

**ANCIENT AND MODERN SOURCES OF ORGANIC CARBON TO
TRIBUTARIES OF THE HUDSON-MOHAWK RIVER SYSTEM,
NEW YORK, USA**

A Thesis Presented

by

BRETT E. LONGWORTH

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

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Department of Geosciences

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DEDICATION

This thesis is dedicated to Jessie Elizabeth Gunnard, who has encouraged, inspired, and just generally stuck with me far longer than I expected this to take.

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ABSTRACT**ANCIENT AND MODERN SOURCES OF ORGANIC CARBON TO TRIBUTARIES
OF THE HUDSON-MOHAWK RIVER SYSTEM, NEW YORK, USA**

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Rivers play an important role in the surficial and geologic carbon cycles. They are the primary link between terrestrial carbon sources and the ocean, and they erode ancient organic matter (OM) and carbonate from sedimentary rock. While much of the organic carbon (OC) contained in rock exposed by erosion is oxidized to CO₂, a significant portion may be transported downriver and reburied in marine sediments. This riverine conduit of sedimentary rock OM to the ocean potentially separates a pool of ancient OC from the contemporary carbon cycle. This “short circuit” in the carbon cycle has important implications for the global carbon cycle over geologic time, which include carbon isotope effects, effects on estimates of carbon reservoir sizes and turnover rates, and ultimately, the composition of Earth’s atmosphere over geologic time.

Chapter one of this thesis reviews the role of rivers in the global carbon cycle: sources of riverine OM; transport and processing of riverine OM; and isotope systematics of riverine OM. Fluvial systems provide the primary transport mechanism from land to water for OM from net ecosystem production stored in soils and from

ancient marine OM in sedimentary rock. This export is divided into dissolved and particulate pools with differing sources, fates and behaviors in the riverine and global carbon cycles. Radiocarbon, stable carbon and nitrogen isotopes, along with bulk composition and molecular analysis, provide the tools to examine these sources, fates and processes.

Chapter two describes the methods and results of a study of fourteen small headwater watersheds of the Hudson-Mohawk River system in upstate New York, USA. Using elemental analysis and isotopic composition, this study examines the sources of particulate organic matter (POM) to headwater streams. To examine the effects of lithology (OM-rich shales vs. OM-free rock) and land use (agricultural vs. forested) on the type and composition of POM exported by rivers, watersheds with varying combinations of OM-rich shales and agriculture were chosen as sampling sites. In watersheds with large areas of agriculture and shale, mean $\Delta^{14}\text{C}$ of POM was depleted by 74‰ relative to samples from forested, shale-free watersheds, while all watersheds had similar $\delta^{13}\text{C}$ values. POM from agricultural watersheds was enriched in $\delta^{15}\text{N}$ of total particulate nitrogen (TPN) by 3.9‰ over forested watersheds. The mean C:N ratio for forested watersheds was double that of agricultural sites. The area of watershed shale and agriculture in a watershed are both factors in controlling $\Delta^{14}\text{C}$ and C:N of POM. Mixing models indicate that shales contribute about 6% of stream POM. Although these results do not clearly separate the influences of land use and lithology, they indicate that both agricultural land use and OM-rich watershed lithology introduce aged POM into the Hudson River system.

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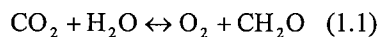
CHAPTER 1

RIVERINE ORGANIC CARBON: SOURCES, PROCESSING, FATES, AND CYCLING

This chapter reviews the role of rivers in the global carbon cycle; sources of riverine organic matter (OM); transport and processing of riverine OM; and isotope systematics of riverine OM. Rivers and streams are important in the movement of OM on both short and geologic timescales. Fluvial systems provide the primary transport mechanism from land to water for OM from both net ecosystem production stored in soils and from ancient marine carbon in uplifted sedimentary rock. This export can be divided into dissolved and particulate pools, which have differing sources, fates and behaviors in the riverine and global carbon cycles. Radiocarbon, stable carbon and nitrogen isotopes, along with bulk composition and molecular analysis, provide the tools to examine these sources, fates and processes.

1.1 Rivers in the global carbon cycle

At the core of the global carbon cycle is the interconversion of carbon between oxidized form and reduced forms (Figure 1.1, Equation 1.1). The balance between these two forms controls concentrations of atmospheric CO₂ and O₂ (Berner, 1989), and moderates global climate through the role of CO₂ as a greenhouse gas (Houghton et al., 2001; Prentice et al., 2001).



In the forward direction, equation 1 converts CO₂ and water to produce OM and release oxygen, while in the reverse direction oxygen and OM are consumed, releasing

CO₂. On land, photosynthetic organisms are the primary agents for reducing, or fixing, atmospheric CO₂ into OM. The majority of this fixed organic carbon (OC) is reoxidized or respired rapidly to provide energy for the photosynthetic organism and heterotrophic communities, but some may accumulate in soils as net ecosystem production. This excess accumulation has three possible fates: 1) storage in soils, 2) oxidization by fire, and 3) export to rivers. In systems that are accumulating OC, this positive net ecosystem production is carbon storage or sequestration. In steady state systems, this excess is removed through a combination of fire and riverine export (Amundson, 2001; Cole and Caraco, 2001).

Riverine export of organic matter to the world's oceans is a small but important part of the global carbon cycle. Total riverine organic carbon (OC) output is estimated to be $0.4 \times 10^{15} \text{ g C y}^{-1}$, and is composed of approximately equal amounts of dissolved organic carbon (DOC) and particulate organic carbon (POC) (Ittekkot, 1988; Meybeck, 1982; Post et al., 1982). River OC export to the oceans is only 0.5% of terrestrial net primary production (Hedges, 1992). Even if the source of all riverine OM were modern terrestrial primary production, a substantial proportion (99.5%) of NPP must be sequestered on land (Stallard, 1998) or remineralized by heterotrophy or fire (Amundson, 2001; Gonzalez-Perez et al., 2004; Levine, 1994). The flux of riverine OM is one to two orders of magnitude smaller than the ocean-atmosphere or terrestrial-atmosphere fluxes of 90 and $120 \times 10^{15} \text{ g C y}^{-1}$, respectively (Schlesinger, 1997); however, it is the primary input of organic matter to the world's oceans, and accounts for a significant term in balancing the movement of carbon between the terrestrial and oceanic carbon cycles.

Figure 1.2 shows a schematic representation of the pools and fluxes involved in riverine carbon transport and cycling.

It is unclear how much of riverine carbon output is remineralized in the oceans and how much is buried in sediments. The balance between these two fates of sedimentary OC controls long-term removal of OC from the Earth's surface. Sediments rich in organic carbon are deposited in environments that limit remineralization of OM prior to lithification. These environments are primarily coastal margins where high sedimentation rates within oxic sediment do not allow time for remineralization of OM, and the anoxic or euxinic bottom waters of seas without deepwater circulation. Anoxic conditions are required to slow or stop remineralization of sedimentary OM (Canfield, 1994; Hartnett et al., 1998). The accumulation rate of OM is generally slow, so a deposition zone must be far enough from shore to avoid excess dilution from detrital clastic material for sediments to have a high organic content (Sageman et al., 2003). The burial rate of OC in ocean sediments is estimated to be 0.1-0.2 Gt y⁻¹ (Berner, 1989).

[With deeper burial, this sedimentary pool is lithified and will remain sequestered from the surface carbon cycle for longer than 10⁶ y until subduction at active plate boundaries and volatilization within the lithosphere or uplift and exposure to weathering or erosion at the Earth's surface (Di-Giovanni et al., 2002; Petsch et al., 2000).

Comment [BEL1]: What percent of total OC burial is terrestrial

The balance between weathering and erosion affects carbon storage in sediments and exerts control on atmospheric concentrations of O₂ and CO₂. Chemical weathering of organic carbon-bearing rock consumes oxygen and releases CO₂, but during erosion without remineralization, organic carbon passes through the cycle and is reburied without affecting atmospheric chemistry, thus decoupling the carbon cycle from climate.

Additionally, if a fraction of OM production remains in reduced organic form through multiple cycles of erosion and deposition, the net amount of OM stored in sediments and rocks should increase. The fact that carbonate reservoirs have not become more isotopically enriched over time (Schidlowski, 2001) argues against a continuous removal of ^{13}C -depleted recalcitrant organic carbon from the surface carbon cycle.

Past work has focused on erosion and weathering of ancient sedimentary OC as separate end members. One hypothesis holds that essentially all ancient sedimentary carbon is remineralized to CO_2 in soils and regolith upon exposure to surface weathering processes and the aerobic environment (Berner, 1989). The other possibility is that weathering of the mineral matrix and erosion frees this ancient carbon pool for transport back to the oceans by rivers without significant remineralization (Blair et al., 2003; Blair et al., 2001; Leithold and Blair, 2001). Two critical factors determine the fate of ancient OM exposed on the continents: reactivity of the OM and time of exposure to surface processes. The nutrient-rich and easily decomposed components of fresh detrital OM in soils and sediments are preferentially utilized in soils and sediments, leaving less bioavailable residues. The resulting sedimentary organic matter should therefore be resistant to further remineralization upon exposure (Blair et al., 2001).

1.2 Source and Composition of Riverine Organic Matter

Riverine organic matter is generally divided into two pools, dissolved organic matter (DOM) and particulate organic matter (POM) (Table 1.1). This division is made by particle size fraction using filtration. DOM is operationally defined as the fraction of organic matter in aqueous solution that passes through a filter membrane. In the literature of soil science, the filter size is generally $0.45\mu\text{m}$ (Herbert and Bertsch, 1995), whereas in

the fields of aquatic geochemistry and biogeochemistry, a 0.6 or 0.7 μ m filter is generally used (Aitkenhead-Peterson et al., 2002; Raymond and Bauer, 2001a). This discrepancy is of potential importance as humus and clay associated organic complexes are within this size range, and excluding or including these compounds may have a large effect on the results of measurements and make comparison with other studies difficult. These larger, more complex organic moieties may be more resistant to remineralization than smaller organic constituents, and therefore also generally have longer residence times in soils (Gaudinski et al., 2001; Rumpel and Kögel-Knabner, 2002). It may therefore be expected that as filter pore size increases, DOM collected will be older and less reactive, while POM should be correspondingly younger and more reactive than the same fractions collected with filters of smaller pore size. While this division seems arbitrary, DOM and POM generally have proven to exhibit different sources, compositions, reactivities and fates in riverine systems. In soils and rivers, dissolved OM is derived primarily from soil leaching (Meybeck, 1982; Meybeck, 1993) and ranges from simple sugars to large molecules with complex structure such as humus and lignin. Particulate organic matter is introduced to rivers by erosion of riverbanks and interfluvies, and produced in rivers by flocculation and biotic activity (Meybeck, 1993).

Comment [BEL2]: 14C and size fraction

Organic matter in rivers can be further divided into categories by source. Autochthonous OM is generated in the river by autotrophic organisms including photosynthetic microorganisms and aquatic plants. Allochthonous OM is produced or stored in the watershed and introduced to the river by erosion or leaching. Humans may also introduce organic material to rivers through pollution. Materials such as sewage and agricultural runoff increase carbon and nutrient loading in river systems due to point-

source carbon in discharged material and fertilization of riverine production by nutrients like nitrogen and phosphorous. The ancient origin of OC in airborne particulate combustion byproducts and petroleum products may have a confounding effect on isotopic studies of organic matter sources when these materials enter rivers through aerial deposition and runoff (Raymond et al., 2004).

1.2.1 Particulate organic matter

Particulate organic matter in rivers has three primary sources: 1) erosion of river channel and interfluvial material, 2) production by riverine autotrophy, and 3) association of DOM with mineral particulates or flocculation (Meybeck, 1993). Deeper soils and rock are introduced to rivers through erosion and downcutting, while surface flow contributes plant litter and surface soils. Export flux and composition of POM varies widely between and within river systems, primarily with discharge, but also due to nutrient availability, and watershed soil conditions.

1.2.1.1 Sources of Particulate Organic Matter

One of the three primary sources of riverine POM is autotrophic carbon fixation. The carbon source for this pool is riverine dissolved inorganic carbon, which in turn is derived from soil CO₂, atmospheric CO₂ and carbonate derived from the weathering of carbonate rock (Meybeck, 1987). Autochthonous POM consists of living or dead autotrophic biomass. Riverine autotrophs generally have a high ratio of functional or photosynthetic biomass to structural biomass compared to terrestrial plants. Autochthonous OM therefore has low C:N ratios and relatively high lability. While

riverine heterotrophy may dominate riverine metabolism, it does not generate new OC, and cannot therefore be considered autochthonous production.

Available light, nutrients, temperature and grazing control production of autochthonous POM. Autochthonous production is usually not the dominant source of riverine POM in all but slow-moving systems with large nutrient inputs (Howarth et al., 1996) In steeper rivers, turbidity, rapid flow and short transit times limit autochthonous production, in many cases reducing it to an insignificant term compared with terrestrial inputs (Blair et al., 2003; Gupta et al., 1997; Martinelli et al., 1999). Autotrophy also exhibits a seasonal cycle, with times of high production corresponding to elevated temperatures and day lengths and to low-flow conditions (Meyer and Poepperl, 2004).

Soil organic matter is a major component of riverine POC and the primary source of riverine DOC. Litter is the organic component of soil with recognizable origin, usually recently dead canopy biomass. Humus is organic material degraded to the point that it no longer resembles plant remains. Together litter and humus make up soil organic matter (SOM). Globally, SOM is the largest terrestrial OC pool, estimated at 1500×10^{15} g C. Soils hold $1.4 - 21.8$ kg C m^{-2} averaging 10.8 kg m^{-2} (Schlesinger, 1997). SOM is the major component of the forest floor and organic layers (Lf and O horizons) and is a minor component of mineral soil layers (E, B, and C horizons) (Herbert and Bertsch, 1995; Rumpel and Kögel-Knabner, 2002).

Soil organic matter is not homogenous in composition, age or reactivity. Fresh litter and root exudates added to the system are highly reactive and have correspondingly short residence times of less than a year. More degraded material, which still has a significant labile component, turns over on timescales of 10^1 - 10^2 y. The slowest cycling

pool contains highly refractory OM and OM occluded by mineral aggregate association. This pool has mean residence times of 10^2 - 10^3 y (Amundson, 2001; Trumbore, 1997; Trumbore, 2000). The reactivity of SOM is a controlling factor in remineralization of SOM to CO_2 and production of DOM, but since erosive export of POM is a mostly physical process, this material can include a far greater fraction of SOM resistant to export by remineralization or DOM (Stallard, 1998).

Ancient sedimentary OM available to rivers is organic matter that has been buried in ocean sediments, lithified, and later uplifted and exposed by erosion. This pool is primarily composed of kerogen, which is defined by its resistance to acid and solvent dissolution (de Leeuw and Largeau, 1993; Hedges, 1992; Tissot et al., 1974). Kerogen is highly resistant to remineralization, but Petsch et al. (2001a; 2001b) showed that microbes can use kerogen as a carbon source, oxidizing it to CO_2 . Precursor organic materials start with the composition of marine OM, but this signal is subsequently altered by selective preservation of resistant biopolymers during diagenesis in surface sediments and the heat and pressure of subsequent burial. The resulting product may be similar to aged soil OM in stable carbon isotopic composition and reactivity (Hedges and Oades, 1997).

Previous data show that riverine organic matter from watersheds underlain by sedimentary rock rich in ancient OM tends to have a greater mean radiocarbon age than material from rivers lacking these lithologies (Tables 1.2 and 1.3) (Raymond et al., 2004). The presence of this older OM suggests that ancient rock OM could play an important role in the riverine carbon cycle and thus affects surface carbon dynamics. Recent radiocarbon analyses of riverine POC by Kao and Liu (1996), Leithold and Blair (2003),

Masiello and Druffel (2001), and Raymond and Bauer (2001b) has shown that a significant portion of riverine OM export may be ancient marine OM released from shales by weathering processes, especially in steep, highly erosive systems. In each of these studies, the radiocarbon ages of POC are older than the oldest watershed materials, making the POC age difficult or impossible to explain by the input of aged soil OM alone. Ancient organic carbon transported in this way may be reburied in marine sediments (Dickens et al., 2004).

1.2.1.2 Composition of Particulate Organic Matter

Riverine POM grades along a continuum between labile, fast-cycling OM mostly composed of living and recently dead organic matter, and refractory, slow-cycling components composed of ancient sedimentary OM and aged soil OM. McCallister et al. (2004) have shown that riverine bacteria in the Hudson River estuary can use aged terrestrial OM, indicating that the lability of POM does not necessarily decrease with increasing POM age. For analytical purposes, however, POM can be divided into labile and refractory pools indirectly by biological oxygen demand or by chemical quantification of proteins and carbohydrates. By these methods, the labile pool makes up 30-75% of total POM and contains significant parts proteins and carbohydrates, 7-29% and 5-17% respectively as percent of total POM (Ittekkot and Laane, 1991). The refractory pool consists of kerogens from ancient sedimentary material and humic and lignic compounds from soils. Physical and/or chemical protection afforded to OM by mineral association and bonding may place otherwise labile OM in the refractory pool.

1.2.1.3 Delivery of Particulate Organic Matter to rivers

Both soils and rock are delivered to rivers by erosion, although they erode at different rates due to their differing physical and chemical natures. River channel and bank versus interfluvial erosion also affect rock and soil differently because soil generally overlies rock and is therefore more available to interfluvial erosion, while rock is more strongly affected by riverine downcutting. Processes such as weathering and mineral association combine with human activity, climate, and landscape factors to exert control on erosive exports. Agricultural practices such as tillage dramatically increase surface runoff by making soils resistant to infiltration (Gregorich et al., 1998). The availability of ancient lithified POM for export is controlled by chemical weathering of its surrounding mineral matrix (Stallard, 1995). High and low flow regimes may selectively liberate different types of OM from the watershed soils and regolith due to varying erosive force, groundwater vs. runoff input, and duration of water contact with substrate (Meybeck 1993). Less dense materials tend to be transported more readily than more dense and mineral associated fractions (Lal, 2003). As a result of these factors, the amount and composition of riverine POM vary tremendously.

1.2.2 Dissolved organic matter

Dissolved organic matter is an important component in the cycling of carbon in soils and in the global carbon cycle. It is the primary form of organic export from soils, and is a major carbon source for aquatic systems. DOM is produced mainly through groundwater leaching of soluble organic compounds from soil organic matter in various stages of decomposition. Many factors, including soil moisture, soil composition,

temperature, and pH interact to control the generation of DOM and its progress through the soil (Judd and Kling, 2002).

Concentrations and fluxes of riverine DOC range from 1mg/L in small alpine streams to greater than 20 mg L⁻¹ in highly productive or wetland environments (Spitzzy and Leenheer, 1991). Global riverine DOC flux is estimated at 0.2×10^{15} g C y⁻¹ (Schlesinger, 1997). This is approximately half of the total riverine OM flux, and is enough to account for the total yearly turnover in ocean DOC (Williams and Druffel, 1987). However, the very different isotopic and elemental composition of riverine and ocean DOC indicate that this is not the case. Average concentration of DOC in river waters is 5 mg C L⁻¹ (river OC flux/river discharge), which is about 3 orders of magnitude less than carbon concentration in most soils. Riverine flux is the primary source of terrestrial DOC to the world's oceans.

1.2.2.1 Sources of Dissolved Organic Matter

Most DOM in rivers is produced in watershed soils and wetlands and exported to rivers by groundwater flow, but inputs from precipitation, canopy throughfall, sedimentary organic matter, and autochthonous production also contribute. The largest flux of DOC to surface waters is from DOC in groundwaters, which is in turn produced by the decomposition of soil organic matter. Concentrations of DOC in soil water, as extracted by pressure in the laboratory or by in-situ lysimeters, vary over three orders of magnitude (10^0 - 10^2 mg C L⁻¹) (Kalbitz et al., 2000) between soil types and horizons. Wetlands produce and store significant amounts of organic carbon. Concentrations of DOC in wetland waters are generally comparable or greater than concentrations in soils, and range from 10 to 100 mg C L⁻¹ (Thurman, 1985). Rainwater has an average DOC

concentration of 2 mg C L^{-1} (Aitkenhead-Peterson et al., 2002; Willey et al., 2000) over North America and consists of pollen, organic dust, and small organic aerosols scavenged by precipitation. DOM is produced in the canopy when precipitation leaches soluble organics from vegetation. This pool has concentrations in the tens of mg C L^{-1} (Aitkenhead-Peterson et al., 2002). Contributions of ancient sedimentary organic matter to the modern DOM pool are uncertain. Petsch et al. (2001a) showed that soil microbes can utilize ancient OM. This could imply that ancient OM is taken up in dissolved form, since soil microbes cannot incorporate material in solid form. This combined with loss of OC during weathering of OM in Devonian age black shales (Petsch et al., 2001b) and DOC present in oilfield brines suggest that DOM may be produced from ancient OM and exported from the soil-rock environment (Thurman, 1985). The size of this flux is unknown.

1.2.2.2 Composition of Dissolved Organic Matter

DOM comprises a wide array of organic moieties of varied size and composition. Compounds that make up DOM vary in complexity from simple polysaccharides to large, complex humic acids of unknown configuration, and vary from 10^2 - 10^5 daltons in molecular weight (Thurman, 1985). Constituents of DOM are polysaccharides, fatty acids, phospholipids, and generally the most abundant, difficult-to-characterize humic substances (Herbert and Bertsch, 1995). Any organic material small enough to be carried in soil solution could be considered to be in this OM pool, but an arbitrary size cutoff is made to exclude suspended particulate matter.

The composition of DOM varies with parent soil organic matter, soil chemistry, and *in situ* processes within the DOM pool. Simple sugars are largely absent from

riverine DOM (Huang et al., 1998), and DOM generally has low concentrations of other highly bioavailable compounds like polysaccharides and N-rich compounds, but may become enriched in these compounds due to flushing of fresh litter, root exudates, or extracellular products of microbial metabolism. More commonly found are resistant substances like lignins, tannins, fatty acids, humic substances, and the degradation products of these compounds (Huang et al., 1998; Page et al., 2002; Rumpel and Kögel-Knabner, 2002).

1.2.2.3 Delivery of Dissolved Organic Matter to Rivers

DOM export is controlled by a combination of abiotic and biologic factors. In field studies, soil moisture appears to be the dominant control. Laboratory studies generally do not accurately portray the role of hydrology in DOM controls, but shed light on the effect of other factors on production and export. Higher concentrations of soil carbon, more labile soil OM, and increased mineralization (oxidation to CO₂) of SOM increase DOM production, while sorption to mineral soil reduces exports. The effects of changing soil chemistry (pH, ionic strength) are variable due to conflicting controls on physiochemistry and biology (Kalbitz et al., 2000).

As a solvent for leaching soluble soil organic matter, water directly controls DOM production and export to rivers. Increased water flow dissolves more of the readily soluble “potential DOM” pool (Kalbitz et al., 2000), increases DOM export and is linked to residence time of DOM within a system. Indirectly, water supports microbial activity in the soil, which in turn produces more DOM. Cycles of wetting and drying seem to have the greatest effect on DOM export, possibly due to buildup of microbial products or

available DOC during dry periods which are then flushed from the system during rewetting (Findlay et al., 2001; Judd and Kling, 2002).

Sorption of DOM in mineral soil horizons is a major control on export. Increased DOM production and flux through soils lead to increased sorption, but also allows more export. Soils with more soil organic matter suppress sorption, possibly due to competition for active sorption sites or simply due to increased DOM availability for sorption and export. Hydrophobic moieties of DOM are preferentially adsorbed onto mineral surfaces, and soils with highly hydrophobic soil organic matter may allow more DOM export by preferential sorption of soil organic matter allowing DOM to remain free (Aitkenhead-Peterson et al., 2002; Kaiser et al., 2000). After production within the soil, hydrologic processes within the streambed and watershed control the physical export of DOM to streams (Figure 1.3). In addition to subsurface flow through riparian soils, exchange of DOM occurs when stream waters recirculate through the stream bottom sediments.

1.3 Transport, Processing, and Fate of Riverine Organic Matter

Far from being a simple conduit from land to ocean, rivers can alter the composition and abundance of organic matter during transport. Downstream transects and incubation experiments show that OM is remineralized and/or reorganized during transit (Raymond and Bauer 2001b). Various pools of OM may be transported downriver at different rates, depending on their densities and sizes, with smaller and less dense particulates traveling faster. OM may change in chemical composition or be converted between POC and DOC. Additionally, rivers are moving ecosystems that fix atmospheric CO₂ to OM by photosynthesis and respire OM as CO₂ while *en route* to the sea (Howarth et al. 1996), creating or destroying POC and DOC.

1.3.1 Transport of Riverine Organic Matter

Velocity and discharge control the flow of water and suspended matter through rivers, and thus control the transport of riverine OM. Velocity varies with the gradient and cross sectional area of the river at any given point. Discharge is controlled by watershed area, land use, hydrology, and precipitation. The time available for production, transformation, and release of riverine OM during transport is determined by its residence time within the system. The residence or transport time of any given parcel of water is determined by integrating its velocity over the length of the river system. In a homogenous section of stream with laminar flow and no inputs or outputs, the residence time is determined by dividing the stream velocity by the distance of the section. In real systems with constantly varying velocity, inputs and outputs, calculating residence time is difficult.

The rate of riverine DOM transport is defined by river flow, assuming no reinfiltration of the hyporheic zone (Kaplan and Newbold, 2000). POM transport in rivers is more complex, because the behavior of suspended matter is dependent on the lifting and carrying capacity of a stream at a given flow velocity (Figure 1.4). Net carbon and nutrient transport are also controlled by a process called nutrient spiraling (Newbold et al., 1982). In this process, carbon and nutrient transport is slowed by continual incorporation into and release from the biota of the streambed. Each time material is released, it flows a short distance before being reincorporated downstream. Association with mineral particles further controls POM transport by increasing density and particle size (Leithold 2001). Overall, DOM and POM export increase with increasing discharge

simply due to greater volume. Stream velocity increases POM transport by allowing the stream to carry larger suspended particulate loads.

1.3.2 River Heterotrophy

Organic matter in riverine systems is far from inert during transport. Heterotrophic organisms constantly remineralize available OM as it moves downstream. Rivers generally have a net heterotrophic metabolism (Cole and Caraco, 2001; Howarth et al., 1996), meaning that the rate of ecosystem respiration is greater than autotrophic production. Net heterotrophic rivers require inputs of terrestrial organic matter. In these systems, terrestrial organic matter is consumed as it travels downstream. Net heterotrophic rivers are also net sources of CO₂ to the atmosphere (Raymond et al., 2000; Raymond et al., 1997; Richey et al., 2002). Selective degradation of riverine OM also alters the bulk composition of the remaining OM. Presumably, heterotrophic organisms will preferentially consume organic matter that is either more easily oxidized or provides more nutrients or energy, but recent evidence from the Hudson and York Rivers show that this may not necessarily mean young OM (McCallister 2005). Hodson and Moran (1995) showed that while refractory DOM can be utilized by bacteria, components containing mono- and polysaccharides and amino acids are preferred. Raymond and Bauer (2001b) determined that radiocarbon-enriched, “younger” DOM was used preferentially in a laboratory incubation of York River waters. Raymond *et al.* (2004) found net enrichment of radiocarbon in both POM and DOM downstream in several transects of the Hudson estuary. This could be interpreted as preferential use of more recalcitrant “older” riverine OM as material flows downstream. This contradicts the 2001

laboratory study (Raymond and Bauer, 2001b) and shows that more work is needed to understand the processes of riverine metabolism.

1.3.3 DOM-POM: Dissolution and Flocculation

An additional pair of processes that affect concentrations and compositions of DOM and POM pools as they move downstream is dissolution of POM to form DOM and flocculation of DOM to form POM. These processes should not affect measurements of total riverine OM, but are important because riverine OM is almost universally divided into dissolved and particulate pools. In a manner analogous to the production of DOM by soil leaching, DOM may be released from POM and river sediments (Komada and Reimers, 2001). This process is poorly understood but may be controlled by release of mineral-bound OM due to chemical weathering of the mineral matrix OM during transport, or by dissolution of acid-soluble POM as riverine pH changes. Microbial exoenzyme activity may also break down POM into DOM-sized fractions (Hopkinson et al., 1998). Smaller constituents may flocculate to become POM by organic-mineral or organic-organic complexing (Droppo, 2001; Droppo et al., 1997; Wilkinson et al., 1997). Small organic constituents are also carried by mineral loading, a process in which low molecular weight OM complexes with mineral grains in highly erosive systems (Leithold and Blair, 2001).

1.3.4 Fate of Riverine Organic Matter in Estuaries and the Ocean

The fate of riverine OM not remineralized in transit is export to the ocean. Estuaries are zones of intensive OM reworking and mineralization prior to export (Bauer et al., 2002; Raymond and Bauer, 2001a). Once in the ocean, OM may be oxidized by

marine heterotrophs or reburied in sediments. The global marine burial flux of OC is estimated at 0.1 Pg C y^{-1} , which is equivalent to approximately one quarter of the riverine flux or less than 1% of primary ocean productivity (45 Pg C y^{-1} , Falkowski et al., 1998). Even though the magnitude of riverine OM exports could completely account for the OM burial flux, it is difficult to find OM with riverine isotopic or compositional signatures in shelf and marine systems (Hedges et al., 1997).

Comment [BEL3]: Shelf vs marine deposition

1.3.5 Steep, Small Rivers vs. Larger Flatter Rivers

Several recent studies have focused on steep rivers draining active continental margins, sometimes called small mountainous rivers as a group (Kao and Liu, 1996; Kao and Liu, 1997; Komada et al., 2004; Leithold and Blair, 2001; Milliman and Syvitski, 1992). All studied rivers of this type carry large sediment loads rich in old OM. These small rivers are responsible for only a small fraction of yearly freshwater discharge, but they carry 40% of the global flux of suspended particulate matter (Milliman and Syvitski, 1992) and 17-35% of global POC load (Lyons et al., 2002). Steep slopes and correspondingly high river velocities provide the highly erosive conditions responsible for this disproportionate importance of small mountainous rivers. Typically, these rivers erode the stream channel more deeply than the larger and slower rivers of passive continental margins, resulting in increased export of deeper, older soils and rock rich in ancient OC (Blair et al., 2003; Kao and Liu, 1996; Masiello and Druffel, 2001). However, passive margin rivers draining lithologies rich in OM such as the Hudson-Mohawk, Susquehanna (PA, USA), and Rappahannock (VA, USA) also have been found to export aged OM (Raymond and Bauer, 2001b; Raymond et al., 2004).

1.4 Isotopic Tracers for Riverine OM

The naturally occurring stable and radioactive isotopes of carbon (^{12}C , ^{13}C & ^{14}C) and nitrogen (^{14}N , ^{15}N) have often been employed as tracers in studies of the carbon cycle. These data are measured and reported as the ratio of the rare isotope (^{13}C , ^{14}C , ^{15}N) to the abundant isotope (^{12}C or ^{14}N), normalized to the isotopic ratio of a recognized standard material. For example, the ratio of rare to common stable isotopes of carbon is expressed as follows:

$$\delta^{13}\text{C} = \left\{ \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{sam}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{std}} - 1 \right\} \times 1000 \quad (2)$$

Values are reported as deviation in per mil (‰) from the ratio of the standard. This system is known as delta notation. Variations in the ratio of heavy to light isotope in a sample are caused by processes which act preferentially on one isotope according to its mass. This fractionation generally results in greater abundance of the lighter isotope in the new pool, and in the enrichment of the parent pool in the heavy isotope. When two pools of differing isotopic composition are mixed the ratio of the isotopes in the resulting whole will reflect linear mixing of the compositions of the parts. This allows determination of the amounts of each part in the whole if the compositions of the parts and the whole are known.

1.4.1 Stable Carbon Isotopes

Ratios of the stable isotopes of carbon are measured as in equation 2 above, using the isotopic ratio of a belemnite from the Pee Dee limestone formation as an international

