributaries and the main channel are summarized in fig. 5. Except for the Wardha, Pranhita and Indravati, tributary concentrations of POC were less than 5 mg C L^{-1} (fig. 5). The annual-mean POC in the main channel is 7.2 mg C L^{-1} near its mouth (fig. 5).

In contrast, the spatial and temporal variations in DOC levels were less pronounced (fig. 4). The main stem DOC ranged from 1.3 to 4.0 mg C L⁻¹ with higher concentrations during lean stages suggesting relatively stronger influence of anthropogenic inputs. In several of the tributaries, DOC accounts for 50%—60% of the total organic carbon (POC+DOC) and is by far the predominant form of organic matter in relatively sediment-poor streams of the upper basin. The DOC concentration in the tributaries varied over a narrow range: 1.0 to 3.3 mg C L⁻¹ (fig. 4); higher concentrations occurring during lean flow stages resulting from agricultural activities and municipal wastes (fig. 4). Tributary DOC levels were comparable to or somewhat lower than the main channel DOC. The annual-average concentration at river mouth is 1.4 mg C L⁻¹ (fig. 5). The C:N ratios in the POC fraction also show extreme variations over time and space. These ratios in the tributaries ranged from 5 to 13.8 (fig. 4); with lower particulate C : N ratio typical of the lean discharge conditions.

2.3.3 Carbon Budget. The above data represent the annual variations in river flow (lean, median and high), while the characteristic variations in DIC and POC abundances and lateral transport in the main stem during high flow (Aug. 1999) are illustrated in fig. 6. Clearly, POC load and transport is dominated by the three tributaries with concentration attaining a maximum at sampling site #9 (fig. 3). The transport of DIC exhibits a near conservative trend influenced by the mixing proportion of the tributaries with the main channel. The DIC content is lowest at a downstream site (# 9) after the confluence of the principal tributaries, Pranhita and Indravati, causing a dilution effect. To determine the relative magnitude of the fluxes to and within the main channel, a mass balance approach has been used based on the discharged-weighted concentrations (fig. 5). The fluxes of DIC, POC and DOC from upriver, tributaries and downriver are calculated as the product of the respective concentration of each species and water discharge for the tributary and sampling sites along the main stem. The DIC export by the tributaries ranged from 123 to 764×10^9 gC a⁻¹, with lowest transport by Sabari and highest export by the major tributary Pranhita (figs. 3 and 5). The individual fluxes of POC and DOC in the tributaries ranged from 2.6 to 620×10^9 gC a⁻¹ and 7.5 to 66×10^9 gC a⁻¹, respectively (fig. 5). It is noteworthy that the DOC export in Purna and Penganga tributaries exceed that of POC flux. Their catchments are characterized by large-scale agricultural activities and ground water irrigation. The POC export is nota-

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bly highest for Pranhita (fig. 5), with high correlation between the transport of POC and TSS. In general, inorganic carbon (DIC) transport is the dominant component in the tributaries and the main stem with the exception of Indravati, wherein the organic carbon flux (a sum of POC and DOC) exceeds that of DIC (fig. 5).



Fig. 6. Downstream variation in the Godavari main channel during high flow season (Aug. 1999): DIC concentration decreases while POC levels increases after the confluence of the principal tributaries, Prahnita and Indravati (see fig. 3). DIC transport exhibits a near conservative trend.

The annual budget for the particulate and dissolved carbon is made for the Godavari basin based on the following fluxes (in 10^9 gC a⁻¹):

Import from upriver:	DIC (990)	POC (8)	DOC (60)
Tributary inputs:	DIC (1130)	POC (970)	DOC (140)
Downriver Export:	DIC (2270)	POC (650)	DOC (130)

These results show near conservative transport of DIC in the river basin with four-fold higher flux than that of POC. The downriver POC and DOC export at the river mouth are nearly 35% less than the import from upriver and tributaries, suggesting non-steady state conditions due to the deposition of sediments in the channel (behind dams) and floodplains of small streams and rivers. Global deposition of river borne organic carbon in floodplain wetlands is at least 6% of the total river flux^[21]. Since large tracts of floodplain wetland are located in the tropical and sub-tropical regions that have received little attention, efforts should be focused towards making organic carbon budgets in these systems.

The distribution of riverine POC is tied to the processes that control sediment transport. The episodic flood events, the import and export of coarse and fine POC, and changes in channel storage are the elements of fluvial geomorphology that define the qualitative and quantitative changes in the organic load. An earlier study with four sampling points^[23] estimated that Godavari river transports about 314×10^{10} g a⁻¹ of particulate carbon, of which POC flux is 280×10^{10} g a⁻¹ and PON flux is 29×10^{10} g a⁻¹. These fluxes are nearly four-fold higher than those derived in this study based on the seasonal and discharge-weighted concentrations. Higher fluxes in ref. [22] could be somewhat biased as monsoon sampling has been used as representative of the suspended sediments and associated POC transport. However, episodic high sediment transport and inter-annual variations could also explain the observed differences. Variations in dissolved and suspended loads need to be monitored, at least, over a period of 10 a in order to document inter-annual variability.

A total carbon flux (DIC+POC+DOC) of 3050×10^9 g C a⁻¹ from the Godavari constitutes about 0.4% of the global transport, while the organic carbon (POC+DOC = 780×10^9 g C a⁻¹) accounts for 0.2% of the riverine export of organic matter from continents to the ocean. The specific transport rate of organic carbon (2.6 t km⁻² a⁻¹) from the Godavari is significantly higher than some of the African rivers (Niger: 0.9, Orange: 0.04, and Gambia: 0.4), while Zaire has a rate of 3.7 t km⁻² a^{-1[19]}. Systematic seasonal data for south Asian rivers, of similar size as Godavari, are not enough to make comparison of organic carbon fluxes to the Indian Ocean.

3 Conclusions

A case study of the biogeochemistry of a large tropical river Godavari (India) shows that the abundance of total carbon in the main stem and tributaries ranged from 13.8 to 50.7 mg C L⁻¹. With the exception of the two tributaries Pranhita and Indravati, the most abundant form of carbon is DIC with an average concentration of 40 mg C L⁻¹, accounting for 85% of the total carbon. Highest values of POC were observed during high flow conditions dominated by southwest monsoon that accounts for 85% of the water discharge in the river basin. A parallel increase in particulate C:N ratios (range: 8 to 12) shows the contribution of allochthonous material due to surface runoff. The impact of anthropogenic DOC signals is pronounced during lean flow stages in up-

river and the feeder tributaries. The total transport of inorganic carbon was 227×10^{10} gC a⁻¹ and accounted for nearly 75% of the total carbon transported in Godavari river, while the contribution of POC flux is 21%. Down river particulate nitrogen flux is about 6×10^{10} g N a⁻¹. The non-conservative trend of organic carbon (POC+DOC) transport, between the upper and lower basins, indicates storage of organic carbon in river channels and dam sites. The effects of land use change on surface runoff, sediment production, nutrient and carbon export are expected to modify the carbon cycle in the tropical Asian rivers. Further studies involving quantitative estimates of various types of sediment influxes will help to predict the effects of perturbations on carbon mobilization and sequestering.

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