202: Global River Carbon Biogeochemistry

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The fluxes of dissolved and particulate carbon from land through fluvial systems to the oceans and to the atmosphere represent important pathways in the global carbon cycle. The processes controlling the distributions of solute species in river waters are established initially by weathering within the watershed, and physical transport via runoff. Superimposed on the underlying geochemical and physical processes is production and mineralization by terrestrial and aquatic biota. These factors play out differentially across the world's river basins, producing chemical signatures that vary from river to river. As a global aggregate, there would appear to be a net sink (between continental sedimentation and marine sedimentation and dissolution) of ~ 1 to $1.5 Pg year^{-1}$. These sinks are partially compensated for by the outgassing. These processes are geographically very dispersed, with the continental sedimentation occurring in northern temperate regions, and much of the marine sedimentation and outgassing occurring in more tropical regions.

BIOGEOCHEMICAL DYNAMICS IN RIVER BASINS

A •significant challenge for global biogeochemistry is to determine how the interaction of hydrological and biogeochemical cycles functions at the land surface, on regional to continental scales, producing the river flow and chemical load delivered to the oceans. Riverine transport represents a major link in the global cycles of bioactive elements, which modulates the biosphere over geological time (Meybeck, 1982). Dissolved and particulate organic matter (DOM and POM) in river systems serve as important heterotrophic substrates (Vannote et al., 1980), provide an integrated continuous record of processes within drainage basins (Meybeck, 1982; Degens et al., 1991), and constitute a major source of reduced carbon to the world ocean (•Olson et al., 1985; Schlesinger and Melack, 1981). The transfer of organic matter (OM) from the land to the oceans is the main pathway for the ultimate preservation of terrigenous production in modern environments, a key link in the global carbon cycle (Ittekkot and Haake, 1990; Hedges et al., 1992). Terrestrial OM losses support significant heterotrophic activity within rivers, estuaries, and marine systems alike (Kaplan and Newbold, 1993; Mayer et al., 1998), while natural and especially anthropogenic nutrient loading promote primary production. Where and when this river-borne OM is finally

At regional scales, river basins are natural integrators of surficial processes (Figure 1). Large rivers owe their flow and chemical loads to a much denser network of small rivers and streams bordered by areas of periodically inundated land, so that upland areas are dissected by corridors of wet soils and flowing water. Hence, understanding the hydrological and chemical patterns observed at the mouths of major rivers requires delineating the sequences of biogeochemical processes operating across multiple time and space scales. As embodied originally by the River Continuum Model, river properties should vary systematically downstream as processes affecting primarily the interactions of flowing water with the landscape give way to within river transport and processing (Vannote et al., 1980; Minshall et al., 1985). They should respond with differing magnitudes and lags to natural or man-made perturbations depending on the processes involved and the downstream transfer rates of their characteristic products. The central premise of a river basin model is that the constituents of river water provide a continuous, integrated record of upstream processes whose balances vary systematically

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respired is of consequence to global carbon models (Stallard, 1998). Thus, understanding the processes that control the pathways from initial source to final mineralization of riverine organic matter is important on both regional and global scales.

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Figure 1 Schematic figure of the major reservoirs and pathways in fluvial systems. Inputs from land occur directly or pass through the riparian zone. Streams coalesce to form larger rivers that exchange with their floodplain. Rivers can pass directly to the coastal zone, or be retained behind dams. Dotted lines indicate exchange with the atmosphere, grounded areas indicate sinks, arrows within boxes indicate internal transformations (adapted from Richey, 2004)

depending upon changing interactions of flowing water with the landscape and the interplay of biological and physical processes (Karlsson *et al.*, 1988; Billen *et al.*, 1991). That is, the chemical signatures of riverine materials can be used to identify different drainage basin source regions, reaches or stages, and can be tied to landscape-related processes such as chemical weathering and nutrient retention by local vegetation (Meyer *et al.*, 1988). Because of the dynamic nature and abrupt moisture gradients of river corridors, the cumulative signal from a series of low-order streams may be manifest by higher-order rivers in a nonadditive manner.

The intent of this article is to develop a quantitative understanding through a heuristic and mass balance model of the sequence of processes from uplands to floodplains that produce the integrated hydrological, chemical, and biological signals at the mouths of the major tributary basins of large-scale river systems. The guiding questions to be addressed in this article include,

- How does a large river system obtain and subsequently modify its biogeochemical composition? This question can be separated into several parts.
- How is the biogeochemical signature which persists through the river system imparted by the (aggregated) land surfaces? That is, where do particular materials enter the river system, and under the control of what process(es). Observations of minimal changes in bioactive element forms and compositions within a study reach suggest that the mainstem of a major river is effectively transporting a complex compositional fingerprint that is imprinted somewhere upstream.
- *How is the land-derived signature modified through transit within the river system?* •That is, are processes within river constant, other than obvious mixing effects,

does not mean that a big river biogeochemically static, it appears simply to be approaching steady state with respect to the surrounding floodplain and atmosphere.

• What are the time sequences of the sources, quantities, and chemical attributes of the river-borne fluxes of C, N, and P to the ocean? What are the physical and chemical controls operating on those fluxes at continental scales? These questions in turn address a central problem in riverine ecology, which is to determine how the dynamics of flowing waters change as they increase in size from first-order springs and seeps to the world's great rivers.

RIVER BIOGEOCHEMISTRY: THE BASIC PARAMETERS AND PROCESSES ACROSS SCALES

A watershed, as the landscape through which all waters flow from their highest source before draining naturally to the sea, can be considered to be a fundamental organizing unit of the land surface. Rain or snow falls to the land surface, some of which is returned to the atmosphere (via evapotranspiration), some is stored in the soil (as soil moisture), and the balance drains into stream networks, mobilizing with it dissolved solutes and particulate materials from the landscape (Figure 2). As streams descend, tributaries and groundwater add to their volume, creating ever-larger rivers. Biological and chemical processes affect the materials in transport. As rivers leave the highlands, they slow down and start to meander and braid, and move between the river's main stream and its floodplain, modifying the flow regime and creating critical ecological (and biogeochemical) niches. The diversity of a river lies not only in the various types of land surfaces (or land uses) it flows through but also in the changing seasons and the differences between wet and dry years. Disruption of the linkages between the landscape and rivers and between rivers and



Figure 2 Grid-based view of land surface processes transferring water and its dissolved and particulate load to streams, where these constituents are subsequently routed downstream A color version of this image is available at http://www.mrw.interscience.wiley.com/ehs

their floodplains through human intervention fundamentally alters the nature of riverine ecosystems. The temporal scales of watersheds cover as much range as do the spatial scales. While the shape of the landscape itself (hills, vallevs) will evolve (on geological timescales), these changes occur much more slowly than the seasonal and yearly evolution of the landcover and land use. These seasonal changes in turn occur much more slowly than a rainstorm, whose characteristic timescale is in the order of minutes to hours. The processes with which we are concerned, for example, the translation of rainfall into runoff across different types of landscapes, are themselves described differently at different space scales. The overall ensemble of these landscape features, which we can observe at multiple scales, can be thought of as the "physical template" upon which the more rapidly dynamic processes can operate.

Hence, the biogeochemistry of rivers is established as the interplay of terrestrial, biological, and geochemical weathering reactions that produce a suite of dissolved and particulate inorganic and organic compounds, via a series of pathways. The fundamental processes controlling the distributions of dissolved inorganic carbon (DIC) and the solute species in river waters are established initially by weathering within the watershed, and physical transport via runoff. Superimposed on the underlying geochemical and physical processes is production and mineralization by terrestrial and aquatic biota. These factors play out differentially across the world's river basins, producing chemical signatures that vary from river to river.

While matter transported by rivers ranges in size from molecules to trees, four broad size fractions are commonly used to characterize the bulk materials. Based operationally on filtration, the fractions include coarse particulate organic matter (CPOM, 63 microns to $\sim 2 \text{ mm}$), fine particulate organic matter (FPOM, $\sim 0.5 \text{ microns}$) and dissolved organic matter (DOM, < 0.5 microns) and dissolved nutrients, and dissolved gases (CO₂, CH₄, N₂O). As summarized (below) by Mayorga and Aufdenkampe (2002), these size classes exhibit very distinct transport dynamics, degradation patterns, and compositional characteristics (Figure 3).

Dissolved Inorganic Species

Watersheds contain soils and rock that consist of a wide variety of different minerals. Weathering of the soil and rock minerals produces runoff containing the common ions (and many other ions in lesser concentration). The major inorganic ion composition of world rivers is controlled largely by geology and weathering regime with minor inputs from precipitation (Stallard and Edmond, 1983, 1987). In general, weathering reactions can be characterized as a weak acid (carbonic acid) slowly dissolving basic minerals. Weathering reactions, such as sodium feldspar or calcite weathering, result in runoff containing dissolved



Figure 3 Fractions of the dissolved inorganic and organic components of the primary biogeochemical constituents of C and N in river water. Dissolved and particulate fractions can be sorted by molecular weight MW (V = very, H high, L low), VHMW DOC (>30 kDa), HMW DOC (1-30 kDa), LMW DOC (<1 kDa), VHMW DON (>30 kDa), LMW DON (>200-1000 Da), and VLMW DON (<200 Da). The reason for such fractions is to break down bulk materials in a manner that can be related to system function

ions, and commonly, undissolved particles of less soluble minerals such as clays. Many of the world's great rivers discharge water that can be characterized as rock-dominated (Gibbs, 1970). Water more or less in equilibrium with the materials in the drainage basin is characterized by higher concentrations of ions and an increased significance of Ca, Mg, and bicarbonate ions. Rivers that receive rainwater and snowmelt with little influence of rock weathering contain water with low concentrations of ions, reflecting rainwater that is (approximately) a dilute solution of carbonic acid with an admixture of a small amount of sea salt. Evaporation and fractional precipitation tend to dominate in more arid regions. The overall concentration of ions increases with evaporation until selected minerals begin to precipitate because their solubility product is exceeded.

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The overall weathering regime in turn establishes the carbonate system, as the sum of the species of DIC, $DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$. Natural waters are buffered with respect to pH mostly because of the content of inorganic carbon species. In turn, pH is an important controlling variable for many important geochemical reactions (e.g. solubility of carbonates). Many important biochemical reactions, such as photosynthesis and respiration, interact with the pH and the carbonate system. Alkalinity, as the approximate imbalance of cations and anions, is a measure of the ability of a water system to resist changes in pH when acid is added to water. A stream that has a high alkalinity is well buffered so that large inputs of acid (from acid rain for instance) can be made with little effect on the stream pH. A stream that has a low alkalinity is poorly buffered and may undergo large, sudden drops in pH in response to acid inputs. Reduction/oxidation (redox) processes, which typically occur in oxygen-depleted zones near streams, will alter alkalinity. Examples of importance to rivers include oxidation of ammonia to nitrate (nitrification), oxidation of sulfide or reduction of sulfate, oxidation or reduction of iron. Precipitation or dissolution of minerals involving participating species will alter alkalinity. For example, the precipitation or dissolution of calcium carbonate can alter alkalinity. Other participating species, such as organic acids, may influence alkalinity, especially in low alkalinity environments. Dissolved inorganic nutrients are closely associated with the cycling of organic matter. Inorganic nitrogen compounds – NO_3^- and NH_4^+ –cycle rapidly via remineralization of organic matter and other microbial process such as nitrification and denitrification. Of the bioactive compounds, PO_4^{3-} shows the least systematic variability, generally $0.4 - 2.0 \,\mu\text{M}$ in turbid rivers as a result of buffering with larger mineral-bound reservoirs in the \bullet FSS. On the other hand, NO₃⁻ and PO₄³⁻ are particularly subject to anthropogenic influences, via fertilizers and domestic and industrial wastes. Dynamics of dissolved gasses, such as O₂, CO₂, CH₄ are also largely controlled by the respiration of organic matter because river, floodplain, and lake waters are dominantly heterotrophic (•Cole et al., 1994; Cole and Caraco, 2001). Thus, the dissolved inorganic constituents of river waters are constantly evolving as a result of interactions with nondissolved phases within the river corridor.

Dissolved Organic Matter

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Perhaps the most important characteristic of dissolved material is that it has the potential to be directly bioavailable. Microbial organisms, plant roots, and many animal tissues transport dissolved molecules across cellular membranes, both passively and actively. Likewise, contaminants exhibit their highest toxicity when in the dissolved phase. The dissolved fraction is particularly characterized by diversity and contrasts. Organics and inorganics exist in both truly dissolved and colloidal phases. DOM exists as a mixture of simple molecules, complex biomacromolecules, their partial degradation products and molecular assemblages or gels. This mixture contains the most labile material carried by the river (e.g. NH_4^+ , free amino acids, etc.) and also relatively nonlabile weathering end-products (e.g. inorganic ions that determine alkalinity, low molecular weight (LMW), DOM, etc.). While the dissolved fraction is generally considered to be $<0.45\,\mu\text{m}$, to better understand the composition and dynamics of DOM, ultrafiltration techniques have employed membranes with pores as small as 1 nm to separate and concentrate DOM into various size fractions (Hedges et al., 1994; •Küchler et al., 1994; Amon and Benner, 1996a,b; •Mounier et al., 1999; •Patel et al., 1999). Generally, ultrafiltered DOM (UDOM) refers to organic material with molecular weights $>1000 \text{ g mol}^{-1}$ or daltons (high molecular weight or HMW), including very high molecular weight subsets variously named very high molecular weight (VHMW) DOM or colloidal organic carbon (COC) by different research groups (1000 daltons is approximately equivalent to a molecule of 1-nm diameter).

Cumulative evidence suggests that DOM is produced largely from the degradation and/or leaching of leaf detritus similar to that in CPOM (Devol and Hedges, 2001). Once in solution, biomacromolecules such as proteins and carbohydrates are easily hydrolyzed (at least partially) by exoenzymes for subsequent microbial uptake. As a result, degradation tends to decrease both the size and bioavailability of HMW DOM to form the low molecular weight (LMW, 200-1000 daltons) fraction (Amon and Benner, 1996a). However, as all particulate and dissolved organic carbon fractions degrade, microbial activity and photochemistry can generate a pool of the smallest molecules (<200 daltons) – free amino acids, free sugars, and organic acids such as acetate and citrate (Amon and Benner, 1996b; Moran and Zepp, 1997). Despite the likelihood that this very low molecular weight (VLMW) DOM represents an exceedingly small proportion of total DOM in rivers, these compounds are generally extremely bioavailable and could drive significant biological fluxes. The relative proportions of VHMW, HMW, LMW, and VLMW DOM fractions would be expected to evolve down river as a result of their different degradation rates. Coagulation and disassociation of DOM in and out of colloidal gel phases or mineral surfaces complicates these size dynamics significantly however, as many of these processes respond to changes in pH and to ratios of polyvalent to monovalent ions in solution (such as Ca²⁺/Na⁺) (Chin *et al.*, 1998; Kaiser, 1998).

Particulate Organic Matter

Coarse suspended river sediments are a heterogeneous mixture of sand-sized mineral grains (coarse suspended sediments, (CSS)) and discrete plant fragments. Because CSS settles quickly to the streambed, suspended concentrations are strongly dependent on streamflow velocities and increase substantially with depth in the river. Thus, CSS transport is highly episodic or seasonal, with most occurring during flood events. In large turbid rivers, the CPOM is a small but important portion of the CSS fraction, comprising only 0.6-3.3% by mass. CPOM is less dense than mineral grains of the same size, hence explaining its higher contribution to CSS in river channels under lowflow. Between 10 and 20% of CPOM can be identified biochemically as amino acids, carbohydrates, and lignins relative to 25-60% within biomass sources (Hedges et al., 1986a; Hedges et al., 1994; Hedges et al., 2000). Biochemical source indicators, such as carbon to nitrogen ratio and the ratio of cinamyl to vanilyl lignin phenols, all show that Amazon basin CPOM, for example, is primarily derived from tree leaves (Devol and Hedges, 2001). Biochemical indicators of degradation, such as the contribution of fucose and rhamnose sugars to total carbohydrates and acid to aldehyde ratios in lignin phenols, all support evidence from microscopic studies and major biochemical composition that CPOM is sparingly degraded and rather fresh. Radiocarbon analysis of CPOM and low density soil particulate organic matter confirms their recent origin (Hedges et al., 1986b; Trumbore et al., 1995). It is clear that CPOM is actively degrading and leaching, supplying microbes with substrate and releasing dissolved organic and inorganic compounds into the river. These rates have not been directly measured, but are likely to be quite high. Stream and river budgets suggest that CPOM continuously enters the river mostly from bank vegetation and detritus falling directly into the water (McClain et al., 1997).

FPOM is essentially the product of diverse dissolved organic and inorganic compounds binding to fine suspended sediments (FSS, as clays and silt materials between 0.45 and $63 \,\mu$ m). The sorption of natural DOM to minerals is the primary pathway in which FPOM is formed (Mayer, 1994; Hedges and Keil, 1995), organic matter contributes only to a small fraction of FSS, generally. As FPOM is, typically, only a small weight-percent of FSS (typically 0.5-2.0% by weight), in the turbid rivers that transport most of the FPOM, the dynamics of FPOM have to start with an understanding of the sources and transport of FSS. FSS is mobilized initially into stream channels by erosion events (especially extreme events, resulting in hillslope failure). As a product of rock weathering, mineral diversity within FSS is very large and depends on the geology (source minerals) and climate (weathering rates) of the watershed. Clays and oxides are aggregated with the larger minerals in important quantities. The clay-size fraction $(0.45-5\,\mu m)$ is composed mostly of phyloalumino-silicate clay minerals, which are the weathering products of primary silicates. As a result, mineralogical compositions within large drainage basins are constantly evolving downstream, with inputs from tributary watersheds and from weathering during temporary storage

on the floodplain. While maintained in suspension by the slightest turbulence, FSS is not transported conservatively downstream. Evidence suggests that within the Amazon, for example, a typical FSS particle passes through floodplain deposits several times between the Peruvian border and the Atlantic (Martinelli *et al.*, 1993; Dunne *et al.*, 1998). Given the patterns of channel migration, each cycle of floodplain deposition and resuspension requires a few thousand years (Mertes *et al.*, 1996). The presence of lakes and especially reservoirs created by dams trap sediment, thereby creating a very large anthropogenic impact on the downstream movement of suspended sediments.

From a biogeochemical perspective, the critical issue is, how does the FSS mineral particle acquire its organic matter composition? The major characteristics of FPOM, as tightly associated with the mineral phase, most likely form within soils prior to erosion into rivers. While mineralogically diverse, FSS is generally high in surface area and high in cation and anion exchange capacity. As such, significant quantities of certain inorganic ions (e.g. NH4+, PO₄³⁻, and most metals) and organic compounds can potentially be adsorbed to the mineral surfaces of FSS. Thus, FSS actively interacts with the dissolved fraction, often acting as a buffer or reservoir for dissolved compounds. Sorbed organic matter affects mineral surface properties significantly by increasing cation exchange capacity and by offering hydrophobic phases into which organic contaminants (e.g. pesticides, petroleum products, etc.) and heavy metals readily sorb (Benedetti et al., 1996). Biochemically, a smaller fraction of FPOM is identifiable as carbohydrates or lignins when compared to CPOM, but often a larger fraction is identifiable as amino acids. It appears that FPOM comes largely from leaf material as does CPOM, but often falls slightly outside of the biochemical range that is possible by mixing biomass alone, as might be expected of diagenetically altered material (Devol and Hedges, 2001). Specific degradation parameters show this clearly; however, riverine FPOM is still relatively fresh compared to riverine DOM or deep-sea sediments (Hedges et al., 1994). Overall, 90% of the FPOM cannot be physically separated from the mineral material (Keil et al., 1997; Mayer et al., 1998). This appears to be the result of physical protection from microbial attack that is offered by the intimate association of FPOM with mineral surfaces (Keil et al., 1994; Baldock and Skjemstad, 2000; Kaiser and Guggenberger, 2000). Whether an organic molecule sorbs or remains dissolved determines, in large part, its transport potential and susceptibility to degradation.

SCALE-DEPENDENT MODELING AND PROCESS DYNAMICS

Clearly, the biogeochemical signature of large-scale river systems is the composite of processes occurring across

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multiple time and space scales. A parcel of river water passing a particular location in network with a particular chemical signature represents the cumulative upstream history of that parcel. That chemical signal is the product of what occurred in the stream segment above that point (internal transformations, such as respiration or primary production, and lateral exchanges, such as riparian interactions or floodplains), plus the addition of mass from upstream segments. That is, the chemical signature at some point in a river is the product of both terrestrial and in-stream processes. To capture these dynamics, it is useful to organize our understanding into first heuristic, and ultimately, computer models. Ideally, we want to develop "first-principle" models, rather than the regression approaches commonly used, relating water flow across the landscape to river chemistry.

First, we must be able to describe the movement of water through the landscape, as a function of the specific physiochemical attribute of the landscape (as discussed qualitatively in the previous section). It is necessary to be able to explicitly represent infiltration, soil moisture, and runoff, and then the downstream routing of a water parcel. The emergence of geospatially explicit landscape and hydrology models is making it feasible to start developing coupled landscape/fluvial biogeochemistry models. At a macro scale, hydrology models such as the Variable Infiltration Capacity (VIC; Liang et al., 1994; Liang et al., 1996; Lohmann et al., 1998) and others described elsewhere in this Encyclopedia describe a vegetation cover type (through parameters including leaf area index, stomatal resistance, root mass distribution with soil depth, and others) and soil attributes in multiple layers for each grid cell. The model solves for a water balance and energy balance simultaneously, producing fields of soil moisture and runoff, with the runoff routed down a river network. Models such as the Distributed Hydrology Soil Vegetation Model (DHSVM; Wigmosta et al., 1994), can recognize the spatial heterogeneity of smaller watersheds (typically less than about 10 000 km²), and compute cell-to-cell fluxes.

Such landscape/hydrology models can now be used to compute chemical properties, as the generation and routing of a chemical substance within the stream network. That is, a chemical substance can enter a river segment laterally or it can enter from an upstream reach (that previously had a lateral input). The combined inputs are then subject to advection (downstream flow) and chemical or physical reactions (respiration, sedimentation) during transport. Schematically, this is represented in Figure 4. Each discrete reach of the network can be represented by connected straight segments, where each segment lies within one of the grid cells used to run the hydrology model (e.g. VIC or DHSVM). The model is built in an Eulerian framework, where each model element is a stream segment. Hence, there are as many model elements as there are



Figure 4 An overall river network (e.g. the Amazon), with the basic source/routing scheme superimposed. A representative segment *i* has two contributing segments, j_1 and j_2 , and one outlet segment, k (Note that a segment can have anywhere from 0 to 7 input segments - more than 4 being rare - but it always has a single output segment). At time step t, input flows to i are $Q(j_1, t)$, $Q(j_2, t)$, and $Q_{\text{lat}}(i, t)$; and input mass fluxes are $F(j_1, t)$, $F(j_2, t)$, and $F_{\text{lat}}(i, t). Q_{\text{lat}}(i, t)$ is the runoff rate entering segment *i* at time step t from the corresponding grid cell, and has previously been computed by a hydrology model. $F_{lat}(i, t)$ is the mass flux of species C entering segment i at time step t from the corresponding grid cell. At time step t, the output flow from *i* is Q(i, t) and the output mass flux from *i* is F(i, t). The travel time in *i* is $\Delta t(i)$. Input streamflows and mass fluxes at time t are used to compute the output streamflow and mass flux at time $t + \Delta t(i)$

stream segments and grid cells. Model elements are treated as control volumes with state variables that are updated at each model time step. There are only two state variables, Q(i, t) (stream flow rate exiting element *i* at time step *t*, m³ s⁻¹) and F(i, t) (mass flow rate of species *C* exiting element *i* at time step *t*, $\mu g s^{-1}$.

The first part of the problem is to compute the lateral inflow term. This is problematic, and depends very much on where in the drainage net, the inflow is. The solute export module of a basin biogeochemistry model needs to estimate the amount and concentration of basin solutes (e.g. dissolved carbon and nitrogen species) exported to a stream via subsurface flow and in-stream concentrations (Figure 5). The control volumes in the basin are the soil solutions in each soil root zone and in the saturated lateral layer. The form of the specific equations can be derived from the relationships illustrated in Figure 3.

For the sake of illustration, let us now consider a hypothetical species C with concentration [C] is assumed to decay exponentially in time as it moves downstream, with decay constant k_1 :

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = -k_1[C] \tag{1}$$



Figure 5 Schematic of lateral inflow (see Figure 4 for definitions) A color version of this image is available at http://www.mrw.interscience.wiley.com/ehs

Integrating equation (1) from time t = 0 to t = T

$$[C](T) = [C](0)e^{-k_1T}$$
(2)

The concentration of species C (given in $\mu g m^{-3}$) in the streamflow exiting a model element *i* at time step *t* is obtained from these state variables, as.

$$[C](i,t) = \frac{F(i,t)}{Q(i,t)}$$
(3)

The equations used to update the state variables are:

$$F_{\text{lat}}(i,t) = k_2 Q_{\text{lat}}(i,t)^{k_3}$$
 (4)

$$\Delta t(i) = \frac{length(i)}{velocity(i)}$$
(5)

$$Q(i, t + \Delta t(i)) = \sum_{j} Q(j, t) + Q_{\text{lat}}(i, t)$$
(6)

$$F(i, t + \Delta t(i)) = \left[\sum_{j} F(j, t) + F_{\text{lat}}(i, t)\right] dt e^{-k1\Delta t(i)}$$
(7)

where:

$$\Delta t(i)$$
 is the travel time in segment i,
 $length(i)$ is the length of segment *i*,
 $velocity(i)$ is the streamflow velocity in seg-
ment *i* (In this first model ver-
sion, $velocity(i)$ is assumed to be
independent of streamflow, making
 $\Delta t(i)$ constant in time for any seg-
ment *i* – an assumption that can
later be relaxed),
dt is the model time step,

$$k_1$$
 is the parameter in equations (1)
and (2) (with units day⁻¹),

 $Q_{\text{lat}}(i, t)$ is the runoff rate entering stream segment *i*, a value previously computed by VIC for the grid cell corresponding to *i*, Flat(i, t) is the rate at which mass of species C is entering stream segment i at time step t from the corresponding grid cell (here assumed to be a function of $Q_{lat}(i, t)$ according to (5)),

 k_2 (units μ g m⁻³) are model parameters, and Q(*, *)and k_3 and F(*, *) are the state variables. (nondimensional)

Equation (7) is directly obtained from equation (2), with the simplifying assumption that the travel distance (and time) for the lateral inputs is the same as for the inputs from tributaries.

Equations (5), (6), and (7) are computed for each model time step.

From equations (3) and (4), we obtain:

$$[C]_{\text{lat}}(i,t) = k_2 Q_{\text{lat}}(i,t)^{k_3 - 1}$$
(8)

From equation (8) we see that the concentration of species *C* in the runoff entering segment *i* from its corresponding grid cell will increase with the runoff rate for $k_3 > 1$, and will decrease with runoff rate for $k_3 < 1$. For $k_3 = 1$, this concentration will be constant (and equal to k_2), regardless of runoff rate.

More specifically, the downstream advection and reaction for the different species can be represented as follows, where the exact form of the equation depends on the degree to which a specific parameter is dependent on its own concentration:

For conservative species (alkalinity, Ca, Si, O^{18} -H₂O) : [C](i, t) = C_o

Add a constant internal, nonconcentration dependent source S (FSS as function of erosion/deposition, production of nitrate): $[C](i, t) = C_o + S \ length(i)/\ velocity(i)$

Source + concentration dependent sink (e.g. PO_4 mineralization and adsorption) $[C](i, t) = s/k + (C_o - s/k) e^{(-k \ length(i)/velocity(i))}$

where *S* represents the aggregate of internal processes (erosion/deposition, mineralization, gas exchange, adsorption)

Gas Exchange: $[C](i, t) = (C_{eq} \pm R/(D/\mu z)) - (C_{eq}]$ $C_o \pm R/(D/\mu z))e^{(-(D/\mu z) \ length(i)/velocity(i))}$

where

 k = gain/loss from mineralization of dissolved organics (respiration/production)

z = thickness of hypothetical stagnant boundary layer.

 $C_{\rm eq}$ = gas equilibrium with the atmosphere

D = molecular diffusion coefficient

While the above framework is still very much under development, it does represent the direction that basin biogeochemical modeling is developing.

RIVER BASIN MASS BALANCES OF CARBON

We will now evaluate the biogeochemical fluxes through global rivers, in terms of the box model of Figure 1. While the primary emphasis will be on carbon, the current export of nitrogen and phosphorus will also be examined. Evaluation of this model can only be approximate; the dynamics are complex, and multiple time constants are involved. Data are scarce, particularly in many of the most anthropogenically impacted systems. The distribution of the constituent processes varies dramatically across the face of the globe (with some of the most important regions being the least measured). This discussion is derived primarily from Richey (2004).

Mobilization from Land to Water and Riparian Zones

The modern terrestrial sediment cycle is not in equilibrium (Stallard, 1998). Meade et al. (1990) estimated that agricultural land use typically accelerates erosion 10- to 100-fold, via both fluvial and Aeolian processes. Multiple other reports in the literature support this conclusion. With the maturation of farmlands worldwide, and with the development of better soil conservation practices, it is probable that the human-induced erosion is less than it was several decades ago. Overall, however, there has been a significant anthropogenic increase in the mobilization of sediments (and associated POC) through fluvial processes. The global estimates of the quantities, however, vary dramatically. Stallard (1998) poses a range of scenarios, from 24 to 64 Pg year^{-1} of bulk sediments (from 0.4 to 1.2 Pg year⁻¹ of POC). Smith *et al.* (2001) estimate that as much as 200 Pg year^{-1} of sediment is moving, resulting in about 1.4 Pg year⁻¹ (using a lower %C than Stallard, 1998).

Where does this material go? Does it all go downstream via big rivers, ultimately to the ocean, or is it stored inland? Stallard (1998) argues that between 0 and 40 Pg year^{-1} of sediments (0 to 0.8 Pg C year⁻¹ POC) is stored as colluvium and alluvium, and never makes it downstream. Smith et al. (2001), using a different approach, estimate that about 1 Pg C year^{-1} of POC is stored this way. If this movement is merely transferring POC from one reservoir to another, with the same residence times, there is no net change in the C cycle. Then the issue is, to what degree can the (remaining) soils sequester carbon by sorption to the newly exposed mineral soils? Both Stallard (1998) and Smith et al. (2001) argue that carbon is removed from the upper portion of the soil horizon, where turnover times are relatively rapid (decades, or shorter), into either of the two classes of environments with longer turnover times; wetlands and smaller, deeper depositional zones, coupled with new carbon accumulation at either erosional or depositional sites. Both assume that oxidation of organic C in transit is minimal, and both use quite conservative

values for total suspended sediment (TSS) export. If true, this sequence of processes would result in a significant C sink, on the order of 1 Pg C year^{-1} .

Within-river Transport and Reaction Processes

Within-river transport processes carry these eroded materials downstream through the river network. Transport is not passive; significant transformations occur along the way. Rivers exchange with their floodplains (depending on how canalized and diked a river is). A significant process within flowing water significantly affects organic matter (OM) – the mineralization to pCO_2 . Most river and floodplain environments maintain pCO_2 levels that are supersaturated with respect to the atmosphere. High partial pressures of CO₂ translate to large gas evasion fluxes from water to atmosphere. Early measurements in the Amazon suggested that global CO₂ efflux (fluvial export plus respiration) from the world's rivers could be on the order of $1.0 \,\mathrm{Pg}\,\mathrm{C}\,\mathrm{year}^{-1}$. Recent measurements of temperate rivers lead to estimates of global river-to-atmosphere (outgassing) fluxes of $\sim 0.3 \,\mathrm{Pg}\,\mathrm{C}\,\mathrm{year}^{-1}$, which is nearly equivalent to riverine total organic carbon (TOC) or DIC export (Cole and Caraco, 2001). Richey et al. (2002) computed that outgassing from the Amazon alone was about $0.5 \text{ Pg C year}^{-1}$. Assuming that the fluxes computed for the Amazon are representative of fluvial environments of lowland humid tropical forests in general, surface water CO₂ evasion in the tropics would be on the order of roughly $0.9 \text{ Pg C year}^{-1}$ (three times larger than previous estimates of global evasion). Factoring in the recent Amazon results, a global flux of at least 1 Pg C year⁻¹ directly from river systems to the atmosphere is likely.

What is the source of the organic matter being respired? Is it labile contemporary organic matter, recently fixed in the water by plankton or nearshore vegetation, or is it some fraction of the allochthonous (terrestrial) matter in transport? The prevailing wisdom is that river-borne organic matter is already very refractory and not subject to oxidation (after centuries on land). The "age" of riverine organic matter yields some important insights.

Thus, preaging and degradation may alter significantly the structure, distribution, and quantity of terrestrial organic matter before its delivery to the oceans. As noted by Ludwig (2001), the OM that runs from rivers into the sea is not necessarily identical to the OM upstream in river catchments. Cole and Caraco (2001) observe that the apparent high rate of decomposition of terrestrial organic matter in rivers may resolve the enigma of why OM that leaves the land does not accumulate in the ocean (*sensu* Hedges *et al.*, 1997). Overall, this sequence of processes suggests that the OM that is being respired is translocated in space and time from its points of origin, such that, over long times and large spatial scales, the modern aquatic environment may be connected with terrestrial conditions of another time.

Input to Reservoirs

Just because dissolved and particulate materials enter a river it does not mean that they reach the ocean; modern reservoirs have had a tremendous impact on the hydrologic cycle. Starting about 50 years ago, large dams were seen as a solution to water resource issues, including flood control, hydroelectric power generation, and irrigation. Now there are more than 40 000 large dams worldwide (World Commission on Dams, 2000). This has resulted in a substantial distortion of freshwater runoff from the continents, raising the "age" of discharge through channels from a mean between 16 and 26 days to nearly 60 days (Vörösmarty et al., 1997). While erosion has clearly increased the mobilization of sediment off the land, the proliferation of dams has acted to retain those sediments. Vörösmarty et al. (2003) estimates that the aggregate impact of all registered impoundments is on the order of 4 to $5 Pg year^{-1}$ of suspended sediments (of the $15-20 \text{ Pg year}^{-1}$ total that he references). Stallard (1998) extrapolates from a more detailed analysis of the coterminous US to an estimate of about 10 Pg year⁻¹ worldwide (versus 13 Pg year⁻¹ efflux to the oceans), for a storage of about $0.2 \text{ Pg C year}^{-1}$ (which he includes as part of his overall calculation of continental sedimentation.

Export to the Coastal Zone

The conventional wisdom is that the flux of POC and DOC are each about $0.2 \text{ Pg C year}^{-1}$, and DIC is $0.4 \text{ Pg C year}^{-1}$ (e.g. Schlesinger and Melack, 1981; Degens, 1982, Meybeck, 1982, 1994; Ittekkot, 1988; Ittekkot and Laane, 1991; Ludwig *et al.*, 1996; Ver *et al.*, 1999). That these analyses converge is not terribly surprising. They are all based on much of the same (very sparse) field data, and use variations of the same statistically based interpolation schemes. Let us evaluate these numbers.

Because direct measurements are few, POC flux estimations are typically a product of the flux of total suspended sediments (TSS) and the (estimated) weight-percent organic C (w%C) associated with the sediment (because the bulk of POC is organic C sorbed to mineral grains). The first problem is an adequate resolution of the TSS flux. Data on TSS are frequently poor and of unknown quality. Many reported data are surface samples, and the depth integrations necessary to accurately characterize sediment flux are on the order of 2-3x higher. Additionally, much sediment moves during episodic storm events, when measurements are almost never made.

Estimates of TSS transport to the oceans have ranged from 9 Pg year^{-1} to more than 58 Pg year^{-1} , with more recent studies converging around $15 - 20 \text{ Pg year}^{-1}$. These estimates are generally based on extrapolations of existing data, which are weighted to the large rivers of passive margins and temperate regions. Milliman and Syvitski

(1992) called attention to the much higher yield rates from steep mountainous environments (without directly computing a global total). More recently, Milliman *et al.* (1999) estimated that the total sediment flux from the East Indies alone (the islands of Sumatra, Borneo, New Guinea, Java, Sulawesi, and Timor), representing about 2% of the global land mass, is about 4 Pg year⁻¹, or 20–25% of the current global values. This type of environment (steep relief, draining directly to the oceans) is found elsewhere in the world, so the results are not likely to be unique. New data from Taiwan support these high levels, with isotopic analyses of the C showing that a significant part of the flux is human-driven (Kao and Liu, 2002).

Then, to obtain POC flux estimates, these values (and their uncertainties) must be multiplied by w%C. Meybeck (1991) divided particulate carbon into inorganic (PIC) and organic (POC) phases, and assumed that high sediment rivers have very low carbon fractions (0.5 w%C), representative of shale; he essentially does not consider the latter to be "atmospherically derived" and hence discounts it from estimates of fluxes to the ocean. More recent values for w%C tend to be in the 1-2% range, and higher for organic-rich systems (Richey *et al.*, 1990; Stallard, 1998; Gao *et al.*, 2002).

To account for this range, POC flux can be computed as an ensemble based on different combinations of w%C and TSS fluxes, resulting in a range of $0.3 - 0.8 \text{ Pg C year}^{-1}$, with a "more likely" value of about $0.5 \text{ Pg C year}^{-1}$ (depending on assumptions used). Therefore, it is possible that the common estimate of $0.2 \text{ Pg C year}^{-1}$ is low, and that the overall value lies in the range of $0.2-0.5 \text{ Pg C year}^{-1}$. The common estimate for PIC of $0.2 \text{ Pg C year}^{-1}$ (Meybeck, 1991; Ver *et al.*, 1999) may also be underestimated if sediment fluxes are higher.

The value of $0.2 \text{ Pg C year}^{-1}$ for DOC export may also be low. DOC is also subject to sparse (and questionable) measurements, without the availability of a proxy like TSS for POC. Aitkenhead and McDowell (2000) developed a model of riverine DOC flux as a function of soil C:N. Using this model, they computed a global flux of $0.4 \text{ Pg C year}^{-1}$, or twice the common estimate. That is, the total organic C output from fluvial systems may well be approximately double the original estimates, in the ~0.8 Pg C year^{-1} range.

Anthropogenic Transient

To what degree have these fluxes been influenced or impacted by human activities, that is, how much of this carbon is an anthropogenic transient? The consensus is that human-induced erosion has dramatically accelerated the movement of sediments (and POC). While some of this material "hangs up" on land (sedimentation, reservoirs), some of it likely escapes to the sea (some of the regions with highest sediment yields have very few dams). There

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is evidence that anthropogenic processes have an affect on DIC. Raymond and Cole (2003) report an increase in the alkalinity of the Mississippi, that implies an increase in the consumption of atmospheric CO₂ through weathering. However, Jones *et al.* (2003) reported a systematic decrease in pCO_2 in rivers across the United States, which they attributed to large-scale declines in terrestrial CO2 production and import into aquatic ecosystems, and not to terrestrial weathering or in-stream processes.

In the case of DOC, there is simply not enough information available to make conclusions. Clair *et al.* (1999) suggested that DOC export from basins in Canada might increase by 14% with a doubling in atmospheric CO₂. An additional factor rarely addressed in rivers is direct loading from urban and industrial sources (Ver *et al.*, 1999; Abril *et al.*, 2002). In evaluating the consequences of continental sedimentation and the potentially higher fluxes of POC, a net transient exported from land of roughly 1 Pg C year⁻¹ is possible, with perhaps half of that going to the sea, and the other half divided equally between outgassing and sedimentation.

Overall Fluvial System – Atmosphere Exchange

Considerable uncertainty remains in the assessment of the carbon cycle of fluvial systems, including the actual magnitude of fluxes, how to include processes not previously considered, and delineation of anthropogenic and natural processes; all with an explicit recognition of geography. The bulk transfer of atmospheric C through the land to fluvial systems (assuming a steady state summation of downstream processes, in a non-steady state environment) ranges from about $0.6 \text{ Pg C year}^{-1}$ (CW) to $2.6 \text{ Pg C year}^{-1}$ (+Outgassing). Continental sedimentation results in a significant sink, but that sink is reduced with CO₂ outgassing (because of the way the sedimentation was computed). The inclusion of continental sedimentation, and then the larger export of OM to the sea (about twice conventional assumptions, under +POC, DOC), yields net sinks of atmospheric CO₂ of up to $1.6 \text{ Pg C year}^{-1}$. However, if outgassing is included, then the fluvial net sink is reduced to $0.2 \text{ Pg C year}^{-1}$. While partitioning the total fluvial fluxes into natural conditions and anthropogenic transients is problematic at best, there is substantial evidence that there has been a dramatic increase in the mobilization of sediments. While much of this material is captured in reservoirs, it is reasonable to expect that a considerable amount escapes to the sea (especially in nondeltaic regions with steep slopes and few dams).

Summarizing all the components of the riverine carbon cycle, several images emerge. As a global steady state aggregate, there appears to be a sink (between continental sedimentation and marine sedimentation and dissolution) on the order of $1-1.5 \text{ Pg C year}^{-1}$, with a significant anthropogenically enhanced component. A return flux to the

atmosphere, on the order of 1 Pg C year^{-1} , reduces the net sink to about 0.2 or $0.3 \text{ Pg C year}^{-1}$. There are significant regional implications in this analysis. With its preponderance of land mass, extensive reservoirs, and agriculture, the bulk of continental sedimentation (and its implications for C sink), is focused in the Northern Hemisphere, between $30^{\circ} - 50^{\circ}$ N. The C sequestration in paddy lands would be closer to the equator. The greatest amount of sediment flux to the ocean (and the greatest uncertainty) is in South and Southeast Asia and Oceania. Outgassing is a function of both pCO_2 concentrations (driven by *in situ* oxidation) and surface area of water. It is likely the most significant in the humid tropics, particularly during the peak of the wet seasons. The highly canalized temperate areas have less area available. The northern latitudes, particularly with warming, are liable to have significant fluxes.

Dissolved N and P

While evaluation of the overall anthropogenic impact on river basin carbon is complex, there is little ambiguity about impacts on dissolved N and P. To establish a baseline for evaluation of the N cycle, Lewis et al. (1999) evaluated yields of total fixed nitrogen and nitrogen fractions for watersheds across the world, over a broad range of watershed areas, elevations, and vegetation types, in which anthropogenic disturbance was small. They found that yields were substantially lower than previously estimated for background conditions, and that yields can be predicted on the basis of general environmental variables such as drainage area or the amount of runoff. However, the production of food and energy has markedly increased the amount of newly fixed nitrogen entering terrestrial and aquatic ecosystems during the last century. As of 1990, the amount of newly fixed N entering terrestrial systems annually had about doubled (Galloway et al., 1995; Galloway and Cowling, 2002). The fraction of this N that reaches rivers and ultimately the coastal oceans has led to the enrichment of coastal ecosystems (e.g. increased phytoplankton production, increased turbidity with subsequent loss of submerged aquatic vegetation, oxygen deficiency, and decrease in biodiversity, and so on (Nixon, 1995; Vitousek et al., 1997; National Research Council, 2000; Cloern, 2001; Rabalais, 2002). Under a "business as usual" scenario, Seitzinger et al. (2002) computed that future DIN loadings to coastal systems could approximately double yet again, by 2050.

Similarly, Harrison *et al.* (in press) used a spatially explicit, global model of river dissolved inorganic phosphorus (DIP) export to evaluate the relative magnitudes of sewage, fertilizer, manure, and weathering P sources, and the inclusion of reservoir retention and consumptive water use terms. Their model computed that of the 34 Tg of P year⁻¹ loaded on watersheds by human activity

globally, approximately 2% (0.71 Tg year⁻¹) reaches river mouths as DIP; of the total predicted annual DIP export (1.1 Tg P year⁻¹), anthropogenic sources account for 65%, with the remaining 35% (0.38 Tg year⁻¹) attributable to natural weathering processes.

SUMMARY STATEMENT

The overall biogeochemistry of river basins at large scales is fundamental in establishing the overall dynamics of the landscape, its linkages to the atmosphere, and ultimately to the oceans. Changes in land use and climate will significantly impact the critical water resources that these basins represent. New tools enable us to make more rapid progress than ever in our understanding. A cautionary note, however, is that the fact remains that there are •far too few field studies as to the actual state of a surprising number of these basins.

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Keywords: rivers; carbon; hydrology; landscape; production; weathering; mineralization; outgassing

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