CHAPTER 13

Interactions of C, N, P, and S in River Systems: A Biogeochemical Model*

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ABSTRACT

Rivers transport dissolved and particulate C, N, P, and S from land to the oceans. Dynamic processes operating on varying time scales within the river system store and transform the elements in transit, such that the fluxes and chemical forms of the elements finally exported are often quite different from those in the headwaters. In terms of the global cycling of elements:

1. Rivers transport organic C from terrestrial sources ultimately to marine reservoirs. The export to the ocean is on the order of 800 Tg C yr⁻¹, which may be considerably less than the rate at which carbon enters the river system, due to oxidation and storage within the river. The rate of burial due to human events, such as upstream disturbances, has increased several-fold, to about 10–20% of the rate of increase in atmospheric CO₂.

2. Rivers supply dissolved inorganic ions to the oceans. The current fluxes are poorly known, but appear to be approximately 500 Tg C yr⁻¹ (dissolved inorganic C), 200 Tg S yr⁻¹ (sulphate), 11 Tg N yr⁻¹ (dissolved inorganic N), and 1 Tg P yr⁻¹ (phosphate). For the nutrients N and P, the pristine fluxes were 2–5 Tg N yr⁻¹ and 0.5 Tg P yr⁻¹. Calculations suggest that the increased nutrient loading to the marine environment increases primary production and leads to an increased marine burial on the order of 200–1000 Tg C yr⁻¹.

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3. River systems, whose often extensive floodplains accumulate organic matter and nutrients from upstream, are very active metabolically. As such, they might be active locations in the production of the gases CO₂, CH₄, NH₃, N₂O, H₂S, and COS.

Rivers play an important role in human activities. They support major agriculture, inland and coastal fisheries, and provide portable water, electricity, and transport. Human-induced events can influence the functioning of river systems and, in turn, the role of river systems in global geochemical cycles.

13.1 INTRODUCTION

Rivers are among the more striking and dynamic of the earth’s ecosystems. Their outstanding function is the transport of water; they also carry the dissolved and particulate products of crustal weathering and erosion from land to the sea (Rzóska, 1980). Rivers are thus a critical link in the global cycling of elements. Data describing them are, however, surprisingly few and their role in cycling is poorly understood. This so-called role has been evaluated traditionally as the global sum of the export of terrestrial organic carbon and minerals to the oceans, with the tacit assumption that rivers are passive conduits.

Rivers act as integrators of basin-wide activities: their loads are a composite of organic and inorganic materials representing a spectrum of sizes and chemical characteristics. These properties influence the fate of the materials over a range of time scales: they enter the river through various pathways, and are subject to within-river utilization, modification, and storage. As a result, the load discharged to the oceans may be very different in quantity and quality from the materials entering the river, and there may be considerable variation from one geographic region to another (Richey, 1981). Further, man has changed the nature of many of the world’s major rivers by controlling their floods, constructing large impoundments, and using them for the export of wastes. As a result, few rivers are pristine or completely free-flowing.

Clearly, rivers are more than passive conduits. The flux of elements into, through, and out of these systems is of considerable importance at both regional and global scales. The intent of this paper is to place some perspective on this issue by exploring the biogeochemistry of C, N, P, and S in rivers. To do this, a conceptual model will be examined in Section 13.2, and the data that do exist will be evaluated within the model context in Section 13.3, with regard to both natural conditions and to conditions due to anthropogenic disturbances. Finally, the appropriate context for the evaluation of rivers in element cycling will be summarized.

13.2 A BIOGEOCHEMICAL MODEL OF RIVER SYSTEMS

The salient features of a river system can be addressed in the form of a
conceptual model (Figure 13.1). The model consists of a description of the physical configuration and dimensions of river systems (Figure 13.1a), the hydrologic regime (Figure 13.1b), the important chemical species and fluxes (Figure 13.1c), and a mass-balance summary of the fluxes (Figure 13.1d). The individual model components are discussed below.

13.2.1 Physical Characteristics of River Systems: Configuration and Hydrology

An individual river system is a network of streams in a discrete drainage basin, fed by ground-water and precipitation run-off (Figure 13.1a). The streams are ordered in size, from the smallest first-order spring, to a second-order stream as the confluence of two first-order streams, and so on, to the main channel exiting the basin (Strahler, 1957). The structure of a river itself involves the flowing water, the river bed, and the floodplain, as well as the dry land of the drainage basin. For a biogeochemical analysis, a river system is divided spatially into a series of discrete sectors, on the basis of the relative homogeneity of each sector's physical and biotic features.

Annual variations in the quantity and distribution of precipitation over a drainage basin produce the characteristic rise and fall in the hydrograph (water level). In small streams one storm can produce abrupt 'spikes' in the hydrograph, whereas a more modulated pattern is observed in large rivers (Figure 13.1b). Over the course of the hydrologic cycle, the configuration of the river system changes, as the water is contained in the main channel or covers the floodplain. Such differences constitute temporal changes in a river system that must be evaluated.

The configuration of the drainage basin, its hydrology, and such parameters as relief and lithology, govern the immediate channel shape and transport of materials. The ability of flowing water to carve a channel, transport materials and ultimately to modify landscapes depends on its force (gravity times water mass) and the resistance offered to it by friction within the channel boundaries (Leopold et al., 1964). The ability of a river to transport its suspended load and bedload is proportional to the product of its force and velocity (power) and the concentration and size distribution of its particles (Rouse, 1950).

The physical properties of a river system operate on several time scales. Seasonal changes (<10^0 years) establish the characteristic hydrographs, while interannual precipitation (10^3–10^4 years) establishes the routine conditions observed. However, major flood events (10^1–10^2) can change the basic structure of a river channel and can export materials stored for decades. Finally, tectonic and glacial events (10^3–10^4 years) can alter the geologic configuration of river basins.

13.2.2 C, N, P, and S: Chemical Species

The total organic matter and dissolved ions in a river consists of material of
(a) A drainage basin consists of a network of streams of increasing order. Analytically, the basin can be divided into sectors, on the basis of discrete subdrainages from tributaries. Each sector has dry land (L), tributaries (Tr), floodplain (Fp) and main channel (MC). The boundaries of the main channel, or reach are located preferably at the sites of gauging stations, where river discharge can be measured.

(b) The river discharge (Q) changes over time, which results in changing water levels. The model of (a) must be evaluated over this hydrograph as processes and physical dimensions change according to stage height. The main conditions are indicated.
The characteristic distributions and fluxes of C, N, P, and S between and within each sector of a drainage basin are identified. The important species include particulate (POM) and dissolved (DOM) organic matter, dissolved inorganic carbon (DIC), dissolved inorganic N, P, and S (NPS), and the reduced species of C, N, and S (red CNS). These occur as the land source materials, in tributaries (which are also dynamic but are represented here as passive), on floodplains in both sediments (when inundated by flood waters) and standing waters, and in the main channel itself. The main channels of large rivers often have a significant bed load, but rarely an established benthos. For each sector i, transport pathways include terrestrial inputs to tributaries via direct (litterfall) or mobilized (ground-water, erosion) routes (Tf), total tributary inputs to the main channel (∑Tr), import from the upriver sector (Ti−1) and export to the downriver sector (Ti+1). Internal fluxes include primary production by phytoplankton (Prn), macrophytes (Prm), and vegetation in contact with water (Prv), seston respiration in the water column (Rw), floodplain sediment respiration (Rs), entrainment (En), deposition and sedimentation (Dp), oxidation–reduction (Rd), nutrient uptake (U) and regeneration (R), flocculation (F), exchange (Ex), and gas evasion (G) and ebullition (Eb). A reach is described by river surface area, sediment surface area, volume, length, concentration of species, river velocity, thickness of boundary layer between air and water, and the diffusion constant across the air–water boundary layer.
CARBON MASS BALANCE IN MAIN CHANNEL

\[ \frac{dPOC^m}{dt} = T_{i-1} + \epsilon T_{i} + P_{R}^{m,P} + En - Dp - Rw - T_{i+1} + F \]

\[ \frac{dDOC^m}{dt} = T_{i-1} + \epsilon T_{i} - Ex - F - T_{i+1} \]

\[ \frac{dDIC}{dt} = T_{i-1} + \epsilon T_{i} + Rw + Rs - P_{R}^{m,P} - G - T_{i+1} + Ex \]

(d) Example mass continuity equations for the fluxes described in (c) for DIC, DOC, and POC in the main channel. Solution of these equations gives the concentration of the respective species in a sector, C(i)

highly varied origin and is subject to many fates (Figure 13.1c). To explain the bulk composition, information is needed on the origin and chemical composition of the constituent fractions.

The organic matter is divided functionally into dissolved and particulate fractions, usually on the basis of what passes through, and what is retained on, a 0.45 \( \mu \)m filter. The bulk of dissolved organic matter apparently exists as brown acidic polymers, known as fulvic and humic acids, that are thought to be produced by the extracellular condensation reactions of organic substances released by the microbial degradation of terrestrial plant material (Beck et al., 1974). The dissolved fraction is utilized as a source of energy by heterotrophic micro-organisms, principally near the terrestrial sources (Manny and Wetzel, 1973; McDowell and Fisher, 1976; Moeller et al., 1979). Depending on the source of the dissolved fraction and the chemistry of the water, a quantity of the material precipitates (Lush and Hynes, 1973). As a result, some characteristic changes may occur from upstream to downstream such as increasing molecular weight and phenolic hydroxyl content (Kaplan et al., 1980). The dissolved organic material subsequently found in downriver sectors and exported to the marine environment is relatively inert and differs in mean half-life and chemical composition from its precursors (Beck et al., 1974). The particulate matter is divided further into ultrafine (<50 \( \mu \)m), fine (<1 mm), and coarse (>1 mm) fractions. In approximate order of increasing refractivity (decreasing availability as a food source) these include phytoplankton, attached flora (periphyton, bacteria, and mosses), non-woody vascular plant tissue and their remains (e.g., tree leaves, grasses, mac-
rophytes), woody plant tissue, fossil organic matter in eroded sedimentary rock and human organic matter.

The concentrations and ratios of elements in the dissolved and particulate organic fractions are highly variable. Concentrations of particulate and dissolved organic carbon (POC and DOC) range from ≤ 1 mg C litre⁻¹ in alpine streams to > 20 mg C litre⁻¹ in some tropical or polluted rivers (Brinson, 1976; Malcom and Durum, 1976; Naiman and Sibert, 1978; Mulholland and Kenzler, 1979). Average DOC:POC ratios can range from 1 to 10 or 20 in rivers of North America (Malcom and Durum, 1976; Naiman and Sedell, 1979) to less than 0.5 in tropical rivers (Richey et al., 1980; Wissmar et al., 1981). The ratio of carbon to the other elements varies from the Redfield ratio for plankton-dominated systems to higher amounts of C relative to the other elements in systems dominated by terrestrial detritus (Wetzel and Mann, 1977; Triska et al., in press).

Certain properties of this heterogeneous mixture of organic fractions provide useful tracers for identifying the sources of the individual components and for assessing how labile or refractory a particular mixture is. The ratio C:N is suggestive of source materials. Hedges and Mann (1979a, b) have demonstrated that the ratios of concentration of the lignin oxidation products cinnamyl, syringyl, and vanillyl phenols provide unambiguous tracers for woody and non-woody tissues of gymnosperms and angiosperms. Differences in the thermodynamic and kinetic properties of the stable carbon isotopes result in measurable variations in the isotopic composition of materials of different terrestrial and aquatic origins (Craig, 1957; Degens, 1969; Wigley et al., 1978).

The major dissolved species include dissolved inorganic carbon (DIC; as CO₂(aq), H₂CO₃, HCO₃⁻, CO₃²⁻), SO₄²⁻, NO₃⁻, NH₄⁺, and PO₄³⁻. Bicarbonate and SO₄²⁻ are among the major dissolved ions in river water, with world average concentrations of about 58 mg litre⁻¹ and 11 mg litre⁻¹, respectively (Livingston, 1963). As in all waters, the distribution of DIC among its constituent species is governed by pH and less importantly by temperature and pressure (Stumm and Morgan, 1970). Of particular note is that the partial pressure of CO₂ (pCO₂) of river water is many times that of the atmosphere (Garrels and Mackenzie, 1971). The resulting evasion of CO₂ from the water to the atmosphere can constitute a significant loss of carbon (Stallard, 1980). Nitrate, NH₄⁺, and PO₄³⁻ vary from mg litre⁻¹ levels in polluted systems to trace levels in pristine waters (cf Table 14.1, Wollast, Chapter 14, this volume). As often limiting nutrients, they are biogeochemically significant, while SO₄²⁻, on the other hand, behaves conservatively. The reactions in which these ions are involved may produce other chemical species that are of relatively minor importance to the river system, but are important elsewhere, e.g. N₂O, NH₃, COS, CH₄, and H₂S.
13.2.3 C, N, P, S: Element Fluxes

The movement of organic matter and nutrients through a river basin can be viewed as a series of steps down the valley as materials are stored temporarily in tributaries, floodplains, and alluvial fans (Likens et al., 1981) (Figure 13.1c). From the drainage basin, particulate organic matter enters headwater streams via litterfall, slumping, and erosion. These inputs tend to concentrate particulate matter in streams in excess of the concentration of their terrestrial sources. Dissolved inorganic carbon is produced by weathering of carbonate and aluminosilicate minerals with atmospheric CO$_2$, oxidation of soil organic matter, and by root respiration. It enters the river through ground-water and overland flow as well as gas exchange. The biogenic fraction of this DIC constitutes a loss of terrestrial organic matter, as does the loss of POC and DOC to rivers. Dissolved organic matter, produced through humus decomposition, enters through ground-water or overland flow. Of the carbon transferred from land to the tributaries, not all reaches the main channel—some is degraded and some is stored within the tributaries.

The elements N, P, and S also enter a river system through various pathways. Depending on the pH and temperature of soils, NH$_4^+$ and NO$_3^-$ are produced in the watershed through such biological processes as nitrification and the ammonification of organic matter, and are mobilized into rivers through run-off. The weathering of apatitic rocks is the major natural source of PO$_4^{3-}$. Atmospheric precipitation is a source of dissolved N and S species. N, P, and S from fertilizer application, sewage and non-point source run-off can be major sources of the dissolved species near human population centres.

Within the different environments of a river system, a sequence of oxidation-reduction reactions can occur. Nitrate, NH$_4^+$, and PO$_4^{3-}$ are taken up along with CO$_2$ during primary production by macrophytes, periphyton, and suspended algae. Regeneration of these ions occurs through respiration, microbial metabolism, and the action of macro-invertebrates and fish, which graze on particulate organic materials. According to the chemical conditions of a particulate environment, microbial oxidation, nitrification, denitrification, sulphate reduction, and fermentation can be optimal pathways for the degradation of organic materials. Very active sites for these pathways, such as inundated floodplains, can be 'hot spots' for the production of the reduced gases of C, N, and S.

There is a direct exchange of particulate matter between the floodplain and the main river through the processes of entrainment and deposition. The rate of change of river stage and peak discharge, channel and floodplain geometry, and floodplain vegetation all interact to determine the nature of floodplain deposition and capture dynamics. These exchanges involve important qualitative changes in microbiology, and quantitative changes in particle size (Cummins et al., unpublished manuscript).
An important feature of rivers is that organic C, N, P, and S may be stored for considerable periods within the river system itself. The balance between entrainment, deposition, and respiration determines the potential of the floodplain to act as a long term source or sink of elements. High rates of organic accumulation occur if rates of production are not compensated by comparable rates of oxidation. The accumulation rate is further affected by aggradation or degradation through particulate transport. These materials may then be subject to extreme flooding events that can operate on a time scale of tens of years, which demonstrates the fallacy of assuming a short term steady-state situation in streams and the importance of discharge history. Flood events, the import and export of large and small organic debris, and major changes in in-channel storage are the elements of fluvial geomorphology that define the substrate basis for the establishment of biological communities.

Organic carbon and nutrients that are not processed or retained within one river sector are exported to the next reach. This process has been referred to as spiralling (O’Neill et al., 1975; Webster et al., 1975; Elwood et al., 1982). Rzóska (1980) argues that rivers are not 'ecosystems' precisely because material is not recycled at the same point in space. While such a view may be somewhat restricted, it does illustrate this special property of rivers.

Eventually, the riverborne C, N, P, and S are transported into the estuary. The organic fractions are probably quite refractory, after the considerable processing within the river, and the particulates are sequestered mostly in near-coastal sediments (Likens et al., 1981). Microbial respiration of the sediments then becomes an important source of nutrients for the water column. This supply occurs by direct regeneration, and through mobilization from inorganic phases as a consequence of changes in redox conditions, and from the production of reduced C, N, and S. Most of the DOC mixes conservatively in estuaries and is exported, although ca. 10-15% may flocculate (Sholkovitz, 1976). After the particulate fractions have settled out, the riverborne nutrients stimulate primary production either directly or after being regenerated in the salt wedge. Substantial changes in speciation can occur in the water column and sediments. Changes in the intensity of nitrification and denitrification may affect the proportions of N₂ and N₂O release, as well as oxygen consumption (Wofsy et al., 1981). Further details on the marine fate of riverborne dissolved and particulate C, N, P, and S are provided by Wollast (Chapter 14, this volume).

13.2.4 Element Mass Balance and Expected Distributions

The concentrations of C, N, P, and S in the water and sediments at any site in a river are dependent on immediate circumstances and on events that have occurred upstream in the channel, tributaries, or in the watershed. Qualitative and quantitative changes in the material load are brought about by specialized
biological communities and by physical retention processes. The analytical problem is to systematically take into account the dynamics of these changes.

This accounting can be done in the format of a mass balance of the respective elements by river sector (Figure 13.1d). The balance, which is made by using suitable tracers to help identify the sources and chemical composition of the different fractions, is expressed as a 'box model'. The systematic data currently available to analyse this model are few, and will be discussed in the next section. Understanding the dynamics is an even more difficult task, requiring a long-time series of data collected at various points along a river system.

This problem has been addressed by Vannote et al. (1980) who suggested that the distribution of ecological events in flowing water is predictable with increasing river order. They developed a 'River Continuum Concept' to formalize the expected distributions of carbon fractions based on the energy equilibrium theory of fluvial geomorphology (Leopold et al., 1964). The concept states that the energy input and organic matter transport, storage, and use by functional feeding groups is regulated largely by fluvial geomorphic processes. As the patterns of organic energy use would be comparable to the dynamic equilibrium of physical energy expenditure, consistent patterns of community structure and function, organic matter loading, transport, utilization, and storage along the length of a river would be expected (Figure 13.2).

From this concept, Vannote et al. suggest that the biological organization in rivers conforms structurally and functionally to the kinetic energy dissipation

![Figure 13.2 Hypothetical distribution of the diversity of DOM compounds and biota and of the ratios CPOM/FPOM (coarse and fine POM) and Pr/Rw (production and respiration) from first through twelfth order rivers (modified after Vannote et al. 1980)]
patterns of the physical streams. Thus, biotic communities would adjust rapidly to any change in the redistribution of kinetic energy by the physical system. A river tends to reduce fluctuation in energy flow and element distribution over space and time, in the face of instability in the physical environment. In large river systems, stability and reduction of organism diversity should be correlated with reduced variance in diurnal temperature and in geomorphic features. On an annual basis, such rivers should tend toward uniformity of energy flow as a temporal progression of biotic functional groups utilize the resources available. Such usage should result in minimum loss of energy, but energy that is lost can be used downstream by communities that have become adapted to these upstream sources. The distributions of C, N, P, and S in rivers should follow these principles.

The ‘River Continuum Concept’ was developed solely with data from northern temperate rivers, so its use may be limited. However, such a qualitative solution to the model (Figure 13.1d) is of considerable heuristic value not only in guiding future research but in extrapolating from what is currently known of rivers to the more general case of determining the role of rivers in the global cycling of elements.

13.3 ROLE OF RIVERS IN THE GLOBAL CYCLING OF ELEMENTS

The data available to evaluate the river model are few. Entire rivers and regions are often characterized on the basis of a few samples from the water surface, with no attention paid to possible spatial or temporal variations. Ratios, with their attendant assumptions, are used often to estimate unmeasured elements relative to measured parameters. Precise calculations of the major riverine fluxes are of questionable reliability, because of the limits imposed by the data base.

13.3.1 Global River Fluxes

Four major morphologic patterns characterize modern river basins—a river may: (1) derive most of its materials from mountains marginal to the flatlands (Amazon and Mississippi); (2) be marginal to a fold belt and flow parallel to it (Ganges and Parana); (3) flow along the strike of a mountain chain (Mekong and Magdalena); or (4) be superimposed across mountain chains (Columbia and Danube) (Potter, 1978). The mouths of most major rivers are located along the trailing edges and marginal seacoasts of their respective continents. This leads to the formation of the characteristic sub-aerial and submarine deltas, where riverborne materials may ultimately be buried.

Within each basin, the interplay of precipitation, discharge, basin area, and suspended load produces results in very different patterns for the world’s major rivers and their respective geographic regions (Figure 13.3). The Amazon is by
Figure 13.3 Water discharge, drainage basin area, and yield of total suspended solids (TSS) from the world’s ten largest rivers. Data are from Holmen (1968), Todd (1970), van der Leeden (1975), Holland (1978), and Richey (1981a). The global totals for these three parameters are $4.5 \times 10^{13}$ m$^3$ yr$^{-1}$, $39.9 \times 10^{12}$ m$^2$, and $7300$ Tg yr$^{-1}$ respectively (Holland, 1978).

The largest river in terms of discharge, accounting for 20% of the global sum. Thereafter, there is more of a continuum in size, with the 20 largest rivers accounting for only about 35% of total discharge (Holland, 1978). The Amazon drainage basin is also the largest, although not by a factor as great as that of discharge. The combinations of precipitation and drainage basin area produce the different discharge regimes. The Asian rivers transport a disproportionately large amount of total suspended solids (TSS), reflecting the high erosion rates and the steep relief of that continent. Although the general patterns of water discharge and the load of TSS are clear in the different geographic regions, the precise quantities are not. Nordin and Meade (1981) have suggested that the basic data of water discharge and TSS loads have been underestimated by a factor of about 2, due to methodological problems in sampling. For example, Curtis et al. (1979) found that the vertical distribution of suspended particulates in the Amazon River was non-uniform and that collection of samples at the surface lead to an underestimation of the true integrated value by a factor of 2 at high water.
13.3.2 River Fluxes by Geopolitical Region

One of the better known river fluxes is the export of total organic carbon (TOC, as the sum of DOC and POC) to the oceans. The greatest export appears to be from the sediment-rich waters of Asia and the high-discharge, organic-rich rivers of Latin America and tropical Africa. The global sum has been variously estimated as 30–1200 Tg C yr$^{-1}$, with recent estimates converging on 400 Tg C yr$^{-1}$ (Williams, 1968; Slopintsev, 1971; Garrels and MacKenzie, 1971; Handa, 1977; Kempe, 1979; Richey et al., 1980; Schlesinger and Melack, 1981; Meybeck, 1981). Likens et al. (1981) suggested 800 ± 400 Tg C yr$^{-1}$ as the best estimate.

That these recent estimates converge is hardly surprising, since they are based on extrapolations from the same, very limited data set, usually using some ratio or regression of total organic carbon to total suspended solids. Uncertainties in the export estimate arise from uncertainties in the discharge and TSS measurements, and in the ratio TOC:TSS. Most river data are for temperate systems, with few data available for Asian rivers. The range of values that different assumptions produce are considerable. Clearly, the variation in the TOC:TSS ratio for Asia has a significant effect on calculated results. What is a likely value for this region? Schlesinger and Melack (1981) assumed a ratio of 0.009%, the carbon content in shale, as representative of a region of intense weathering. V. Subramanian (University of New Delhi, personal communication) has measured the POC:TSS ratio at 0.2 to 0.4 % in the Ganges, and POC values in tributaries of the Ganges are as high as 100 mg litre$^{-1}$ (G. Saunders, U.S. Department of Energy, personal communication). Clearly, the dense human populations in Asia affect the carbon export by rivers.

Several studies of within-system nutrient fluxes have been done (Hobbie and Likens, 1973; Elwood et al., 1982; Triska et al., in press), but there are not sufficient data to calculate the fluxes of N and P for whole regions. However, the productivity of the extensive floodplain of the Amazon is attributed to the nutrients supplied from the annual flooding (Sioli, 1975). Rzóska (1980) attributes the fertility of the floodplains of the Shatt el-Arab, Zaire and Nile to riverborne nutrients. Welcomme (1979) relates the dependence of the fisheries of the floodplain rivers of Latin America, Africa, and Southeast Asia to the annual patterns of nutrient supply and production.

Estimates of the other significant river fluxes on a global or geographic basis are even more tenuous. Richey and Salati (in press) estimated that the export of organic C from the Amazon River (6 Tg C yr$^{-1}$) is only about 30% of the terrestrial input to the river. The difference is apparently respired or stored within the river system itself. From such observations, Likens et al. (1981) estimated that about 800–2000 Tg C yr$^{-1}$ enters rivers from land. Of this