Organic Matter and Nutrients in the Mainstem Amazon River

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The Amazon, like smaller rivers, is the daughter of its drainage basin. Local climate and interactions over time with the template of topography, geology, and vegetation determine the size and flow of rivers. Likewise, the compositions of the particulate and dissolved materials carried by rivers result from initially similar rainwaters that have been uniquely imprinted by contact with almost every plant, animal, and mineral in the catchment. Rivers thus provide a continuously flowing signal, recorded by isotopes, ions and molecules, of the cumulative effects of drainage basin processes such as weathering, oxidation/reduction, gas exchange, photosynthesis, biodegradation, and partitioning. This recording is complementary to more classical methods of remote sensing based on electromagnetic radiation, but is composited over a wider range of time and space scales and includes effects of subcanopy and subsurface processes. The Amazon River is similar to other rivers in this regard, but is unusual in the size and extent of different environments its waters touch.

The Amazon River is the world’s largest river and drains the world’s largest single catchment (~6,000,000 km²). It discharges an average of about 200,000 m³ of water per second to the Atlantic Ocean. This volume is about 5 times more than the Congo, the second largest river. The Amazon has 1100 major tributaries, three of which are nearly as large as the Congo. From its origins at about 5200 m in the Andes about 200 km from the Pacific Ocean, the Amazon goes through at least 10 name changes as it snakes its way 6500 km eastward to the Atlantic Ocean (Schreider and Schreider 1970). The flooded areas along the lower mainstem are important sources of greenhouse gases such as methane (Bartlett and Harriss 1993, Devol et al. 1994) and the latent heat release from convective precipitation in the basin is sufficient to influence global climate.

The Amazon drainage basin contains 40% of the world’s tropical rain forest (dos Santos, 1987) and is home to countless species of plants and animals. The river itself contains some 2000 described species of fish. Nevertheless, the Amazon is a classic river basin, with a vast central plain bordered by highlands and an extensive floodplain (várzea). Even now, the Amazon is largely undisturbed by anthropogenic activity and includes a series of hydrological and chemical regimes that are representative of world rivers.

The diverse natural ecosystem of Amazonia supports a large resource-based economy. Deforestation for lumber and agriculture has made perhaps the greatest impact on Amazon ecosystems. Extensive road-building during 1960–1980 converted
large areas of forest to crop land and cattle pasture. Between 1978 and 1988 the amount of deforested land in Amazonia increased from 78,000 to 230,000 km\(^2\) (Skole and Tucker 1993). Mining and extraction of gold and aluminum have severely impacted the chemistry of certain Amazon River subcatchments. Development has resulted in elevated concentrations of mercury in the river, sediments, fish, and some humans. This input is associated with both gold mining (Martinelli et al. 1988) and increased erosion of mercury-rich surface soils due to land clearing (Roulet et al. 1998). Another developmental activity that has directly impacted the Amazon River system is dam building. The main purpose of these dams is to produce inexpensive electricity to attract investment (Bunyaard 1987). However, the reservoirs create also produce methane gas that is eventually emitted to the troposphere (Martinelli et al. 1993).

Because of its immense size, the Amazon River basin plays a key role in global biogeochemical cycles. In order to predict the consequences of land use change both locally and globally, it is necessary to understand how the Amazon interacts with its geological environment, component ecosystems, and the atmosphere, as well as how these interactions might change as a consequence of anthropogenic impacts. This is the central question that has guided Amazon River research for the past several decades.

In this chapter we present an overview of current knowledge about the geochemistry of biologically active elements, (e.g. C, N, P, and O) in the Amazon River mainstem. The data and concepts upon which this summary is based result primarily from the CAMREX project (Richey et al. 1990, Richey and Victoria 1993). This ongoing study has included a series of 13 seasonal cruises between 1982 and 1991 which covered the Amazon mainstem between Vargem Grande and Óbidos (1800 km), as well as a time-series record collected at Machantera near Manaos (Devol et al. 1995). Sampling and analytical methods will not be reiterated here, but are discussed in detail in the various cited CAMREX references.

Geologic and Hydrologic Setting

Several major geomorphological zones distinguish the Amazon drainage basin (Fig. 15.1), each with a distinctive geology, vegetation, and local climate. The basin is flanked to the north and the south by two Precambrian shields, the Planalto das Guianas and the Planalto Brasileiro. The Andean Cordillera and the Subandean Trough constitute the western boundary. In between lies the nearly flat central plain of the Amazon trough where elevation changes only about 120 m in 3400 km.

These different source regions imprint distinct chemical signals on the various tributaries to the Amazon mainstem (Fig. 15.1). West of the Brazilian border, the Rio Ucayali and Marañón come together to form the Rio Solimões, as the Amazon mainstem is called above its confluence with the Rio Negro. These rivers drain primarily Andean regions. The two largest of the lower tributaries are the Rio Negro, which drains highly weathered lowland terrain, and the Rio Madeira, with headwaters in the Bolivian Andes. The Rios Trombetas, Xingú, and Tapiáos in the lower course of the river drain primarily shield areas.

Rainfall in the basin is seasonally and geographically variable due to the movement of the intertropical convergence zone (Salati et al. 1979). Maximal rainfall (~7000 mm yr\(^{-1}\)) occurs on the eastern flanks of the Andes. Rainfall decreases to about 3500 mm yr\(^{-1}\) in the northwest lowlands and about 2000 mm yr\(^{-1}\) in the northeast. There is a distinct local dry season that extends from June-August in the South and from January—March in the North. As a result, the seasonal flood cycles of the north and south tributaries are not in phase (Richey et al. 1990). The inflows of large tributaries from the south and north produce a mainstem hydrograph that becomes progressively more damped downstream (Fig. 15.2). Within Brazil, the hydrograph is reasonably sinusoidal, with no sharp spikes. Upstream, near the border with Peru and Colombia, discharge varies from a low of about 20,000 m\(^3\) s\(^{-1}\) in September to a high of about 50,000 m\(^3\) s\(^{-1}\) in April. The minimal and peak discharges increase dramatically downstream and at the city of Óbidos (~800 km from the sea, Fig. 15.1) vary annually from about 100,000 m\(^3\) s\(^{-1}\) to 225,000 m\(^3\) s\(^{-1}\).

The seasonal cycle of discharge in the Amazon mainstem is accompanied by a dramatic change of roughly ten meters in river height. At high water the river overflows its banks and enters the surrounding floodplain through a complex network of channels (paranáis). Within Brazil the floodplain is typically 10–50 km wide (Mentes et al. 1996) and is occupied by numerous permanent and seasonal lakes. Extensive flooded forests and beds of floating grasses plus other macrophytes also cover the mainstem floodplain (várzea). The expanse of floodplain along the Amazon mainstem has been estimated at 94,000 km\(^2\) (Sippel et al. 1992), but accounts for less than one third of the total floodplain area within the Amazon basin (Junk and Fich 1993). The Amazon floodplain has been compared to a

![Figure 15.1 Map of the Amazon River drainage basin. Major tributaries are denoted by open circles with numbers. Locations referred to in the text are referenced by filled circles with letters. Major geologic provinces are also noted.](image-url)
capacitor, which stores water during rising water and releases it during falling water (Fischer and Parsley 1979). At high water as much as 20,000 m$^3$ s$^{-1}$ of water enter the floodplain, as compared to a net downstream discharge of about 170,000 m$^3$ s$^{-1}$ at Óbidos (Richey et al. 1989). As the river drops, floodplain water drains back into the mainstem. This seasonal flooding results in expansive areas of inundated and waterlogged soils, as well as extensive exchanges of water and chemical signals between the mainstem and its floodplain.

Elemental Biogeochemistry of the Amazon Mainstem

Early on, the linkage between the geology, biology and hydrology of the Amazon River mainstem was recognized from visually observable features of the waters and was formalized into an Amazon river "typology" by Sioli (1950, 1951, 1956). This classification consists of visually distinct whitewater, clearwater, and blackwater rivers. Whitewater rivers are ochre colored due to their high suspended sediment content, a prime example being the Rio Madeira. These rivers have a major portion of their drainage in the Andes mountains where physical and chemical erosion of the basement rock are sufficiently intense to produce high turbidity and dissolved ion contents. At the opposite end of the spectrum are the clearwater rivers, such as the Tapajós, that drain highly weathered, low-gradient shield areas. Clearwater rivers are generally low in suspended and dissolved solids and have high transparencies due to low concentrations of suspend-

![Figure 15.2 Amazon River discharge at three locations within Brazil between 1988 and 1992: (1) OBI = Óbidos, (2) MAN = Manacapuru, and (3) VG = Vargem Grande. The horizontal dotted line represents the overbank condition at Manacapuru.](image)

![Figure 15.3 Distributions of carbon, nitrogen, and phosphorus between dissolved inorganic, particulate, and dissolved organic fractions in the Amazon River mainstem, its major tributaries and floodplain waters. Inorganic carbon in the mainstem is divided into its free CO$_2$ and alkalinity components. The total concentration of each species is given below each individual pie diagram and the percentages of the total attributable to the different forms are given next to each pie segment. For carbon the major dissolved inorganic species are alkalinity, which is almost exclusively bicarbonate ion, and dissolved CO$_2$ (Devol et al. 1987). The dissolved inorganic nitrogen is virtually all NO$_3^-$ and phosphorus is mainly PO$_4^{3-}$.](image)
ed sediment and DOC. Blackwater rivers, such as the Rio Negro, have low concentrations of suspended solids and are typically the color of tea due to staining by high concentrations of dissolved organic matter. These rivers drain in low-gradient areas of the central basin that contain podsols rich in bleached sands. These highly weathered soils are typically covered by a characteristic castaings vegetaion and frequently lack a distinct B-horizon. Although this classification was derived from visual characteristics of the rivers, subsequent analysis of dissolved and particulate constituents has shown that the three water types are distinctly different in patterns that reflect upstream processes.

Biogeochemical reactions transform elements between particulate, dissolved organic, and dissolved inorganic phases. Therefore, it is instructive to look at the relative sizes and distributions of these various pools in the three major water types and their influence on elemental cycling in the mainstem, its tributaries and floodplain. The highest total levels of carbon, nitrogen, and phosphorus are found in the mainstem, with progressively lower levels in tributary and várzea waters (Fig. 15.3). Dissolved inorganic carbon (DIC) in Amazonian waters takes primarily two forms, carbonate alkalinity, derived mostly from whitewater Andean drainage (Devol et al. 1995, Stallard and Edmond 1983, Gibbs 1972) and dissolved CO₂ gas. In the mainstem (pH ~6.2-7.2) the dominant DIC species are dissolved CO₂ and bicarbonate, with virtually no carbonate (Devol et al. 1987). Consequently, particulate forms of inorganic carbon are virtually absent. Alkalinity, defined as the total equivalents of dissolved weak bases, is essentially equivalent to bicarbonate concentration and composes about 82% of the DIC in the Amazon mainstem. However, bicarbonate (alkalinity) percentages drop to an average of 57% in tributaries and 50% in the várzea due to generally decreasing pH in these waters. The CO₂ gas component of the DIC is directly involved in biogeochemical cycling through the processes of respiration and photosynthesis. Due to the lack of carbonate or carbonate ion to buffer respiratory CO₂ production, respiration drives the dissolved CO₂ up and the pH down. Therefore, the high CO₂ concentrations in várzea waters reflect active respiration.

The second largest carbon reservoir in all environments is dissolved organic carbon (DOC), which increases as a percentage of total carbon from the mainstem, to tributaries and the várzea. Conversely, particulate carbon, which is essentially all organic, decreases in the same sequence, comprising less than 2% of the total carbon in várzea waters. Nitrogen and phosphorus both decrease continuously from the mainstem to the tributaries to the várzea. All three forms of nitrogen are present in significant quantities in all environments. The dissolved inorganic nitrogen is primarily NO₃ and the particulate nitrogen is exclusively organic (Hedges et al. 1986a). In contrast, most phosphorus is present in particulate phases in all environments. The particulate P shown in Fig. 15.3 is equivalent to a concentration 7.8 µM and is similar to the total particulate P values reported by Berner and Rao (1994) of about 22 µg/g of sediment given 4.6 g of average sediment load of about 250 g/l (Devol et al. 1995). According to Berner and Rao, about one quarter to one third of the particulate P is organic, with the remainder composed of several inorganic phases.

The distributions of C, N, and P in the mainstem, tributaries, and várzea are related to the white-, black-, and clearwater types. The high concentrations of alkalinity in the mainstem indicate that much of this white water originated in the Andes where fresh, mineral-rich rock is being weathered. This Andean contribution to the mainstem also is seen in the higher fractions of C, N, and P in the particulate phase and the generally greater total concentrations of all elements. The lower amounts of almost all constituents in the tributaries reflect increased influences of black- and clearwater rivers that drain weathered ion-poor basins. Due to settling, particulate phase concentrations decrease even further in quiescent waters on the floodplain. Carbonate alkalinity, however, is a conservative property in the lowland Amazon system (Devol et al. 1987) and remains relatively concentrated. This persistence indicates that the fraction of mainstem water stored on the floodplain is large relative to local contributions from black- and clear water streams.

Downstream distributions of suspended particulate material and associated bioactive constituents are shown in Figs. 15.4, 15.5 and 15.6, which compare falling and rising water distributions. These distributions are subdivided into coarse and fine-size fractions, where coarse fraction is that material that was retained on a 65 µm mesh sieve and the fine fraction is that which passed through the sieve but was captured on a 0.5 µm filter. The rising and falling portions of the hydrograph are characterized by distinctly different suspended sediment distributions. During falling water, concentrations of both fine suspended sediment (FSS, 0.5-65 µm) and coarse suspended sediment (CSS, > 65 µm) are relatively uniform throughout the mainstem. FSS varies between about 100 and 200 mg l⁻¹, while CSS is about 25% as abundant. During rising water, however, concentrations of both particle size fractions are higher and generally decrease downstream. At the upstream stations, FSS and CSS concentrations are nearly twice as high as during low water. CSS concentrations decrease proportionally more than FSS concentrations and actually fall below their corresponding falling water values at the downstream end of the reach.

The previous distribution patterns reflect variations in both sources and transport of particulate materials during different stages of the hydrograph. To some extent, FSS and CSS concentrations simply reflect water sources, because a greater fraction of water flowing through the lower Amazon during rising water is derived from turbid Andean tributaries (Devol et al. 1995). Physical processes, however, modulate this pulsed input by differential particle storage and mobilization within the mainstem. The power of a river to suspend transport sediments increases with turbulent energy, and hence with river surface slope (Richards 1982). The surface slope of the Amazon mainstem is greater during rising versus falling water periods (Devol et al. 1995), creating higher particle concentrations and transport at this time (Dunne et al. 1996).

In most cases, distributions of particulate bioactive elements within the mainstem correspond directly with changing abundances of particles in the two size fractions. This relationship indicates that most particulate species bioactive elements are closely associated with mineral particles whose compositions are relatively uniform throughout the hydrograph (Keil et al. 1997, Richey et al. 1993). Thus, fine particulate organic carbon (PPOC) concentrations vary upstream from about 200 µM (falling water) to 400 µM (rising water). Coarse particulate organic carbon (CPOC) concentrations reach about 60 µM (falling water) and 120 mM (rising water) in the upper half of the reach. During rising water there is a pronounced decrease to values as low as 10 µM at the downstream end. Distributions of fine and coarse particulate nitrogen parallel those of carbon, both between rising and falling water and among cruises within each period. Particulate phosphorus concentrations (PP, Fig. 15.6) follow the trends of FSS, likely because most particulate phosphorus is in the fine-size fraction.
Figure 15.4 Downstream distributions of various particulate species between Vagem Grande and Óbidos (~1800 km) in the Brazilian Amazon. Distributions for each species are given for both rising-water and falling-water periods, with the particular concentration scale applicable to both periods. Species defined as follows: FSS = fine (<65 μm) suspended sediment; CSS = coarse (>65 μm) suspended sediment; FPOC and FPON = fine particulate carbon and nitrogen, respectively, and FPON and CPON = fine and coarse particulate nitrogen, respectively. For falling water, the solid black line is CAMREX cruise 5, dotted line is cruise 8 and thick gray line is cruise 2. For rising water, the solid black line is CAMREX cruise 4, dotted line is cruise 7, and thick gray line is cruise 3 (see Richey et al. 1990). All variables are mM except FSS and CSS, which are mg l⁻¹.

Figure 15.5 Downstream distributions of dissolved species between Vagem Grande and Óbidos the Brazilian Amazon. Distributions for each species are given for both rising-water and falling-water periods, with the particular concentration scale applicable to both periods. ALK = alkalinity, pCO₂ = dissolved CO₂ gas, O₂ = dissolved oxygen, PO₄ = phosphate ion, DOC = dissolved organic carbon and NO₃ = nitrate ion. Solid dashed and thick gray lines are as defined in Fig. 15.4. All units are μM except alkalinity, which is μeq l⁻¹.
Covariations among concentrations of suspended sediment, POC, PN, and total particulate phosphorus suggest that the mechanisms controlling their downstream distributions are closely linked. Indeed, plots of particulate carbon and nitrogen for the different fractions (including the major tributaries) all show a clear dependence on suspended sediment concentration (Fig. 15.7). However, there are differences between C and N and P. Phosphorus shows the strongest relationship with an intercept of zero P at zero FSS. In contrast, both the C and N regressions have significant positive intercepts (C and N are present at zero FSS). Although this difference might be due to a small component of organic debris that is not sediment associated, it is more likely a result of the way the organic matter is associated with the sediments. Keil et al. (1997) have shown that much of the particulate organic matter in the Amazon mainstem exists in association with mineral grains and is thus a fraction of the total surface area of suspended sediment particles (Fig. 15.8). Consequently, low overall FSS concentrations in more quiescent rivers may correspond to smaller remnant particles with proportionately more surface area than an equivalent mass of larger particles. This relationship would generate downward curvature to the FPOC v. FSS relationship, thereby causing a higher intercept on the carbon axis.

As has been noted previously for other rivers (Meybeck 1982), weight % total POC decreases sharply with TSS concentration in the Amazon River system (Fig. 15.9). Although all plots of this form (A/B versus B) have a boomerang shape (Berges 1997), Amazon basin waters have only about half the carbon content per unit weight compared to the rivers in the Meybeck compilation (noted by a line in Fig. 15.9). One reason for this offset may be that the Amazon samples are depth-integrated composites (Richey et al. 1986), as opposed to more conventional surface grab samples of the type largely compiled by Meybeck. Because larger particles are concentrated

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**Figure 15.6** Downstream distributions of total particulate phosphorus (PP) between Vargem Grande and Óbidos in the Brazilian Amazon. Distributions are given for both rising- and falling-water periods. Solid dashed and thick gray lines are as defined in Fig. 15.4. All concentrations are μM.

**Figure 15.7** Fine (< 65 μm) and coarse (> 65 μm) particulate organic carbon (POC, top), particulate organic nitrogen (PON, middle), and particulate phosphorus (PP, bottom) versus their respective fine or coarse sediment concentration. The symbol key in the lower panel applies to the entire figure.
lower in the river channel (Meade et al. 1985) and typically are poorer in organic carbon than fine particles (Hedges et al. 1994, Keil et al. 1997), depth-integrated samples will tend to exhibit lower percentages of organic carbon.

Although there is a good correlation between POC and PN for the entire data suite, the fine and coarse fractions have distinctly different relationships (Fig. 15.10). The slopes of the two regression lines correspond to atomic N:C ratios of 0.093 (correlation coefficient = 0.96, n = 165) for the fine fraction and 0.037 (correlation coefficient = 0.84, n = 133) for the coarse fraction (see also Hedges et al. 1986a, 1994). Neither regression has a statistically significant intercept, indicating that PN is primarily organic rather than inorganic. Dissolved organic matter isolated by ultrafiltration (UDOM) has a N:C ratio of 0.028 (Hedges et al. 1994), and hence is more nitrogen depleted than organic matter in either particulate fraction. Phosphorus shows no relationship with organic carbon. The good relationship between C and N within the individual coarse and fine fractions indicates that their compositions are internally uniform throughout the lower mainstem. The lack of a corresponding relationship for particulate phosphorus indicates that the phosphorus fraction is primarily inorganic (Berner and Rao 1994, Devol et al. 1991, Devol et al. 1995).

The downstream distributions of the dissolved species of the bioactive elements are distinctly different from those of the particulate forms (see Figs. 15.4 and 15.5). Alkalinity is high in the upper mainstem and decreases continuously downstream regardless of flood stage, although the decrease is greater for falling versus rising water periods. This trend reflects the high percentage of Andean white water upstream and continuous dilution downstream by lower ionic strength clear and blackwater tributaries (Stallard 1980, Gibbs 1972). In contrast, CO₂ generally increases during falling water and remains relatively constant during rising water. The mainstem Amazon is supersaturated in CO₂ gas (150–250 μM) by more than an order of magnitude (atmospheric equilibrium CO₂ concentrations ∼10 μM). Dissolved oxygen concentrations are the mirror image of the CO₂ distributions. During falling water, O₂ concentrations decrease downstream. During rising water they are constant, with concentrations below atmospheric equilibrium (∼250 μM) at all times. Patterns for dissolved nitrate and phosphate are similar, with downstream decreases during falling water and relatively constant concentrations during rising water.

Three processes primarily control the forms and fluxes of particulate and dissolved materials in the Amazon mainstem: input, mixing, and within-reach processing. With respect to the data presented, the CAMREX program has taken the upstream input to the Brazilian Amazon as the measurements made at Vargem Grande (Fig. 15.1). With the notable exception of the Rio Madeira, all the lower tributaries are more dilute in most chemical species than the upstream input. Consequently, the downstream decreases seen in most variables are due primarily to mixing of Andean white water with dilute, less turbid lowland water (Gibbs 1972, Richey and Victoria 1993, 1992).
Stallard and Edmond 1983). However, other processes must come into play. For example, distributions of most particulate components (and dissolved nitrate and oxygen) are relatively uniform during falling water. This constancy demonstrates the importance of physical processes, such as particle resuspension and in-channel chemical reactions.

While it is possible to see seasonal signals in the mainstem data, e.g. rising versus falling water trends, a clearer seasonal picture is available from time series data (Fig. 15.11) obtained at the Marchanteria station (Fig. 15.1) ~50 km downstream of Manacapuru (Devol et al. 1995). At this location the rising stage of the hydrograph extends from about the beginning of November through mid-June, after which the river falls through October. At this site near the midpoint of the Brazilian Amazon, water discharge varies from about 150,000 m³s⁻¹ at high water to about 70,000 m³s⁻¹ at low water. Among the dissolved chemical species, oxygen, carbon dioxide and nitrate all show seasonal patterns that are either directly or inversely related to discharge. Dissolved phosphorous is the only bioactive element that does not show this pattern. Concentrations of particulate nitrogen, carbon and phosphorus are directly proportional to total suspended sediment (see Fig. 15.7). Alkalinity has a distribution intermediate between other particulate and dissolved constituents.

To understand the mechanisms governing the seasonal cycles of bioactive elements it is helpful to know the geographic sources of mainstem water as a function of time. Devol et al. (1995) used water discharge data (from the Brazilian Departamento Nacional de Águas e Energia Eletrica) to calculate the fractions of water in the

Figure 15.11 Average discharge (Q) and 'composite hydrographs' for fine (< 65 µm) suspended sediment (FSS), coarse (< 65 µm) suspended sediment (CSS), dissolved oxygen (O₂) fine particulate organic matter (FPOM), coarse particulate organic matter (CPOM), free dissolved CO₂ gas (pCO₂), alkalinity (Alk), phosphate, nitrate, and respiration (resp) at the Marchanteria time series station. The composite hydrographs were constructed from the time series (~10 year) data by plotting all data for a given variable by day and month as though they were all collected during a single year. The mean trend is given by the solid line and the standard deviation around that mean is the dashed line. The lower right graph shows the seasonal variation in fraction of the total mainstem discharged at Marchanteria derived from Andean drainages, major tributaries, and local lowland drainages throughout the year (redrawn from Devol et al. 1995).
The relationship between alkalinity and FSS concentration and Andean source waters was expected because >80% of suspended materials and dissolved solids in transport in the Amazon are derived from Andean regions (Gibbs 1972, Stallard 1980, Meade et al. 1985). Although the Andes are also the dominant source of CSS, its seasonal cycle is tied more to the river surface slope than the percent Andean water. In fact, the seasonal pattern of river slope has a nearly identical shape to CSS concentration (Devol et al. 1995). Deposition occurs during periods of low slope (low turbulence), whereas resuspension predominates during high slope (Meade et al. 1985). This changing balance would also explain the relationships between coarse particulate carbon and nitrogen and river slope. The corresponding relationship between fine particulate carbon and nitrogen and river slope is not so clear. Although there was a partial regression association with the percent Andean water, the primary regression parameter was river slope. This pattern also may result from deposition of organic poor larger particles during periods of low slope, and resuspension at high river surface slope.

The seasonal distributions of $O_2$ and $CO_2$ are related to respiration rate and gas exchange across the river surface. In situ photosynthesis within the turbid mainstem is virtually zero (Wissmar et al. 1981, Richey et al. 1990). Both Quay et al. (1992) and Devol et al. (1987) suggested that the Amazon mainstem is in quasi steady state with respect to dissolved $O_2$ and $CO_2$. If the respiration rate per unit volume is approximately constant, as it appears to be at the time series site (Fig. 15.11), then the total respiratory consumption of oxygen in the water column is almost exactly balanced by invasion of $O_2$ across the air-water interface. Consequently, as areal respiration increases with increasing river depth, oxygen concentration is drawn down and the saturation deficit (and the gas-exchange rate) increases until the two processes balance. Thus, the seasonal cycle of dissolved oxygen is driven primarily by river depth. Devol et al. (1995) used the time series data to test the quasi steady state hypothesis in a model where change in oxygen concentration with time was equal to the integrated respiration rate plus air-water-gas exchange and a residual term (d$O_2$/dt = respiration + gas exchange + residual). The model was then solved numerically, given the initial condition that dissolved $O_2$ was equal to the observed value during early January, respiration rate was 0.5 µmol h⁻¹, and the residual was zero (Fig. 15.12). The best fit to the data was obtained with a gas exchange boundary layer of 78 µm, a realistic value for a turbulent river. The model clearly reproduced the shape and timing of the observed distributions, but was only able to produce about 60% of the amplitude. The remaining variation is the residual term and could be due to seasonal fluctuations in respiration, gas exchange across the river surface or lateral exchange with the floodplain (Devol et al. 1995). Lateral exchange with the floodplain seems likely and also would help explain seasonal $NO_3$ distributions. Further evidence for mainstem floodplain exchange is seen in the stable carbon isotope data presented by Quay et al. (1992). They show that $^{13}C$ depleted FPOC of Andean origin is gradually replaced with more $^{13}C$-enriched material as the river flows across Brazil to the Atlantic Ocean. PO₄ concentrations exhibited little seasonality possibly due to buffering by sorption reactions (Berner and Rao 1994, Froelich 1988, Fox 1991).

These data suggest that the cycling of biogeochemically important elements in the Amazon mainstem is influenced by three primary factors: source, physical processing, and biogeochemical reaction (Fig. 15.13). The ultimate source for most of the material in transport in the Amazon is the Andes. Consequently, as distance from the Andes increases, concentrations of most constituents decrease due to dilution by sediment- and ion-poor lowland tributaries. Superimposed on the source imprint, however, are the effects of physical and biochemical alteration. Particulate materials undergo a series of physical deposition-remineralization cycles as they move downstream, age, and undergo chemical alteration (see also next section). DOM enters the river from the adjacent floodplain and contributes significantly to the total organic carbon pool (Richey and Victoria 1996). While in the river, the different forms of carbon are subject to oxidation and

Figure 15.12 Oxygen concentration versus time at Marchanteria. The solid line is the solution to the numerical model discussed in the text, while the filled circles are the time series average data from Fig. 15.5 (redrawn from Devol et al. 1995).
modification. Carbon-driven respiration consumes dissolved oxygen from the river and produces CO₂ and NO₃. Consumption of O₂ and the production of CO₂ sets up concentration gradients across the air-river interface that drive gas exchange. In the mainstem it appears that gas exchange is counter-balanced by in situ respiration such that the river is in quasi steady state with respect to dissolved O₂ and CO₂. The lowland mainstem contains virtually no mineral carbonates, thus at typical pH values (6.4–7.2) nearly all of the titration alkalinity occurs as bicarbonate. Thus, it is the relative concentrations of dissolved CO₂ gas and alkalinity that pose the pH of the mainstem, which is highly sensitive to respiratory CO₂ injection. Respiration also liberates organic N and P. Remineralized nitrogen is quickly nitrified to nitrate, which produces a NO₃ flux at Óbidos that is about 30% greater than the accumulated upstream inputs (Bichey and Victoria 1996). To gain further insight into the nature of the physical and chemical control one can examine Amazon mainstem biogeochemistry as reflected by organic constituents.

![Figure 15.13 Schematic representation of processes affecting the cycling of biogeochemically important elements in the Amazon River. The ultimate source of most particulates is the Andes mountains. Mineral material and fine particulate carbon are transported downstream but are deposited and eroded from local floodplains many times before being discharged to the ocean. Coarse particulate material (CPOM) enters and dissolved organic matter (DOM) enters from the floodplain. Within the river some fraction of these carbon sources are respired consuming oxygen and producing carbon dioxide. A byproduct of the organic matter oxidation is nitrate. The dissolved oxygen and carbon dioxide levels in the river come to quasi steady state concentrations that are maintained by gas exchange with the atmosphere.](image)

![Figure 15.14 Ratio of fine particulate organic carbon (FPOC) to dissolved organic carbon (DOC) versus fine suspended sediment (FSS). Capital letters denote the mainstem stations at Óbidos (O), Manacapuru (M), and Vargem Grande (V) and lowercase letters are tributaries: Negro (n), Madeira (m), Jurua (j), Japurà (g), Purús (p), and Içá (l).](image)

Amazon Biogeochemistry from an Organic Perspective

The isotopic, elemental, and molecular composition of organic matter carried by the Amazon River provide a continuous recording of the sources and reactions of biogenic matter in the drainage basin. Although only a tiny fraction of the organic recording flowing through the Amazon system has as yet been viewed, it is clear that the data stream is extremely detailed and provides information complementary to that obtained from nutrients, gases, and other inorganic substances. The observed organic compositions indicate that fine and coarse particulate organic matter (FPOC and CPOM) have contrasting histories and dynamics throughout the Brazilian mainstem. In contrast, organic compositions within individual size classes are relatively uniform throughout different seasons and stages of the hydrograph (Hedges et al. 1986a, 1994). These patterns are consistent with a model in which organic matter is progressively degraded to smaller units, which upon becoming submicron in size distribute selectively between water and the surfaces of minerals. The interplay of microbial degradation and dynamic partitioning between dissolved and particulate phases modulates the forms, compositions and reactions of organic substances in the Amazon River and sets the stage for their fates following discharge into the ocean (Keil et al. 1997).

**Forms**

The amount of organic matter carried in particulate form by the Amazon depends largely on concentrations of total suspended particles (Fig. 15.7). The partitioning of riverine organic matter between fine particulate and dissolved forms as a function of fine suspended solids is illustrated in Fig. 15.14. The direct relationship of FPOC/DOC
with FSS (by far the predominant particle form) indicates that an increasing fraction of transported organic matter occurs in fine particles as the overall concentration of suspended fine solids increases. There are at least two possible explanations for this relationship. One is that FPM occur as discrete organic particles whose concentrations vary in proportion to the total amount of physically separate mineral particles in suspension. This parallel relationship, however, would have to hold over a large range of hydrodynamic conditions and for discrete organic and mineral particles of sharply contrasting origins and densities. Such close coupling is not the case for CPOM, which includes a component of discrete plant debris that is concentrated versus sand when water velocities drop in the mainstem (Richey et al. 1990).

A second possibility is that the organic matter in the 0.5-63 μm size range is physically associated with minerals, so that a direct covariation of FPM with FSS is “locked in.” This relationship would explain the remarkably uniform %OC within the size-fraction (1.2 ± 0.2%, n = 50), versus coarse suspended solids (1.0 ± 0.5%), throughout the mainstem and year. Keil et al. (1997) have recently found that the %OC of size fractions of fine suspended solids from throughout the lower Amazon mainstem vary directly with the surface area (SA) of the component mineral particles at a slope in the range of 0.5-1.0 mg OC/m² (Fig. 15.8). Such a direct OC/SA relationship is the hallmark of organic matter associated with mineral surfaces (Mayer 1994a,b). The observed organic concentration of 0.5-1.0 mg OC/m² (Fig. 15.8) is typical of mineral particles suspended in many rivers (Keil et al. 1997) and coastal marine sediments and may correspond to an environmentally stable loading (Mayer 1994a,b, Keil et al. 1994). Sorption of organic molecules from natural waters onto mineral surfaces might also contribute toward the observation that the FPOC/FSS relationship for Amazon system rivers (Fig. 15.8) is more linear when the particle loading is normalized to ambient DOC.

Sources

Organic substances in river systems have many potential sources and are subject to extensive alteration as they pass from their origins to the lower river. Because of these challenges and the physical complexity of drainage basins, the biological and geographic provinces of riverine organic substances are best assessed on the basis of multiple characterizations at different chemical scales (nuclear, atomic, and molecular). Source inferences are most likely to be accurate when drawn from concordant information provided by multiple tracers with contrasting sensitivities to natural processes and their rates. The sources of organic materials in the Brazilian Amazon have now been assessed based on the elemental (N/C), stable carbon isotopic, radiocarbon, and major biochemical (lignin, carbohydrates, and amino acids) compositions of dissolved organic matter isolated by ultrafiltration (UDOM) and fine and coarse particulate organic matter (CPOM and FPM: Entel et al. 1986, Hedges et al. 1986a, b, 1994). These characterizations indicate that each of the three organic forms is uniform in its composition throughout the Brazilian mainstem, although each is compositionally distinct from the other two. Stable carbon isotopic compositions are among the most persistent characteristics of organic substances (Fry and Sherr 1984). The averages and ranges (± 1 standard deviation) of the delta 13C values of dissolved, coarse, and fine particulate organic matter from the Amazon mainstem (Fig. 15.15a) are in the range of -26 to -30‰, with UDOM falling toward the negative extreme (Fig. 15.15a). These values are within the delta 13C range of woods and leaves from local angiosperm trees (n = 15), all of which fix carbon by the conventional C-3 pathway (Fry and Sherr 1984). In contrast, the two C-4 grasses, Paspalum repens and Echinochloa polystachya, which account for 80-90% of the floating grasses predominating vegetation of the Amazon várzea, have a delta 13C range of 12.0 to -12.4‰. At the "light" carbon isotopic extreme are phytoplankton recovered from várzea lakes that exchange water with the mainstem during high water. These algae incorporate 13C-depleted CO₂ of respiratory origin and resultantly have delta 13C values in the range of -30 to -36‰ (Araújo-Lima et al. 1985). Based on these comparisons (Fig. 15.15a), organic matter carried by the Amazon mainstem is not derived predominantly from either floodplain grasses or plankton en-trained from surrounding lakes. Although a grass/plankton mixture cannot be ruled out isotopically, it seems unlikely that these two disparate sources would be so well balanced throughout 1800 km of the mainstem. In addition, organic matter has similar 13C compositions in the major intervening tributaries (Quay et al. 1992), including those of the blackwater type (for example, Rios Negro and Jutai) that do not have várzea C-4 grasses. Thus, stable carbon isotope measurements point toward trees, which cover about 80% of the drainage basin, as the most likely ultimate source of organic remains carried by the lower Amazon.

All three forms of organic matter in the Amazon mainstem include appreciable amounts of vascular plant remains, as indicated by substantial yields of total lignin-derived phenols per 100 mg of total organic carbon (A = 1-9 mg). This result is definitive because lignin polymers only occur in vascular plants, which are the sole source of vanillyl, syringyl, and cinnamyl phenols (Hedges and Mann 1979, Goñi and Hedges 1992). It is evident from the vertical ranges in Fig. 15.15a that coarse suspended sediments include appreciably more vascular plant remains than fine sediments and UDOM. Comparison of these ranges to those for potential plant sources indicates that neither plankton nor angiosperm woods can be the predominant organic matter source. Tree leaves appear to be a major source of all three forms of riverine organic matter, although some addition of
wood, or preferential loss of nonlignin components (for example, polysaccharides) from leaves, would be necessary to explain the higher lignin content of CPOM.

Additional resolution of these potential sources is possible via a combination of elemental and lignin phenol analysis. For example, the four potential organic matter sources vary characteristically in their average atomic C/N ratios (Fig. 15.15b). Plankton from várzea lakes are nitrogen-rich, as reflected by low C/N values of about 5-8. Microorganisms such as bacteria and fungi, are also nitrogen-rich (C/N < 10). Tree leaves and várzea grasses have much higher C/N ratios averaging about 25 and 70, respectively. Woods contain high concentrations of N-free biopolymers such as polysaccharides and hence exhibit extremely high (> 100) C/N ratios. As with the previous figure, the compositional ranges of the three forms of riverine organic matter are remarkably small within the elemental spread of the different likely sources. Again, coarse and dissolved organic matter plot near the C/N range of tree leaves. FPOM, however, is considerably more nitrogen-rich, with an average C/N near 11. This high nitrogen content could result either from the presence of a major fraction of plankton or microbial remains, or from some process that has selectively added nitrogen to fine particulate material.

The other axis of this property/property plot is the C/V lignin ratio (Fig. 15.15b), which is the weight ratio of total cinnamyl phenols to total vanillyl phenols. This tracer is based on the general relationship that cinnamyl phenols are obtained from the CuO oxidation of nonwoody plant tissues, whereas vanillyl phenols are produced by all vascular plant tissues, including woods. Phytoplankton do not produce either cinnamyl or vanillyl phenols, and hence have no effect on C/V ratios. Woods produce only trace amounts of cinnamyl phenols and have C/V ratios of effectively zero. In contrast, leaves of trees from the Amazon basin and the two floodplain grasses yield C/V ratios on the order of 0.2 and 1.3, respectively. All three forms of riverine organic matter produce measurable amounts of cinnamyl phenols (C/V > 0.1), and hence contain remains of nonwoody vascular plant tissues. The measured values are within the range of local tree leaves and over an order of magnitude lower than for floodplain grasses. Although not shown, the syringyl/vanillyl phenol ratios (S/V) of these samples are also similar to those of leaves. Thus all the measured isotopic, elemental, and lignin parameters indicate that leaves of locally predominant angiosperm trees are the major source of dissolved and particulate organic materials in the lower Amazon mainstem. Lack of evidence for input from the C-4 grasses that predominate in the várzea, point toward upland (terra firme) forests as the geographic province of these leaf remains.

Degradation

In spite of similar sources, the coarse, fine, and dissolved organic components of Amazon River water exhibit consistent biochemical patterns that reflect sharply contrasting degradation histories. For example, CPM, FPOM, and UDOM yield markedly smaller percentages (18, 15, and < 5%) of total sugars (aldoses) than their angiosperm leaf source. This sequence of depletion is accompanied by distinct compositional trends among individual sugars. One of the most outstanding differences is a consistent decrease with particle size in the relative concentration of glucose, and a corresponding increase (on a glucose-free basis) in the percent yields of the two deoxy sugars, ramifications, and fucose (Fig. 15.16a). The four potential sources of riverine organic matter yield 30-70% percent of their total aldoses as glucose. Glucose levels among total sugar mixtures from CPOM fall near the center of this range. Glucose yields from FPOM (~55%) lie at the bottom extreme of this interval and UDOM produces less glucose (20-30%) than any source. In comparison, percentage yields of deoxy sugars increase from the middle of the source field for CPOM, to the upper extreme for FPOM, to well beyond all the measured sources for UDOM. Since glucose percentages characteristically decrease, and deoxy sugar percentages increase, with advancing degradation of carbohydrate-containing materials (Cowie and Hedges 1994, Hedges et al. 1999), the pattern in Fig. 15.16a suggests that coarse, fine, and dissolved riverine organic matter become increasingly degraded. Because this size-related trend extends well beyond the limits of the measured sources in the case of UDOM, it appears to be caused by selective alteration of leaf remains. However, an unmeasured additional source rich in deoxy sugar, such as bacteria (Cowie and Hedges 1986), cannot be ruled out on the basis of these data alone.

Complementary information on the diagenetic histories of organic fractions in the Amazon mainstem can be drawn from comparisons of their lignin and amino acid compositions (Fig. 15.16b). This approach is particularly useful because all the measured sources give low yields (< 2 mole %) of the two nonprotein amino acids, b-alanine and g-aminobutyric acid, and low ratios (0.1-0.3) of vanillic acid to vanillin. As before (Fig. 15.16a), CPOM exhibits a composition that is in the range of the natural sources. FPOM and UDOM plot at increasing offsets along a trajectory that again leads away from all measured potential sources. Although not illustrated, the same size fractions from major Amazon tributaries exhibit similar patterns (Hedges 1994). The elevated nonprotein amino acid and vanillic acid yields of Amazon UDOM are characteristic of heavily degraded organic matter in soils (Hedges et al. 1986a) and deep marine sediments (Cowie and Hedges 1994, Cowie et al. 1995). In the case of these two parameters (Fig. 15.16b), there are no known examples of fresh biological materials having such high values. Thus, organic matter in the Amazon mainstem becomes increasingly degraded as the size of the associated particles becomes smaller. Amon and Benner (1996) report a similar
situation for DOC. They isolated high molecular weight DOC (\(> 1 \text{ kDa}\)) and low molecular weight DOC (\(< 1 \text{ kDa}\)) and found that the bacterial availability of high molecular weight DOC was significantly greater. The observation that the large diagenetic offsets among the size fractions are observed in the major tributaries and do not increase downstream within the mainstem, indicates that degradation occurs predominantly on the landscape or in much lower order streams.

**Partitioning**

Consistent patterns among the nitrogen contents of organic matter in the Amazon mainstem suggest that the previous source and degradation signatures are overprinted by a third process, selective fractionation of organic substances between water and solid phases within the catchment. In addition to the previously presented concentration patterns (Fig. 15.3), compositional evidence for selective partitioning occurs at three levels of nitrogenous organic materials. Elementally, the atomic N/C ratios of UDOM (0.2-0.25), CPOM (0.30-0.45) and FPOM (0.45-0.55) become progressively greater. The carbon-normalized yields of total hydrolyzable amino acids (THAA) also increase in the same order (Fig. 15.17). This sequence (FPOM > CPOM > UDOM) is seen even at the molecular level (Fig. 15.17), where nitrogen-rich basic amino acids (for example, lysine and arginine) are concentrated in FPOM at increased ratios to the sum of basic plus acidic amino acids (aspartic and glutamic acids). These patterns are consistent throughout all the measured tributaries (Hedges et al. 1994), even though higher relative yields of amino acids from FPOM than CPOM goes against the general trend that advanced degradation results in lowered biochemical concentrations (Cowie and Hedges 1994). Because all other diagenetic parameters indicate that smaller organic materials are more degraded (Fig. 15.16), the pattern in Fig. 15.17 suggests a fractionation of the degradation products of CPOM, such that nitrogenous substances are concentrated in FPOM at the expense of UDOM.

The previous patterns in nitrogen distribution may result from preferential uptake of dissolved nitrogenous organic substances from natural waters onto minerals. It is known from experiments with pure biochemicals (Theng 1979, Hedges and Hare 1987), artificial polymers (Hedges 1978, Leet 1994) and natural organic matter (Henrichs and Sugai 1993, Wang and Lee 1994) that clay minerals sorb nitrogenous organic substances in preference to nitrogen-free counterparts, as well as basic amino acids over acidic amino acids. The primary explanation for this affinity appears to be that most organic amines carry locally positive charges at the pKs of environmental waters, whereas clay minerals are negatively charged. Opposite charges lead to long-range attractive forces and tend to

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**Figure 15.17 Ratio of basic amino acids (B), (lysine and arginine) to the sum of basic plus acidic amino acids (B+A), (aspartic and glutamic acids) versus carbon-normalized yields of total hydrolyzable amino acids (THAA).**

**Figure 15.18 The \(\Delta^{14}C\) of atmospheric CO\(_2\) versus year, plotted with 1981 values for the FPOM (F), CPOM (C), and UDOM (D) from the Amazon mainstem.**

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guide and anchor nitrogen-bearing molecules to clay mineral surfaces (Hedges et al. 1994). Once tethered, large molecules can then spread onto mineral surfaces, leading to multiple-site binding that is entropy driven and difficult to overcome because all attachment must be broken simultaneously before release. This mechanism, however, applies only for organic molecules that are sufficiently small and polar to dissolve in water. Insoluble organic particles will be affected primarily by gravity, which is not charge specific.

**Dynamics**

Although only a small number of radiocarbon analyses have been published for organic materials from the Amazon mainstem (Fig. 15.18), the observed compositions reflect dynamics which are as different as the previously discussed chemical compositions. A mainstem CPOM sample collected in the early 1980s from about 400 km upstream of Manaus (Fig. 15.1) had a \(\Delta^{14}C\) (+227%) that was indistinguishable from contemporary atmospheric CO\(_2\) (Fig. 15.18). This similarity indicates material exhibiting a short (< 5 yr) cycling time between biosynthesis and degradation in the basin (Hedges et al. 1986b). FPOM from the same water had a \(\Delta^{14}C\) near +20%. This lower activity reflects a large fraction of older (prebomb) carbon, and hence a slower average turnover time in the basin. Such radiocarbon contents are often exhibited by soil organic matter, which also has C/N and lignin compositions typical of riverine FPOM (Hedges et al. 1994). One striking result of this study was that dissolved total humic substances isolated from two sites in the mainstem (Ertel et al. 1986) exhibited \(\Delta^{14}C\) values of +265 to +289% (Hedges et al. 1986b). Although dissolved humic substances (isolated by hydrophobic sorption onto a resin column)
and ultrafiltered DOM are not necessarily the same material (Hedges et al. 1994), both fractions represent more than two-thirds of Amazon DOC and are likely to have similar overall radiocarbon contents. The measured Δ14C of the two DOM samples are substantially higher than for atmospheric CO2 at the time of collection (Fig. 15.18), meaning that a major portion of mainstream DOM had to be synthesized between 1960 and 1980, when the radiocarbon content of local atmospheric CO2 was higher.

A specific "age" cannot be assigned to these samples. However, division of the maximal time since photosynthesis (~50 years), by the minimal fraction of radiocarbon that could have been fixed in this time (for example, 25% divided by the highest possible 14C input at +750‰), yields a ratio of ~30/1/3, or about 100 years (Hedges et al. 1986b). This is the maximal estimated residence time of dissolved organic matter in the Amazon basin prior to export by the river. Much shorter (decadal) lags between photosynthetic uptake of DOM carbon and its discharge to the ocean are more likely. Even though CPOM, DOM, and FPOM from the same litter of mainstream water all appear to share a predominant leaf source, their average residence times between formation and export are dramatically different. The presence of contemporary CPOM indicates the potential for rapid organic matter export with minimal attending degradation. Since the time required to transport water directly down the mainstream into the ocean is on the order of a month, the older carbon in the FPOM and UDOM fractions must age somewhere on land, or in pooled groundwaters. Storage may also provide time for the extensive degradation evident from the compositions of these smaller components. The mean residence times and extents of degradation of organic matter forms in the Amazon basin, however, are not always strictly parallel. For example, FPOM moves through the basin more slowly than UDOM, and yet is less degraded.

Model

One challenge for formulating a conceptual model for organic matter processing in the lower Amazon is to explain how leaf-derived remains of contrasting size from the basin might exhibit such consistent differences in their compositions and rates of export. The model must also explain how nitrogenous organic matter, which is often considered to be relatively reactive, might be concentrated in the "oldest" FPOM fraction, possibly at the expense of a more degraded, but faster moving, dissolved fraction. Because the Amazon mainstream discharges precipitation too fast to explain the long residence times of the fine and dissolved organic materials it carries, the mechanism responsible for the observed dynamics (and presumably the corresponding compositions) must temporary storage at upstream sites within the basin.

Our current attempt to explain how the previously discussed patterns might be generated is illustrated in Fig. 15.19 (see also Hedges et al. 1986a, 1994). This hypothetical scenario involves leaves from the upland forest as the predominant organic matter source. Although clearly an oversimplification, this starting point is consistent with the previously discussed compositional information and the observation that the Amazon basin is 80% covered with hardwood forest where leaves constitute a major fraction of long-term productivity. This assumption also aligns with the lack of evidence for a strong influence of varzea vegetation. Upon falling to the forest floor, tree leaves are subject to rapid and extensive degradation. Advancing breakdown of leaves (and woods) by animals and microorganisms is attended by stepwise reduction in the size of the tissue remains, and an increase in their extent of chemical alteration, thereby imprinting the diagenetic relationships seen throughout the river (Fig. 15.8). Although parallel and 99% complete overall (Richey et al. 1990), the processes of physical and biochemical breakdown are not necessarily uniform or stepwise on all scales.

A scheme for selective storage and transport of surviving organic substances is now needed to carry the previously imprinted degradation signal to the river and impose the additional dynamic and nitrogen signatures. The process we envision involves selective transport based on the size and nitrogen content of the degradation products. Being physically intact at the micron to millimeter scale, CPOM is the most likely of the size fractions to retain the biochemical composition of its parent plant tissues. Even this fraction, however, has suffered extensive polysaccharide loss. Since organic particles in the sand-size range are too large to infiltrate the soil, they must be transported by throughfall, wind, or sloughwash into the river system. Because the half-life of physically intact leaf tissue is short in wet tropical settings, only relatively fresh debris will be available for export to streams. More complete degradation of vascular plant remains to dissolved intermediates is the rule, because this is the only pathway to uptake through the cell walls of microorganisms. Since respiration is the fate of 99% of the organic production in the Amazon basin, at least that fraction of all biomass must at one time or another become

Figure 15.19 A conceptual model of organic matter processing in the Amazon basin.
dissolved. The possible fates of degradation byproducts dissolved by leaching or microbial breakdown of forest litter are more varied than for coarse debris because DOM can percolate into the soil and interact with minerals. Many nitrogen-rich organic molecules are preferentially sorbed onto minerals and will be preferentially retained in soils until mobilized into streams by colloid infiltration (Kaplan et al. 1993) or erosion (Hedges et al. 1994). In contrast, highly soluble organic substances with neutral or net negative charges should pass rapidly through the soil (if not degraded) via groundwater and into local streams and rivers. Supporting this "regional chromatography" model is growing evidence that organic substances sorbed to soil and sedimentary minerals are physically protected from microbial degradation (Nelson et al. 1993, Keil et al. 1994). Such shielding would greatly improve the odds that nitrogenous organic matter might persist unusually long in association with soil minerals on the landscape and after erosion into streams and rivers. The elevated concentration of amino acids in the older FPM fraction might be thus explained. The direct relationship of organic carbon concentration with surface area within fine particulate material suspended in the lower mainstem (Fig. 15-3) is equivalent to 10 large (>2000 molecular weight) organic molecules from every square centimeter in the entire drainage basin. Given that every molecule of this size itself carries thousands of "bites" of structural and isotopic data, the immense wealth of environmental information provided by the river remains almost completely untapped.

Conclusions

The emerging picture of the Amazon is an enigmatic one of a metabolically active mainstem transporting predominantly refractory organic materials (Benner et al. 1995, Amon and Benner 1996). The studied reach of the Amazon mainstem (Fig. 15.1) receives on average about 26 Tg yr\(^{-1}\) of DOC and 13 Tg yr\(^{-1}\) of total POC from its tributaries and varzea. The corresponding outputs at Óbidos are 22 Tg yr\(^{-1}\) for DOC and 12.5 Tg yr\(^{-1}\) for total POC. Independently measured rates of respiration and CO\(_2\) evasion in the Brazilian reach are both order of 18 Tg yr\(^{-1}\) (Richey et al. 1990), suggesting the lower Amazon mainstem is in quasi steady state. The observed respiration rates of 1.0–0.5 \(\mu\)mol C h\(^{-1}\) (Benner et al. 1995, Devol et al. 1995) are sufficient if unaltered to completely oxidize all transported organic matter within a period of 25–50 days, which is shorter than the mean water travel time through the ~1800 km reach. Corresponding rates on in situ organic nitrogen oxidation are sufficient to generate a nitrate flux past Óbidos that is 30% greater than the sum of all the tributary and varzea inputs (Richey and Victoria 1996). Given that most DOM and DOM in transport appears relatively refractory (Hedges et al. 1986a, 1994), the half-life of the small organic fraction that is reactive must be much shorter, on the order of hours to a few days. This model of a small pool of highly reactive substrate is in agreement with experimental evidence that bacteria in the river are limited by low concentrations of oxidizable organic carbon (Benner et al. 1995).

Such fast cycling substrates must either come from a nearby source on the floodplain, or express a much greater reactivity within the river than during transport to its waters. One proximate source of potentially reactive organic matter is the C4 grasses that occupy much of the varzea. Based on the \(^{13}\)C-rich composition of CO\(_2\) evading the lower mainstem, Quay et al. (1992) have calculated that as much as 40% of the respired carbon may be derived from C4 varzea grasses, which compose a minor (<10%) component of the total organic carbon in transit (Hedges et al. 1986a, 1994). Another potential source of labile substrates may groundwaters directly entering the mainstem. This pathway is indicated for methane, which must come from a reducing subenvironment outside the river and expresses strong concentration gradients from the banks toward the center of the mainstem (Bartlett et al. 1990). Suboxic groundwaters would be a particularly effective route of introduction of methane, ammonia, and low molecular weight organic acids whose reaction rates might be sufficiently slow in the absence of dissolved \(O_2\) to allow large-scale storage and longer distance transport.

The contrasting distributions and dynamics of the different types of biogenic materials borne by the Amazon mainstem reflect a large range of sensitivities to different processes at work within the basin and their anthropogenic perturbations. For example, dissolved \(O_2\) and \(CO_2\) maintain a delicate balance between rapid rates of substrate input from the landscape, respiration within the turbulent mainstem, and gas exchange across the river surface. Because these small pools of dissolved gases and labile organic molecules turnover on the scale of hours to days, they reflect predominately active processes occurring locally. Such chemical species could therefore indicate perturbations such as loading with sewerage and agricultural wastes or changes in biological activity due to introduction of toxic materials. Nitrate and methane can be similarly responsive, whereas dissolved phosphate is buffered by exchange with a huge pool of mineral-bound ion and responds little if any to local changes. The amounts of suspended particulate materials are so strongly swayed by water turbulence, and hence hydrographic stage, that environmental effects of human activities such as deforestation, mining, and cultivation are difficult to sort out based concentrations.
alone. Compositions of particulate materials, especially within specific size classes, are much more uniform, establishing a background of relatively diagnostic ratios against which human alterations can be more sensitively detected. The 14C compositions of organic matter in the coarse and fine-size fractions indicate, however, that characteristic response times will vary with particle size. Coarse particle debris in the sand fraction is exported on an annual time scale—slow enough to represent major regions of the landscape, yet sufficiently rapid to denote recent activities such as forest clearing. In contrast, organic matter associated with fine particles will change in composition on a decadal to century time scale. Such cycle periods are more apate with processes related to extensive alterations in land and water usage, as well as local climate change. Dissolved organic constituents probably have the greatest diagnostic potential because of the information richness of the complex molecular blend, the spectrum of residence times represented, and the sensitivity of the chemical recording to myriad subsurface processes that are invisible to electromagnetic radiation.

Literature Cited


