

## CHAPTER 1

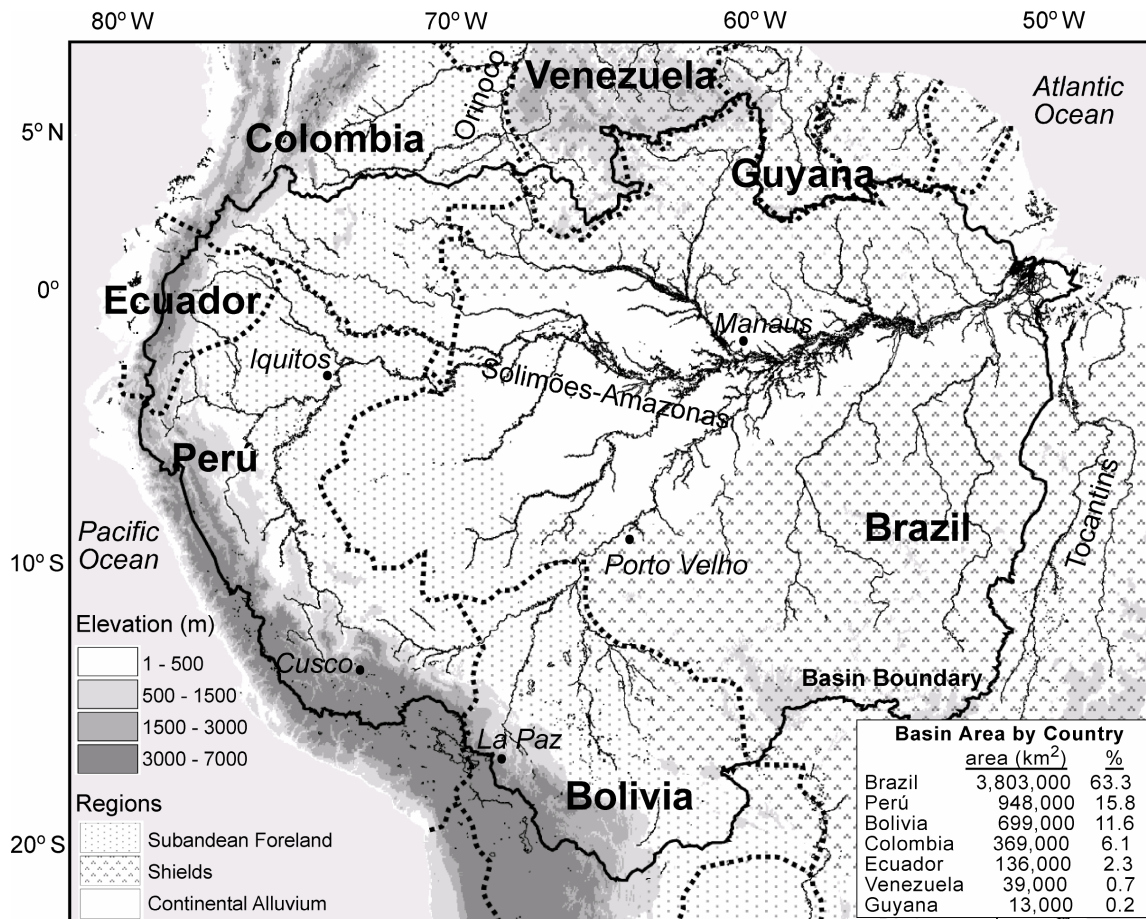
**PROCESSING OF BIOACTIVE ELEMENTS IN THE  
AMAZON RIVER SYSTEM****Emilio Mayorga & Anthony Aufdenkampe**

The Amazon basin drains a vast and heterogeneous region of northern South America, encompassing large areas of seven nations and important population centres such as Manaus, Porto Velho, Iquitos, Cusco, and La Paz (Fig. 1.1). Despite the acceleration of human impact in the form of deforestation and land-use change, mining and oil extraction, dam construction, and urbanization, larger tracts remain relatively pristine, and the main river channels remain largely unaffected by engineering (Lewis *et al.*, 1995; Richey *et al.*, 1997). The Amazon is of undeniable importance for local communities in particular, and Amazonian nations in general; but as the largest river system in the world it also plays a significant continental and global role in modulating climate, biogeochemical cycles, and terrestrial inputs to the ocean (Devol *et al.*, 1994; Meade, 1994; Devol & Hedges, 2001; Marengo & Nobre, 2001).

An understanding of biogeochemical dynamics and controls in river systems is a central requirement of any effort to rationally manage fluvial resources and minimize the impact of human activity on riverine ecosystems. The cycling of bioactive materials (oxygen, carbon, nitrogen, phosphorus, etc.) in rivers, however, is mediated by physical and biological components, such as hydrology, sediment dynamics, and bacterial metabolism. In addition, the linkages between a river and the land it drains are often complex. An integrated approach that crosses disciplinary and landscape boundaries is required to fully elucidate the biogeochemistry of a river system.

In this chapter we review and synthesize current understanding of the biogeochemistry of the Amazon River system. Our goal is to provide a conceptual framework from which watershed managers can evaluate observations, rather than summarize all available data as has been done in the extensive reviews by Guyot (1993) and Lewis *et al.* (1995). In this overview, no new data or analyses are presented nor are observations discussed in extensive detail. Rather, we provide numerous references to the many papers that do so.

We begin by briefly introducing the geography of the Amazon basin and the history of geochemical and related research on the region's rivers. We then describe the principal fractions of bioactive materials carried by rivers—their characteristics, sources and interactions—paying special attention to the role of size in fate and transport. Finally, we illustrate with examples largely from the Amazon mainstem the principal patterns of spatial and temporal variability typical of river systems and discuss how their controls can change regionally and with river scale. Through such a presentation we hope to facilitate the interpretation and use of natural riverine biogeochemical observations in tropical river systems like the Amazon, a task that is of critical importance for evaluating likely impacts of human perturbations. While we refer to relevant research by other groups, we write this chapter from our perspective as members of the CAMREX (Carbon in the AMazon River EXperiment) project, with origins in oceanography that are evident in our view of river processes.

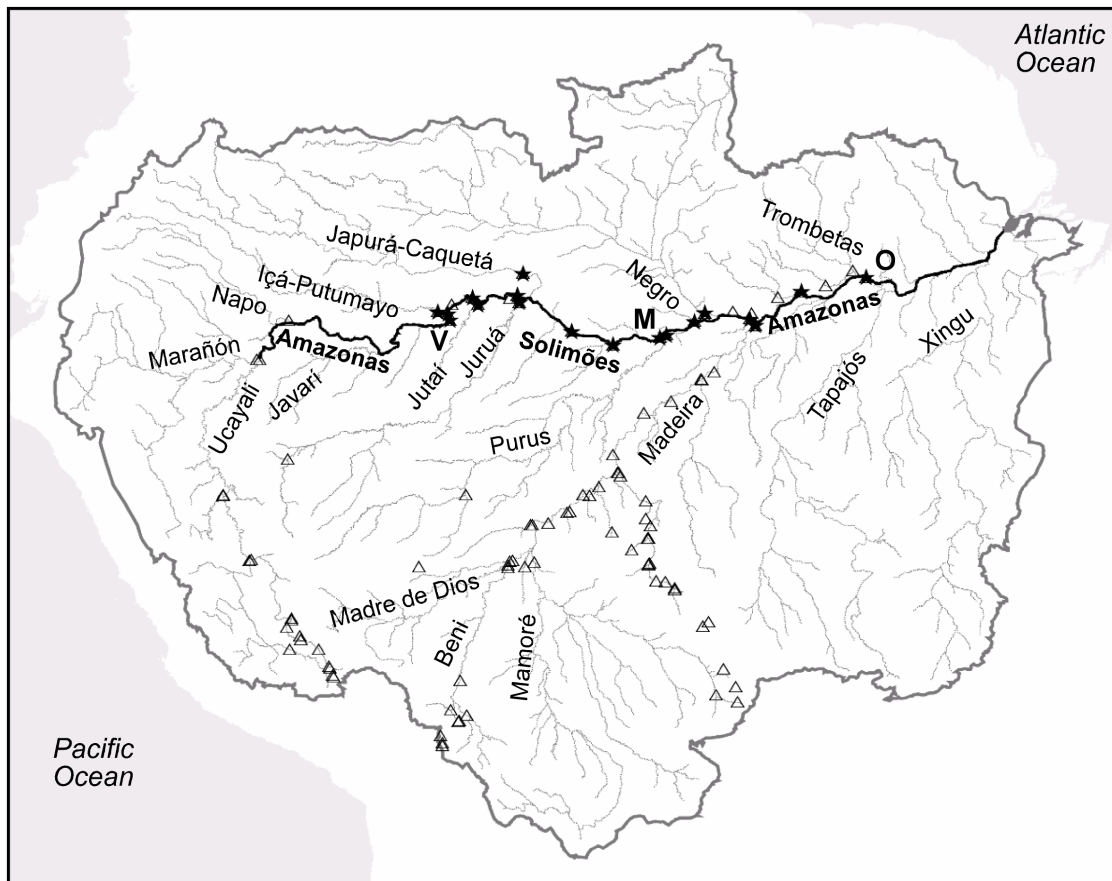


**Fig. 1.1** General physiographic features of the Amazon basin. The basin boundary is shown as a thick black line. National boundaries are shown as thick dotted lines. Major cities in the basin are included. The portion of the total basin area encompassed in each country is listed in the inset table; total basin area is 6 007 000 km<sup>2</sup>. Also shown are elevation and the main morphostructural regions.

## GEOGRAPHICAL AND HISTORICAL PERSPECTIVES OF THE AMAZON

### The Amazon River and its basin

The Amazon basin covers a continental-scale region of approximately six million km<sup>2</sup> (not including the Tocantins basin; Figs 1.1 and 1.2). Such a large area will inevitably encompass very dissimilar environments, climates, and ecosystems. The main physiographic features of the basin and the river system have been extensively reviewed elsewhere (Sternberg, 1975; Sioli, 1984b; Lewis *et al.*, 1995), and we provide only a brief outline. The main structural elements include the Precambrian, highly weathered Guayana and Brazilian shields, the Andean mountains to the west, the Andean alluvial foreland, and a central continental alluvium or trough (Fig. 1.1). Soils in the lowlands are generally deep and highly weathered, with prominent occurrences of sandy podzols in the shields. The soils in flood plains and alluvial regions around mainstems draining the Andes originate in the cordillera and are much less weathered. The climate is generally humid, with mean annual rainfall of approximately 2000 mm. However, precipitation in some regions in the northwest and the Andean piedmont can be much larger, whereas large regions in the east, south, and the high Andes can be drier or arid. More specifically, 10–15% of the basin



**Fig. 1.2** Amazon River network and CAMREX river sampling sites. The names of the mainstem and major tributaries are shown. The Amazon mainstem (thick black line) first begins under the name of “Amazonas” at the confluence of the Uçayali and Marañón in Peru. As it enters Brazil, its name changes to “Solimões”, and becomes the “Amazonas” again after the confluence of the Rio Negro. The total length of the river is about 6500 km, from its mouth to its source in the Uçayali headwaters south of Cusco. CAMREX mainstem sampling stations are shown as solid stars, from Vargem Grande (V) to Óbidos (O). Eleven mainstem sites and the mouths of the seven major tributaries were sampled through cross-sectional composites during 12 cruises between 1982 and 1991. All other CAMREX sampling sites are shown as open triangles. The site of the Marchantaria–Manacapuru time series is labelled “M”.

receives less than 1500 mm of rainfall per year, while 6–10% receives at least 3000 mm of rainfall per year (unpublished data). The length of the dry season in particular has a large role in determining the type of vegetation that may be sustained. The lowlands are primarily covered by evergreen to semi-deciduous rainforest, but large regions have distinct savanna-like vegetation systems, often seasonally inundated in lowlying areas. River discharge generally displays strong seasonality, with changes in stage height of as much as 10 m in the Amazon mainstem driving changes in the extent of inundation within the central lowlands from 100 000 km<sup>2</sup> in November to 350 000 km<sup>2</sup> in May (Richey *et al.*, 2002). Discharge to the ocean is approximately 220 000 m<sup>3</sup> s<sup>-1</sup>.

## History of geochemical research in the Amazon

The variety of environments, massive scale of drainage areas and rivers, and relatively low levels of human impacts, has long attracted geochemical and ecological researchers to the region. Initial investigations centred on large rivers in the Brazilian Amazon, especially the Solimões–Amazonas mainstem, surrounding flood plains and major tributaries, and the

region around Manaus (Sioli, 1984b). Early observations of three types of river water based on colour (Wallace, 1853) were later developed extensively and classified by H. Sioli (Furch, 1984; Sioli, 1984a). White-water rivers have a characteristic muddy colour, relatively high concentrations of dissolved solids, and alkaline to neutral pH; their high sediment load originates in Andean or alluvial regions. Examples include the Ríos Solimões and Madeira, and other lowland rivers draining mountainous Andean regions. Black-water rivers are tea-coloured from high concentrations of dissolved organic matter (DOM), have negligible suspended sediment loads and medium transparencies, are very dilute in dissolved ions, and are usually acidic; they typically drain areas of low relief and sandy podzol soils. The Río Negro is the classic example. Finally, clear-water rivers can have high transparencies and are clear or olive-green in colour. Their dissolved load is typically low but varies across systems, and they have a wide range in pH, from acidic to alkaline, and low suspended sediment loads. Examples are the Ríos Tapajos and Xingu. The group led by H. Sioli, K. Furch, W. Junk and associates from the Max-Planck Institut für Limnologie (Plön, Germany) and the Instituto Nacional de Pesquisas da Amazônia (Manaus, Brazil) is responsible for most of the early studies on the geochemistry and ecology of rivers and flood plains in the central Amazon (reviewed in Sioli, 1984b). Others made important contributions to the characterization of inorganic and organic constituents of these rivers of the central basin (Klinge & Ohle, 1964; Williams, 1968), and Gibbs (1967) extended his surveys of river mineralogy and inorganic geochemistry from the lowlands to the Andes.

The cruises of the Research Vessel *Alpha Helix* in 1976–1977 from the Atlantic to Iquitos comprised one of the most influential initiatives in early Amazon research. These expeditions united researchers from diverse fields and nationalities, spawning a substantial number of important publications on sedimentology (Curtis *et al.*, 1979; Meade *et al.*, 1979; Nordin Jr *et al.*, 1980; Sholkovitz & Price, 1980), biogeochemistry (Fisher & Parsley, 1979; Richey *et al.*, 1980; Longinelli & Edmond, 1983; Stallard & Edmond, 1983; Cai *et al.*, 1988), and biology (Fisher, 1979; Wissmar *et al.*, 1981). The Alpha Helix project gave birth to the CAMREX research group, which has continued to unite researchers in Amazon biogeochemical research for the last 20 years. The more than 120 CAMREX publications have focused on understanding physical and biogeochemical dynamics throughout the basin using a large variety of approaches. These include studies of cross-sectionally integrated fluxes of water, sediments and bioactive elements (Meade *et al.*, 1985; Richey *et al.*, 1986; Ferreira *et al.*, 1988; Richey *et al.*, 1990); flood-plain sediment dynamics (Mertes *et al.*, 1996; Dunne *et al.*, 1998); sediment diagenesis in river bars, flood plains and deltas (Victoria *et al.*, 1989; Johnsson & Meade 1990; Martinelli *et al.*, 1993; Keil *et al.*, 1997); nutrient dynamics in rivers, flood plains and *terra firme* streams (Forsberg *et al.*, 1988; Martinelli *et al.*, 1992; McClain *et al.*, 1994; Devol *et al.*, 1995; McClain *et al.*, 1997); biogenic gas production rates and air–water exchange fluxes (Devol *et al.*, 1987; Richey *et al.*, 1988; Devol *et al.*, 1994; Richey *et al.*, 2002); biochemical tracers of organic matter (OM) sources and processes (Ertel *et al.*, 1986; Hedges *et al.*, 1986a; Hedges *et al.*, 1994; Hedges *et al.*, 2000; Aufdenkampe *et al.*, 2001); isotopic tracers of organic matter sources and cycling (Araujo-Lima *et al.*, 1986; Hedges *et al.*, 1986b; Martinelli *et al.*, 1991; Quay *et al.*, 1992; Victoria *et al.*, 1992; Forsberg *et al.*, 1993; Quay *et al.*, 1995; Brandes *et al.*, 1996); isotopic tracers of water cycling (Martinelli *et al.*, 1996); microbiological metabolism of organic matter (Benner *et al.*, 1995; Amon & Benner, 1996a,b); and remote sensing driven models of hydrology, sediment dynamics, and carbon cycling (Mertes *et al.*, 1993).

Other groups have made very substantial contributions to biogeochemical research in the Amazon basin. Several studies have focused on hydrological, nutrient and geochemical dynamics on hillslopes and in small catchments north of Manaus (Franken & Leopoldo, 1984; Brinkmann 1985; Nortcliff & Thornes, 1988; Nortcliff *et al.*, 1990; Forti & Neal

1992; Konhauser *et al.*, 1994). Others have examined the sources and mechanisms yielding high DOM concentrations in the sandy soils of the Río Negro basin (Leenheer, 1980; St John & Anderson, 1982). In the flood plains of the central Amazon, J. Melack and associates have carried out extensive biogeochemical, hydrological, and ecological studies in lakes, small catchments, and the inundated area (Lenz *et al.*, 1986; Lesack & Melack, 1996; Williams & Melack, 1997; Sippel *et al.*, 1998). Studies in other regions of the basin have been primarily focused on terrestrial, hillslope and stream processes. These include the work in the upper Río Negro at San Carlos, Venezuela (Stark & Jordan, 1978; Tiessen *et al.*, 1994); in the Caquetá basin at Araracuara, Colombia (Duivenvoorden & Lips, 1995); and in the Pachitea basin in the Andean piedmont of central Peru (Elsenbeer *et al.*, 1996). In the Peruvian Amazon a group from the University of Turku, Finland, maintained long-term studies of the relationships between geomorphology, river evolution, succession, and flood-plain mineral nutrients (Salo *et al.*, 1986; Puhakka *et al.*, 1992; Kalliola *et al.*, 1993). In the Bolivian headwaters of Río Madeira, from the 1980s the PHICAB (Programa Hidrológico y Climatológico de la Cuenca Amazónica de Bolivia) project conducted extensive research on the hydrology, sediment dynamics, and geochemistry of rivers (Guyot, 1993; Guyot & Wasson, 1994; Guyot *et al.*, 1999). This French-led project has been extended into the Brazilian Amazon, where it is currently active as HiBAm (**H**idrologia e **G**eoquímica da **B**acia **A**mazônica) (Guyot *et al.*, 1998; Mounier *et al.*, 1999; Patel *et al.*, 1999; see Chapter 2 of this book). Additional research in the Andean Amazon has been reviewed by McClain *et al.* (1995).

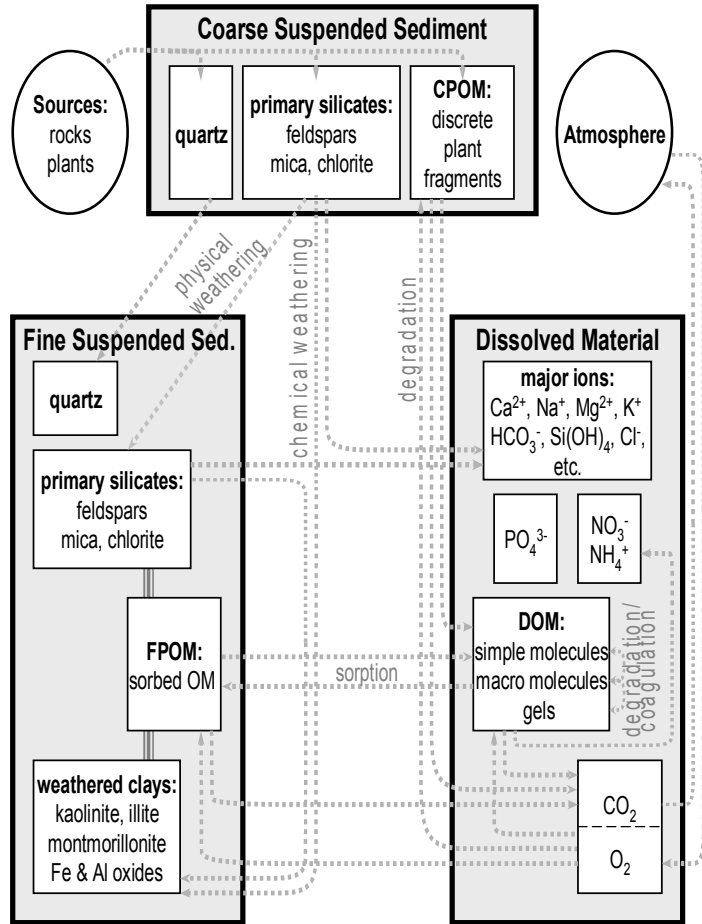
## ROLE OF SIZE ON FATE AND TRANSPORT

### Three distinct physical size classes of material transported in rivers

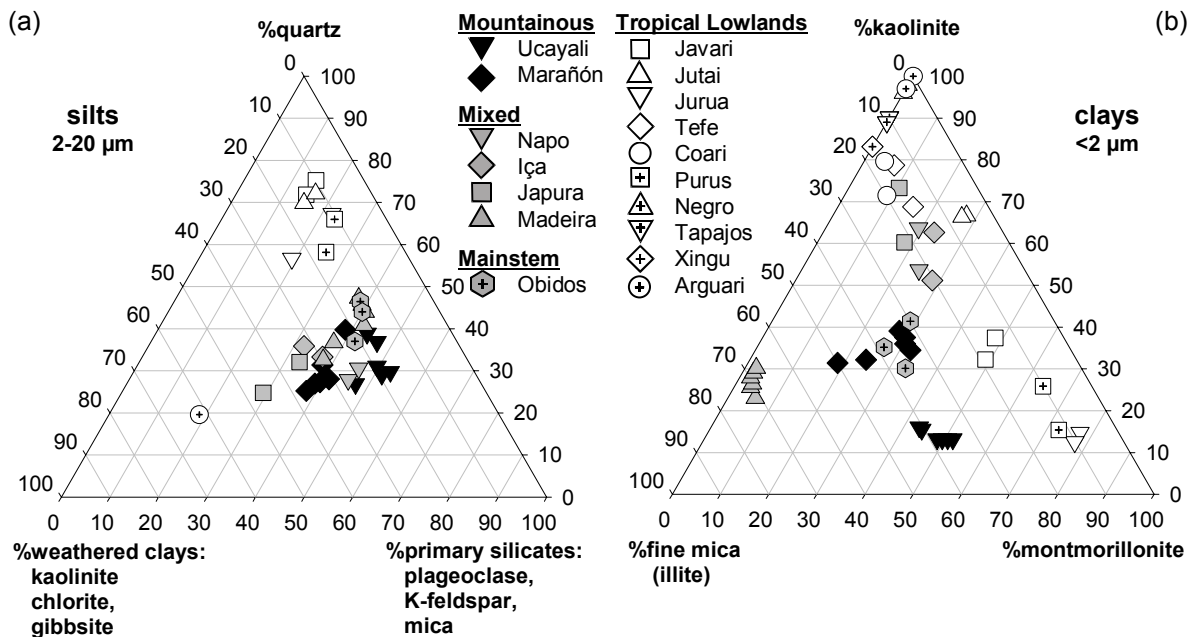
Riverine transport of bioactive elements from land to sea forms a major link in the global biogeochemical system. The diversity of matter carried in river water is extraordinary—weathered products of rocks and plants sustain all forms of living organisms. The entire continuum of material size is represented, ranging from individual molecules to boulders and trees. Early on in the study of rivers, materials in water were separated into fractions by size (Williams, 1968; Meybeck, 1982). Coarse particulate, fine particulate, and dissolved fractions were thus operationally defined using sieve pore sizes ranging from 20 to 65  $\mu\text{m}$  to separate particulate fractions, and filter pore sizes ranging from 0.1 to 1.0  $\mu\text{m}$  to isolate dissolved constituents. These exact size cutoffs often differ slightly between research groups, chosen arbitrarily and largely out of convenience. In nature the size distribution of materials across these ranges is actually quite smooth. Despite this, the three size classes—coarse, fine and dissolved—consistently exhibit very distinct transport dynamics, degradation patterns and compositional characteristics. In addition, these three fractions remain compositionally distinct despite interacting with each other on a continual basis (Figs 1.3, 1.4 and 1.5).

### Coarse particles

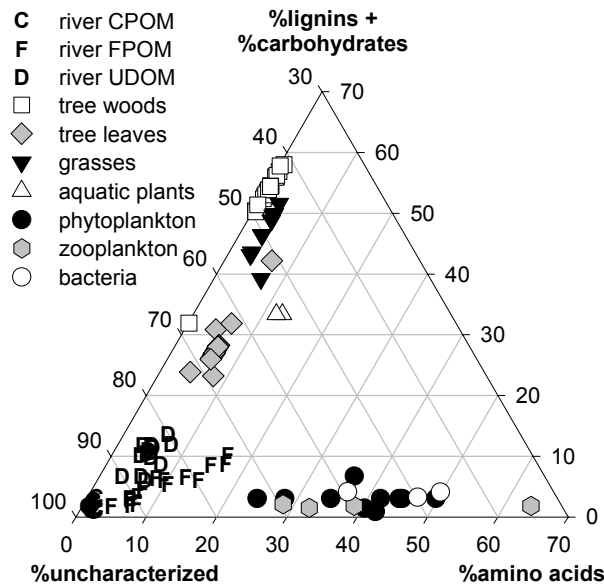
Essentially all the material transported by rivers starts out in the coarse particulate size class. Rock and decaying vegetation are physically and chemically weathered and eroded until they finally reach the river. While the coarse size class includes boulders and dead trees, most riverine studies have focused on sand sizes (defined as 63  $\mu\text{m}$ –2 mm within CAMREX).



**Fig. 1.3** Conceptual model for the composition of the three principal size fractions carried by rivers, and the processes that are responsible for continuous interactions between them. Microbial mediation of these processes is implicit for many of these arrows. Bars connecting boxes within the fine particulate fraction represent the physical associations between mineral and organic components.



**Fig. 1.4** Major mineralogical composition of (a) silt-sized sediments (2–20 μm) and (b) clay-sized sediments (<2 μm) within the Amazon basin. “Mixed” refers to river basins that drain both mountainous and lowland environments. Data from Gibbs (1967).



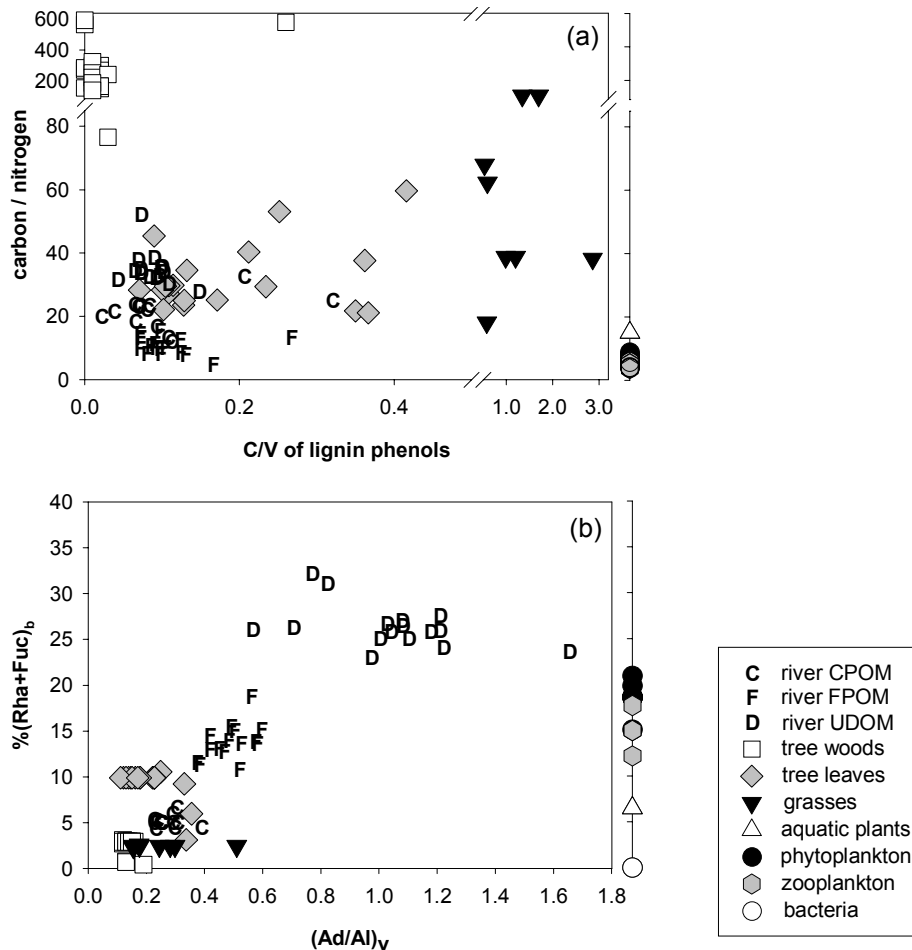
**Fig. 1.5** Major biochemical composition of coarse and fine particulate organic matter (OM) and ultrafiltered dissolved OM carried by rivers of the Amazon basin, relative to the composition of source materials. River data from Ertel *et al.* (1986), Hedges *et al.* (1986a), Hedges *et al.* (1994), Hedges *et al.* (2000) and source data from these papers and from Cowie & Hedges (1984, 1992), Goni & Hedges (1992) and unpublished data. Notice that upper and right axes terminate at 70% of the respective biochemicals, due to all samples containing at least 30% of OM not identifiable in these biochemical classes. All DOM compositions fall in the grouping at >95% uncharacterized.

Because these coarse suspended sediments (CSS) settle quickly to the streambed, suspended concentrations are strongly dependent on streamflow velocities (Meade *et al.*, 1985; Devol *et al.*, 1995) and increase substantially with depth in the river (Curtis *et al.*, 1979; Richey *et al.*, 1986). Thus CSS transport is highly episodic or seasonal, with most occurring during flood events. For instance, the mainstem of the Amazon near Manaus has depth-averaged CSS concentrations of 10–20 mg l<sup>-1</sup> during low water and 45–70 mg l<sup>-1</sup> at high water (Devol *et al.*, 1995). The bed load, or the CSS travelling very close to, or even as part of, the fluid riverbed, is estimated to be a small fraction of total coarse sediment flux in the Amazon mainstem (Dunne *et al.*, 1998) but it may be important in smaller rivers. As for all the size classes, coarse particulates consist of both inorganic mineral material and organic material derived from the remains of living organisms.

Within the Amazon basin, quartz is the dominant mineral in CSS, forming 25–75% of the total (Gibbs, 1967); other primary silicates such as feldspars, micas, and chlorite comprise the remainder at 2–25% each. These primary minerals in rivers, surrounding soils and aquifers each exhibit distinctive weathering rates and products. Thus through weathering processes, the lithology, relief and climate of a watershed together determine the composition of the finer, secondary minerals such as alumino-silicate clays and iron and aluminium oxides and the composition of major dissolved inorganic ions, such as Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and Si species (Fig. 1.3) (Stallard & Edmond, 1983, 1987). The composition of CSS as a function of a hydrograph remains unstudied, but hydrodynamic sorting of CSS components would be expected to produce spatial and temporal variations in CSS composition within a reach.

In the Amazon mainstem and other large turbid rivers, organic matter (OM) is a small but important portion of the CSS fraction, comprising only 0.6–3.3% by mass (Richey *et al.*, 1990; Devol *et al.*, 1995). However as CSS concentrations decrease in rivers, OM contributions increase to as high as 10–30% in the clearest waters (Hedges *et al.*, 1994, and unpublished data). In all cases, microscopic studies reveal that most coarse particulate organic matter (CPOM) in rivers resembles partially degraded plant fragments, often retaining visible cell structure (Keil *et al.*, 1997). CPOM is less dense than mineral grains of

the same size, hence explaining its higher contribution to CSS in river channels under low flow. Between 10 and 20% of CPOM can be identified biochemically as amino acids, carbohydrates and lignins—the primary molecular building blocks of living organisms—relative to 25–60% within biomass sources (Fig. 1.5) (Hedges *et al.*, 1986a; Hedges *et al.*, 1994; Hedges *et al.*, 2000). Biochemical source indicators, such as carbon to nitrogen ratio and the ratio of cinamyl to vanillyl lignin phenols, all show that Amazon basin CPOM is primarily derived from tree leaves (Fig. 1.6(a)) (Devol & Hedges, 2001). Several other lines of evidence, including stable carbon isotope compositions, confirm these conclusions but also show minor contributions from grasses for certain rivers (data not shown; Quay *et al.*, 1992; Victoria *et al.*, 1992). Biochemical indicators of degradation, such as the contribution of fucose and rhamnose sugars to total carbohydrates and acid to aldehyde ratios in lignin phenols, all support evidence from microscopic studies and major biochemical composition that CPOM is sparingly degraded and rather fresh (Fig. 1.6(b)). Radiocarbon analysis of CPOM and low density soil particulate organic matter confirms their recent origin (Hedges *et al.*, 1986b; Trumbore *et al.*, 1995). It is clear that CPOM is actively degrading and



**Fig. 1.6** Biochemical parameters commonly used to interpret (a) organic matter sources and (b) organic matter degradation. Riverine coarse and fine particulate OM and ultrafiltered dissolved OM are again presented relative to common source materials. In (a) the ratio of cinamyl to vanillyl lignin phenols ( $C/V$ ) clearly distinguishes between woods, leaves, grasses and all aquatic organisms (which contain no lignin and are thus plotted to the right). In (b), FPOM and UDOM are outside the range of plant sources with respect to both the acid to aldehyde ratio of lignin phenols,  $(\text{Ad}/\text{Al})_v$ , and the percent contribution of sugars rhamnose and fucose to total carbohydrates,  $\%(\text{Rha} + \text{Fuc})_b$ —two parameters that increase with increasing degradation within sediments. Data obtained from the references listed for Fig. 1.5. Average  $\%(\text{Rha} + \text{Fuc})_b$  values were used for some woods and leaves for which no measurements were made.



leaching, supplying microbes with substrate and releasing dissolved organic and inorganic compounds into the river. These rates have not been directly measured, but are likely to be quite high. Stream and river budgets suggest that CPOM continuously enters the river mostly from bank vegetation and detritus falling directly into the water (McClain *et al.*, 1997).

Coarse suspended river sediments are thus a heterogeneous mixture of sand-sized mineral grains and discrete plant fragments (Fig. 1.3). Both inorganic and organic constituents of CSS are generally fresh and supply the dissolved component (or “pool”) as they degrade. CSS deposits on the river bed and in sand bars form a relatively porous sediment buffer or “hyporheic” zone (Boulton *et al.*, 1998) that acts as a biological reactor, supplying the river with its products and forming new riverine environments that can be colonized by vegetation.

## Fine particles

Fine suspended sediments (FSS) consist of clays and silts, material between 0.45 and 63  $\mu\text{m}$  in size as defined by CAMREX. Maintained in suspension by the slightest turbulence, FSS is often referred to as the “wash load” by geomorphologists, because once introduced to a stream or river, FSS will generally not settle. Notable environments that often prevent FSS from washing directly out to sea are lakes, reservoirs, and flood plains. For instance, evidence suggests that within the Amazon—with its extensive annually flooded plains—a typical FSS particle passes through flood-plain deposits several times between the Peruvian border and the Atlantic (Martinelli *et al.*, 1993; Dunne *et al.*, 1998). Given the patterns of channel migration, each cycle of flood-plain deposition and re-suspension requires a few thousand years (Mertes *et al.*, 1996). Because FSS is mobilized by erosion events, concentrations are also a function of river discharge, although the tendency for FSS not to be re-deposited results in weaker correlations than those observed for CSS (Devol *et al.*, 1995). The mainstem of the Amazon near Manaus exhibits FSS concentrations of 70–120  $\text{mg l}^{-1}$  during low water and annual maximums of 210–340  $\text{mg l}^{-1}$  during the rising hydrograph (Devol *et al.*, 1995).

Mineralogy within the FSS fraction can be quite diverse. Silt-size grains (5–63  $\mu\text{m}$ ) often retain many of the characteristics of the CSS fraction while at the same time showing signs of being more weathered (Fig. 1.4(a)). Fine quartz is important in more weathered lowland basins whereas other primary silicate minerals dominate in rivers draining the Andes (Gibbs, 1967). Clays and oxides are aggregated with the larger minerals in important quantities. The clay-size fraction (0.45–5  $\mu\text{m}$ ) is composed mostly of phyllo alumino-silicate clay minerals, which are the weathering products of primary silicates (Figs 1.3, 1.4(b)). As can be seen in Fig. 1.4(a) and (b), mineral diversity within FSS is very large and depends on the geology (source minerals) and climate (weathering rates) of the watershed. As a result, mineralogical compositions within the Amazon are constantly evolving downstream with inputs from tributary watersheds and from weathering during temporary storage in the flood plain (Johnsson & Meade, 1990; Martinelli *et al.*, 1993). All FSS samples do have common characteristics however. This size fraction is generally high in surface area and high in cation and anion exchange capacity. As such, significant quantities of certain inorganic ions (e.g.  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$  and most metals) and organic compounds (e.g. natural organic matter, contaminants, etc.) can potentially be adsorbed to the mineral surfaces of FSS. Thus FSS actively interacts with the dissolved fraction, often acting as a buffer or reservoir for dissolved compounds (Fig. 1.3).

As with the CSS, organic matter contributes only a small fraction of FSS, generally 0.5–2.0% by weight in turbid rivers (Richey *et al.*, 1990; Devol *et al.*, 1995). Unlike CPOM

however, fine particulate organic matter (FPOM) is tightly associated with the mineral phase (Fig. 1.3). In the Amazon and other rivers of the world, generally over 90% of the FPOM cannot be physically separated from the mineral material (Keil *et al.*, 1997; Mayer *et al.*, 1998). With low-density material removed, the organic surface loadings of these sediments is consistently 0.5–1.1 mg C m<sup>-2</sup> of mineral surface area, leading in part to the conclusion that sorption of natural DOM to minerals is the primary pathway in which FPOM is formed (Mayer, 1994; Hedges & Keil, 1995). Evidence suggests however that mineral-associated organic matter does not form uniform coatings over the surfaces, but organic gel-like assemblages that cover <20% of the surfaces (Mayer, 1999; Filius *et al.*, 2000). However, sorbed organic matter affects mineral surface properties significantly by increasing cation exchange capacity and by offering hydrophobic phases into which organic contaminants (e.g. pesticides, petroleum products, etc.) and heavy metals readily sorb (Benedetti *et al.*, 1996). Biochemically, a smaller fraction of FPOM is identifiable as carbohydrates or lignins when compared to CPOM (Fig. 1.5), but often a larger fraction is identifiable as amino acids. It appears that FPOM comes largely from leaf material as does CPOM (Fig. 1.6(a)), but often falls slightly outside of the biochemical range that is possible by mixing biomass alone, as might be expected of diagenetically altered material (Devol & Hedges, 2001). Specific degradation parameters show this clearly (Fig. 1.6(b)), however riverine FPOM is still relatively fresh compared to riverine DOM or deep-sea sediments (Hedges *et al.*, 1994). This appears to be the result of physical protection from microbial attack that is offered by the intimate association of FPOM with mineral surfaces (Keil *et al.*, 1994; Baldock & Skjemstad, 2000; Kaiser & Guggenberger, 2000).

Fine suspended sediment is thus a diverse but tightly associated mixture of minerals and organic matter that interacts strongly with other size fractions (Fig. 1.3). Fine minerals are formed from the weathering of coarse minerals, and FPOM largely results from sorptive interactions with dissolved organics. However, the major characteristics of FPOM most likely form within soils prior to erosion into rivers. Mineralogical and biochemical evidence points to this conclusion (Devol & Hedges, 2001), including carbon-14 dates hundreds to thousands of years old (Hedges *et al.*, 1986b, and unpublished data). However, whereas high relief source basins are the ultimate source for >90% of river-borne FSS (Meade, 1994), stable carbon isotopes show that at Óbidos >60% of the associated FPOM originates in the lowlands (Quay *et al.*, 1992; Hedges *et al.*, 2000). With such high levels of surface exchange and activity, deposited FSS forms highly fertile soils and sediments, often far from the river channel.

## Dissolved matter

Just as for the particulate size classes, the dissolved fraction (<0.45 µm as defined by CAMREX) is composed of matter spanning a continuum of sizes, from truly dissolved individual molecules to colloidal minerals and organic gels. The distinguishing physical feature of material in the <0.45 µm size class is that it will stay in suspension indefinitely due to Brownian motion alone. Thus, the transport of material in the dissolved pool is determined by the advection and mixing of the waters that carry it. However, fluxes are not only determined by hydrology but also by processes that transfer material in and out of the dissolved phase, such as degradation, adsorption and coagulation. Perhaps the most important characteristic of dissolved material is that it has the potential to be directly bioavailable. Microbial organisms, plant roots, and many animal tissues will transport dissolved molecules across cellular membranes, both passively and actively. Likewise, contaminants exhibit their highest toxicity when in the dissolved phase. The only way to

measure the mass of the entire dissolved pool is by evaporation, however it is much more typical to measure the concentration of individual compounds or compound classes.

The inorganic material within the dissolved fraction includes all major ions, nutrients, dissolved gases, and colloidal minerals. The major inorganic ion composition of the Amazon mainstem is very similar to the world river average, dominated by  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Si}(\text{OH})_4 + \text{SiO}(\text{OH})_3^-$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  in order of importance (Stallard & Edmond, 1983). Diversity within the Amazon basin parallels the pattern of other rivers of the world, with a wide range of ionic compositions and concentrations controlled largely by geology and weathering regime with minor inputs from precipitation (Stallard & Edmond, 1983, 1987). Once within the river, these ions mix conservatively, such that conductivity and alkalinity serve as excellent tracers for water sources (Stallard & Edmond, 1983; Devol *et al.*, 1995). Of the bioactive compounds, phosphate shows the least systematic variability, generally 0.4–2.0  $\mu\text{M}$  in turbid rivers as a result of buffering with larger mineral-bound reservoirs in the FSS (Forsberg *et al.*, 1988; Devol *et al.*, 1995). On the other hand, inorganic nitrogen compounds— $\text{NO}_3^-$  and  $\text{NH}_4^+$ —cycle rapidly via remineralization of organic matter and other microbial process such as nitrification and denitrification (McClain *et al.*, 1994; Brandes *et al.*, 1996; Boulton *et al.*, 1998). Dynamics of dissolved gasses, such as  $\text{O}_2$  and  $\text{CO}_2$ , are also largely controlled by the respiration of organic matter because river, flood-plain and lake waters are dominantly heterotrophic (Cole *et al.*, 1994; Cole & Caraco, 2001). These within-river fluxes (more below) are in quasi-steady-state balance with atmospheric gas exchange (Quay *et al.*, 1992; Devol *et al.*, 1995). Waters of the Amazon are characteristically supersaturated in  $\text{CO}_2$  with respect to atmospheric equilibrium (commonly by a factor of 20–50) and act as a significant source of  $\text{CO}_2$  to the atmosphere (Richey *et al.*, 2002). Thus the dissolved inorganic constituents of river waters are constantly evolving as a result of interactions with non-dissolved phases within the river corridor.

Dissolved organic matter (DOM) exists as a mixture of simple molecules, complex biomacromolecules, their partial degradation products and molecular assemblages or gels. Total concentrations, measured as dissolved organic carbon (DOC), depend strongly upon the mineralogy of the basin, highlighting the importance of sorption to DOM dynamics. Watersheds with soils dominated by quartz sands having low surface area produce black-water rivers with 7–40  $\text{mg l}^{-1}$  of DOC, whereas watersheds rich in clays produce surface waters with low DOC (2–7  $\text{mg l}^{-1}$ ) (Sioli 1984a; Nelson *et al.*, 1993; McClain *et al.*, 1997). To better understand the composition and dynamics of DOM, ultrafiltration techniques have employed membranes with pores as small as 1 nm to separate and concentrate DOM into various size fractions (Hedges *et al.*, 1994; K uchler *et al.*, 1994; Amon & Benner, 1996a,b; Mounier *et al.*, 1999; Patel *et al.*, 1999). Generally, ultrafiltered DOM (UDOM) refers to organic material with molecular weights  $>1000 \text{ g mol}^{-1}$  or daltons (HMW, or high molecular weight DOM in the CAMREX convention), including very high molecular weight subsets variously named VHMW DOM or colloidal organic carbon (COC) by different research groups (1000 daltons is approximately equivalent to a molecule of 1 nm diameter). Inorganic colloids also appear in UDOM fractions, comprising from 5–10% of the total mass in the Amazon lowlands to as much as 80–90% in the high Andes (Hedges *et al.*, 2000).

In Amazon lowland rivers, 70–90% of total DOM can be isolated as UDOM (Hedges *et al.*, 1994), with yields decreasing upstream to 40–50% in the Andes (Hedges *et al.*, 2000). Relative to the two particulate classes, UDOM contains the smallest fraction, 2.5–4.5%, identifiable as major biochemicals (Fig. 1.5), although UDOM also appears to be largely derived from tree leaves (Fig. 1.6(a)). DOM shows the most extensive signs of degradation of all three fractions (Fig. 1.6(b)) (Ertel *et al.*, 1986; Hedges *et al.*, 1986a; Hedges *et al.*, 1994), yet radiocarbon analysis places the average age to be less than decades (Hedges *et*

*al.*, 1986b, and unpublished data). Care must be taken however when interpreting many biochemical trends between DOM and FPOM. It is known that biochemical fractionation of DOM occurs during sorption. Newly sorbed OM tends to be higher in molecular weight, more hydrophobic, more enriched in nitrogen and hydrolysable amino acids, and have different amino acid compositions than the DOM from which it came (Gu *et al.*, 1995; Kaiser & Zech, 1997; Aufdenkampe *et al.*, 2001). Other untested biochemical parameters may also result in part from sorptive fractionation.

Cumulative evidence suggests that DOM is produced largely from the degradation and/or leaching of leaf detritus similar to that in CPOM (Devol & Hedges, 2001). Once in solution, biomacromolecules such as proteins and carbohydrates are easily hydrolysed (at least partially) by exoenzymes for subsequent microbial uptake. As a result degradation tends to decrease both the size and bioavailability of HMW DOM to form the low molecular weight (LMW, ~200–1000 daltons) fraction (Amon & Benner, 1996a). However, as all particulate and dissolved organic carbon fractions degrade, microbial activity and photochemistry can generate a pool of the smallest molecules (<200 daltons)—free amino acids, free sugars, and organic acids such as acetate and citrate (Amon & Benner, 1996b; Moran & Zepp, 1997). Despite the likelihood that this very low molecular weight (VLMW) DOM represents an exceedingly small proportion of total DOM in rivers, these compounds are generally extremely bioavailable and could drive significant biological fluxes. The relative proportions of VHMW, HMW, LMW and VLMW DOM fractions would be expected to evolve down river as a result of their different degradation rates. Coagulation and disassociation of DOM in and out of colloidal gel phases or mineral surfaces complicates these size dynamics significantly however, as many of these processes respond to changes in pH and to ratios of polyvalent to monovalent ions in solution (such as  $\text{Ca}^{2+}/\text{Na}^{+}$ ) (Chin *et al.*, 1998; Kaiser, 1998).

The dissolved fraction is particularly characterized by diversity and contrasts (Fig. 1.3). Organics and inorganics exist in both truly dissolved and colloidal phases. This mixture contains the most labile material carried by the river (e.g.  $\text{NH}_4^+$ , free amino acids, etc.) and also relatively non-labile weathering end-products (e.g. inorganic ions that determine alkalinity, LMW DOM, etc.). Some material is swept away with the water directly to sea, whereas transit times for other components are delayed considerably by interactions with mineral particles.

## River metabolism

The CSS, FSS and dissolved fractions are compositionally distinct, yet interact with each other on a continual basis through the processes of degradation and sorption. The dynamics of one fraction cannot be completely understood without considering the dynamics of the other two. Likewise, when considering whole-river processes, such as river metabolism, all three fractions must be considered together because nutrients and substrates (or pollutants) can reside in more than one fraction. A notable omission in the above discussion of river-borne material is microorganisms. Bacterial biomass accounts for only 15–50  $\mu\text{g OC l}^{-1}$  ( $0.75\text{--}2.5 \times 10^9$  cells  $\text{l}^{-1}$ ) or <5% of total organic carbon (Wissmar *et al.*, 1981; Benner *et al.*, 1995), thus contributing insignificantly to the mass of any fraction. However, the microbial community mediates nearly all biochemical transformations in the natural environment, including the weathering of rocks, and as such the activity of microorganisms is implicit in every discussion of biogeochemistry.

Just as rivers provide microorganisms with a wide array of substrates, nutrients and energy sources, rivers contain within their corridors a diverse set of physicochemical environments within which nearly all biochemical transformations can occur. Most rivers in

the Amazon are dominated by heterotrophic respiration over photosynthesis ( $R/P$  ratio  $> 3$ ) due to low light penetration in turbid rivers and in canopy-covered streams (Quay *et al.*, 1995). Community respiration rates in the Amazon and major tributaries show a wide range, from 0.2–2  $\mu\text{mol C l}^{-1} \text{ h}^{-1}$  (Richey *et al.*, 1990; Benner *et al.*, 1995; Devol *et al.*, 1995), with no consistent seasonal or river-type patterns. These rates appear to be substrate limited rather than nutrient limited (Benner *et al.*, 1995), further evidence that the bulk of dissolved and particulate OM in rivers is of limited bioavailability but that a small pool of labile compounds fuels the majority of respiration (Amon & Benner, 1996a). Water flow in and out of suboxic and anoxic hyporheic zones in river beds is a likely source of labile fermentation products to the river. Methane gradients from banks to the main river channel can be quite large (Richey *et al.*, 1988; Devol *et al.*, 1994), but quantification of fluxes for other associated fermentation products has not yet been attempted. Lastly, in less turbid waters photochemical reactions can be important in both oxidizing DOM and in releasing VLMW organic compounds from more recalcitrant material for bacterial consumption (Amon & Benner, 1996b; Moran & Zepp, 1997). As light penetration increases, so does photosynthesis. In flood-plain lakes, grassland streams, clear-water rivers and to some extent black-water rivers, respiration to photosynthesis ratios approach one (Quay *et al.*, 1995). Depth integrated gross photosynthesis in these waters is comparable to the more productive regions of the oceans, with rates as high as 160  $\text{mmol C m}^{-2} \text{ day}^{-1}$  (Wissmar *et al.*, 1981; Quay *et al.*, 1995). All of these various biological processes are cumulatively important. Concentrations of  $\text{CO}_2$  over the Amazon surface exhibit a diurnal cycle with amplitudes of from 70 to 150 ppm (Quay *et al.*, 1989). Thus, to say that large rivers “breathe” is not simply metaphorical.

## VARIABILITY AND SCALE IN THE RIVER SYSTEM

### Importance of natural variability and river scale for biogeochemical processing

The conceptualization of bioactive materials as interacting size classes with distinct properties has led to invaluable insight regarding dominant biogeochemical transformations in riverine environments (Devol & Hedges, 2001). A fuller understanding of biogeochemical dynamics in a river system, however, requires an additional dimension: an examination of the range and patterns of natural variability in concentrations, compositions, and process rates, and of their principal environmental sources and controls (Meyer *et al.*, 1988). In a fluvial system draining a continental-scale basin, natural variability is manifested across all spatial and temporal scales. Most obviously, concentrations and compositions usually vary within a channel cross-section, both laterally and with depth (Richey *et al.*, 1986). This observation is especially relevant for suspended sediments (Curtis *et al.*, 1979), and for highly labile molecules with well-defined sources in the form of discrete inputs or diffusing from the sediment-water interface, such as  $\text{CH}_4$  (Richey *et al.*, 1988; Devol *et al.*, 1994). Such variability highlights the need for careful, channel-integrated quantitative sampling in order to obtain representative cross-section averages, especially in larger rivers (Richey *et al.*, 1986).

Regional differences in climate, soils, geomorphology, and vegetation also lead to dramatic contrasts, such as the river water typology already discussed. The progressive downstream growth of rivers that in Amazonia leads to massive channels and vast drainage areas results in not only the mixing of river waters draining dissimilar terrains, but also the creation of geomorphologically distinct riverine landforms and flood plains (Gregory *et al.*,

1991), and longitudinal biogeochemical trends. Likewise, episodic events, the seasonal evolution of climate, and subsequent ecosystem and sediment responses, can result in substantial temporal changes in the biogeochemical functioning of rivers.

Some dominant forms of biogeochemical variability in Amazonian rivers will be described, focusing on the Amazon mainstem and mouths of major tributaries where more data are available and where CAMREX concentrated its efforts in the past. This large-river bias is a common feature of tropical South American research, in contrast with a focus on small catchments in temperate regions (Lewis *et al.*, 1995). River size and system scale are important considerations that will be interwoven in this discussion. We will also emphasize factors such as the interactions of bioactive materials with geomorphology, sediment, and hydrological dynamics, and the sensitivity of different species to reach *vs* basin-scale controls.

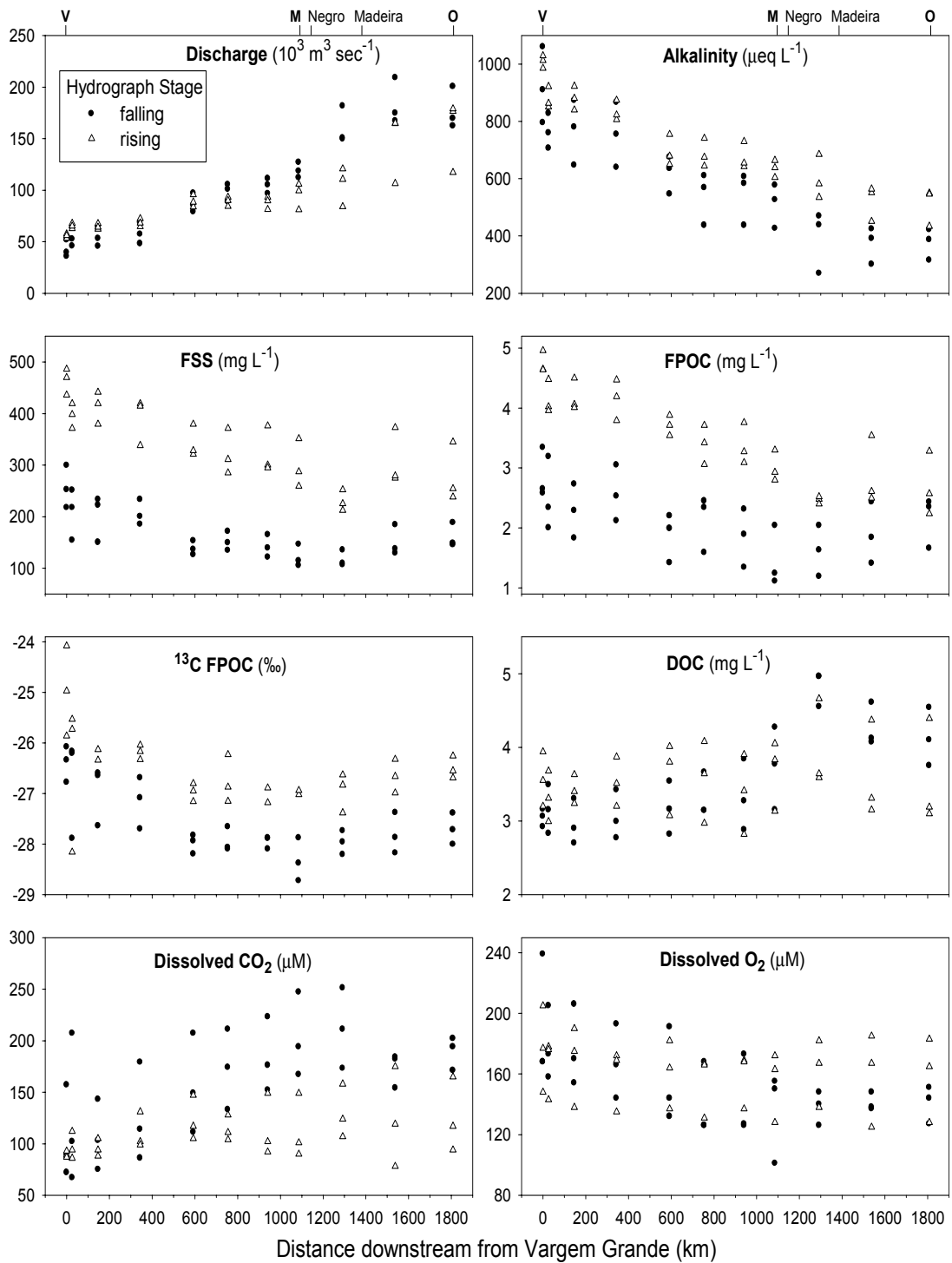
## **Regional heterogeneity, downstream evolution, and large-scale structure**

The biogeochemistry of running waters in the Amazon basin is exceedingly diverse. Several examples of this diversity have already been discussed. Spatial heterogeneity can be manifested at multiple scales, from large regional differences between Andean and lowland streams, through downriver longitudinal geochemical trends and interactions with a changing flood-plain environment, down to sub-regional variability and microscale changes. The value of broad classification schemes such as the visual water typology described earlier is diminished when considering subtle sub-regional changes in biogeochemical composition and controls. For example, turbid white-water rivers closer to their Andean headwaters in Peru and Bolivia display substantial contrasts in the sorptive partitioning history and proportion of HMW DOM (Hedges *et al.*, 2000); these differences may be attributable to differences in climate, terrain, and especially lithology and mineralogy (see Fig. 1.4, Ucayali, Marañón, and Madeira rivers). Moreover, smaller rivers at high elevations are often not turbid at all during the dry, low-water season (personal observation; Kvist & Nebel, 2001). Similarly, streams within each of the lowland physiographic domains (Fig. 1.1) can display geochemical composition and dynamics unlike those of the assumed norm, as a result of localized features (Sioli, 1984a; Kvist & Nebel, 2001). Larger rivers tend to average out these small-scale fluctuations and result in the expected water colour type.

The downstream growth of a river yields important biogeochemical consequences, including: a progressively diminishing role of local impacts and inputs compared to upstream influences; mixing of waters from dissimilar regions through the confluence of large tributaries; and creation of particular flood-plain environments through the geomorphological action of the river and its water and sediment regimes (Vannote *et al.*, 1980; Leopold, 1994). Longitudinal trends and “resetting” of the biogeochemistry of the channel often result from these factors. In the Río Beni, Bolivia (Fig. 1.2), such a pattern is seen in the increasingly finer suspended sediment sizes downstream as the river reaches the piedmont area (Guyot *et al.*, 1999); it is also observed in the  $^{13}\text{C}$  content of organic matter, which evolves from relatively enriched values in the highlands resulting from an elevation isotopic effect on C3 vegetation (Körner *et al.*, 1988), to a progressive decrease towards the lowlands, followed by a sharp increase in  $^{13}\text{C}$  of UDOM that may be a result of input from C4 grasses, and finally a sharp decrease after confluence with the larger Río Madre de Dios (see Fig. 1.6(a) in Hedges *et al.*, 2000).

On a larger scale, CAMREX has investigated changes in concentration, composition, fluxes, and process rates along a 1800-km reach of the Solimões–Amazonas mainstem (Fig. 1.2). While there are often clear differences between longitudinal trends during rising

and falling stage (see below), some patterns are persistent (Fig. 1.7). Most biochemical tracers of OM composition, sources, and degradation show relatively insignificant changes downstream, despite the input of very large tributary fluxes and flood-plain exchanges (Hedges *et al.*, 1986a; Hedges *et al.*, 1994); these tracers suggest that organic matter dynamics are operating in an apparent steady-state.  $^{13}\text{C}$  of FPOC, on the other hand,



**Fig. 1.7** Longitudinal trends along an 1800 km reach in the Solimões–Amazonas mainstem from Vargem Grande to Óbidos in Brazil. The data have been divided into falling (closed circles) and rising (open triangles) stages according to major hydrograph periods, to highlight seasonal differences. Variables shown are river discharge, alkalinity, fine suspended sediment (FSS), fine particulate organic carbon (FPOC), carbon-13 content of FPOC, dissolved organic carbon (DOC), dissolved  $\text{CO}_2$  gas, and dissolved oxygen. The sampling station labels at the top of the graph are the same as in Fig. 1.2. Data from Richey *et al.* (1990) and Quay *et al.* (1992).

generally becomes more depleted from Vargem Grande to Manacapuru, reflecting the gradual replacement of Andean FPOC with lowland-derived organic carbon from C3 plants (Quay *et al.*, 1992). Suspended sediment concentrations generally decrease to Manacapuru, though sediment fluxes may follow different patterns and the channel exchanges vast amounts of sediments with the flood plain (Meade *et al.*, 1985; Dunne *et al.*, 1998). Associated particulate species usually track the trends in suspended sediment concentrations (Hedges *et al.*, 1986a; Richey *et al.*, 1990). Conservative dissolved species such as alkalinity, originating primarily in the Andes and alluvial foreland rivers, present primarily a downstream dilution effect from the input of lowland tributaries with low base cation content. For many bioactive dissolved species such as CO<sub>2</sub>, on the other hand, the contribution of lowland tributaries and the flood plain is often the opposite, resulting in persistent increases downstream (Richey *et al.*, 1990). DOC concentrations are relatively unchanging in the mainstem, except for substantial increases due to the confluence of the black-water Río Negro. In fact, the input of such a large and distinctive tributary often results in substantial changes in the biogeochemical signature of the mainstem.

Several studies have indicated that the Amazon flood plain is a source of respiration products as well as highly labile organic matter that fuels respiration in the channel, but this input does not appear to affect the composition of bulk river organic matter (Devol & Hedges, 2001). The biogeochemical impact of the flood plain, however, is likely to be variable across the mainstem, given the diversity of geomorphological and ecological functioning of the flood plain in different reaches, driven by large-scale morphotectonic features (Mertes *et al.*, 1996; Dunne *et al.*, 1998). This diverse and changing role is also likely to be important in other flood-plain regions throughout the basin (Puhakka *et al.*, 1992; Guyot, 1993; Kvist & Nebel, 2001).

At a small scale, the extrapolation and regionalization of intensive stream and hillslope studies remains a difficult problem. Few studies of this type have been carried out in the basin (Nortcliff & Thornes, 1988; Elsenbeer *et al.*, 1996; Lesack & Melack 1996; McClain *et al.*, 1997), and their research emphases have varied. A dual challenge exists: defining the appropriate boundaries for regionalization of results from stream studies, and scaling small-stream results to their resulting larger rivers—and conversely, down-scaling from large to small rivers. These issues remain largely unexplored in the Amazon basin, though studies in North American rivers are beginning to point the way forward (Smith *et al.*, 1997; Peterson *et al.*, 2001).

## Temporal variability and episodic disturbance

Variability in biogeochemical processing with time can have important ecosystem impacts and must be considered in designing sampling or monitoring systems. It can occur at all temporal scales, from short rainfall events, to regular diurnal cycles and seasonal changes in rainfall; and from interannual climate variability driven by El Niño, to rare episodic disturbance such as earthquakes and mass wasting of hillslopes in the Andes. The consequences in a river are regulated by hydrological regimes and ecosystem and geomorphological responses. In large rivers, the relative timing and magnitude of events in different tributary basins also play a role.

Longitudinal trends along the Amazon mainstem often show marked contrasts between rising and falling stages, resulting from the combined effect of changing relative contributions of tributaries vs Andean source waters, local hydraulic conditions, and the contribution of the flood plain in comparison with in-channel transformations (Richey *et al.*, 1990; Devol & Hedges, 2001). Trends in suspended sediment concentration and associated bioactive constituents vary with the hydrograph, showing relatively uniform



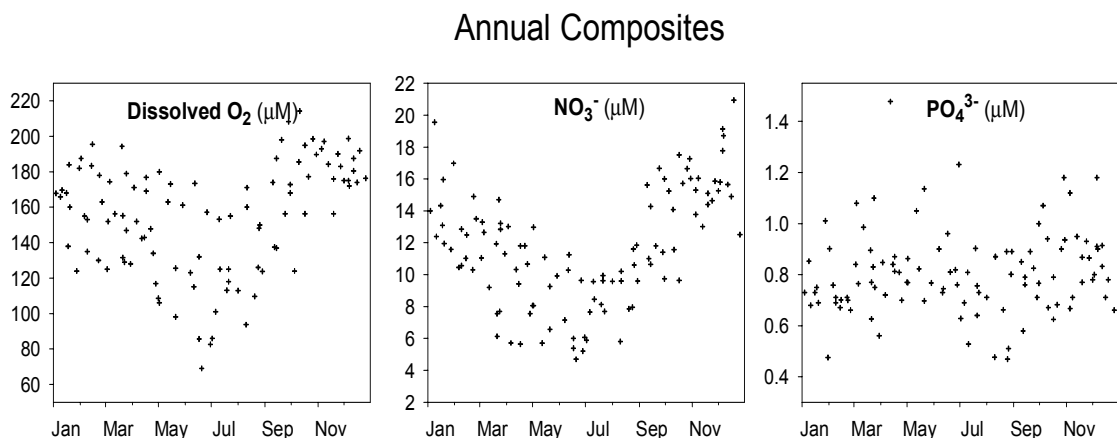
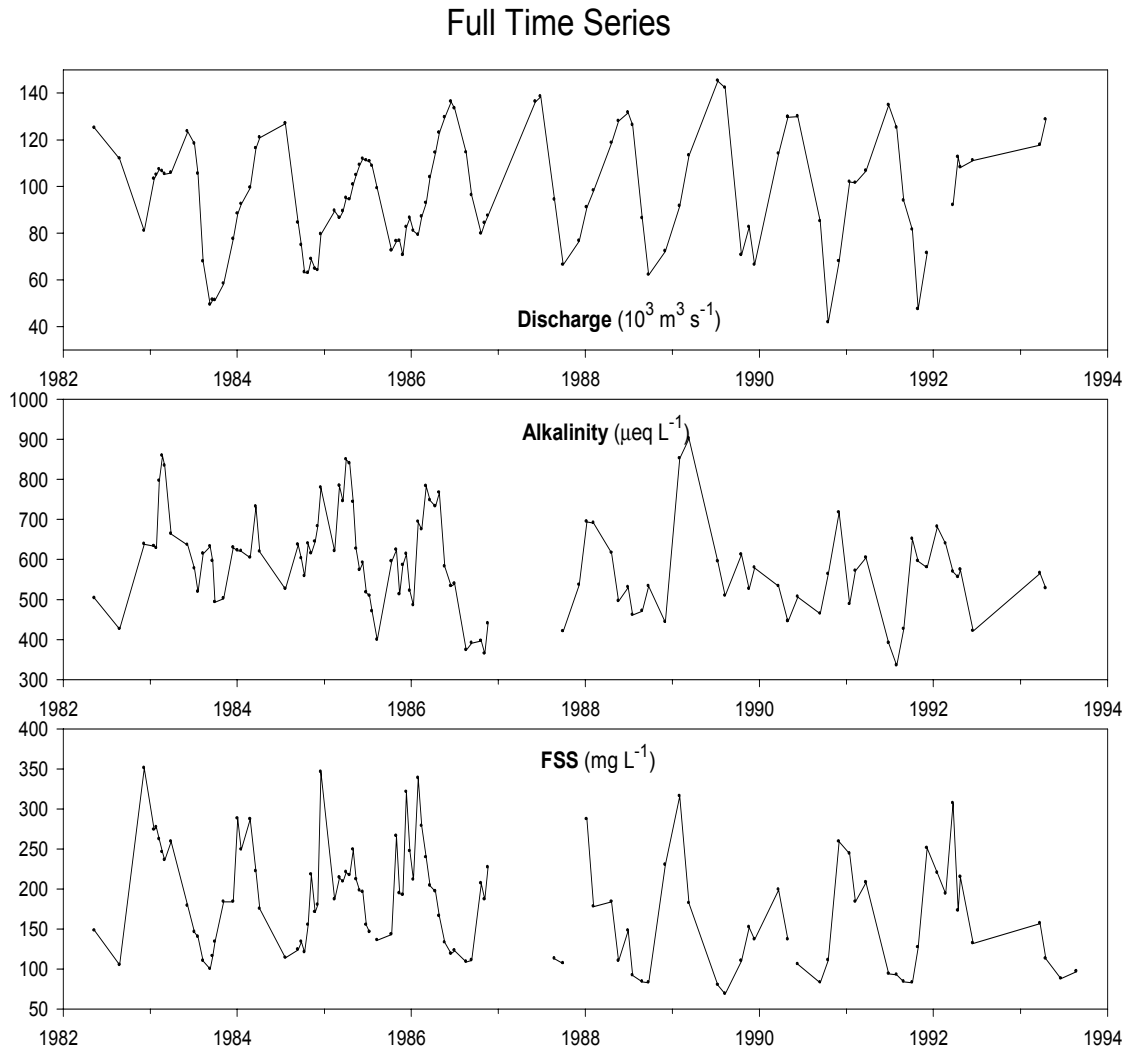
distributions or lack of clear longitudinal patterns during falling water, but higher concentrations and downstream decreases during rising portions of the hydrograph (Fig. 1.7). These seasonal changes reflect variations in both sources and transport of particulate materials during different stages of the hydrograph, the role of local hydraulic and turbulent conditions as measured by river surface slope, and large-scale changes in sediment dynamics and geomorphological functioning of the flood plain (Meade *et al.*, 1985; Devol *et al.*, 1995; Dunne *et al.*, 1998). However, such well-defined patterns often break down after the confluence of the Ríos Negro and Madeira, the two largest tributaries.

Dissolved conservative species with sources in the Andes, such as alkalinity and  $\text{Ca}^{2+}$  (Fig. 1.7), show only a dilution effect downstream, where their seasonal variations are controlled largely by the relative contribution and timing of the hydrographs from the headwaters and the major tributaries (Richey *et al.*, 1990). Dissolved bioactive species, on the other hand, are controlled largely by river stage, where stage is a proxy for channel–flood-plain interactions (Richey *et al.*, 1990; Devol *et al.*, 1995). As discussed earlier, oxygen and  $\text{CO}_2$  show a local steady-state between transport, respiration, and gas exchange across the river surface. Changing river stage results in variations in the longitudinal patterns of these dissolved gases, with increasing  $\text{CO}_2$  super-saturation and decreasing  $\text{O}_2$  concentrations downstream observed primarily during falling waters (Fig. 1.7). Lastly, DOC and  $\text{PO}_4^{3-}$  show little seasonal variability in their upstream–downstream distributions.

A more detailed picture of temporal variability in the mainstem is obtained from a 10-year time series of monthly measurements at the Marchantaria sampling station, in the Río Solimões before its confluence with the Río Negro (Fig. 1.2). Many species present regular, damped variability (Fig. 1.8). This decadal time series facilitated a more rigorous empirical examination of factors controlling the seasonal changes in river constituents (Devol *et al.*, 1995). Sediment and geochemical constituents were regressed against likely controls based on water provenance and hydraulic characteristics: % of water derived from Andean inputs, % derived from “local” water (flood plains and small tributaries feeding the mainstem), river slope, and discharge. Three groups of species with similar controls were found (Table 1.1). Particulate species are controlled by source strength and the hydrodynamics of sediment deposition and remobilization. Conservative dissolved species reflected their sources and dilution effects, and bioactive species vary with the discharge hydrograph. These results are congruent with those gleaned from mainstem cruises.

Variability in streams and mid-sized rivers has been scarcely studied in the Amazon basin. In contrast to large rivers, changes in these systems can occur rapidly in response to storms, often resulting in large and rapid changes in concentrations (Elsenbeer *et al.*, 1996; Lesack & Melack, 1996). In the Bolivian Andes, Guyot (1993) has shown that most annually averaged organic carbon transport occurs in particulate form and is dominated by very high concentrations during a short period of time when FSS concentrations are extremely high. Concentrations of both particulate and dissolved species can vary widely within a few days.

Little is yet known about riverine biogeochemical responses to interannual forcings in the Amazon basin. Richey *et al.* (1989) showed that the mainstem discharge data near Manaus presents substantial variability at frequencies of about 3 years, corresponding to El Niño and La Niña events. Marengo & Nobre (2001) have shown that the impact of ENSO (El Niño Southern Oscillation) events on climate and river hydrographs vary across the basin. Tian *et al.* (1998) and Asner *et al.* (2000) have recently demonstrated via models and remote sensing that carbon cycling in terrestrial ecosystems in the basin also varies with ENSO events. This combined evidence of hydrological and terrestrial biogeochemical responses to interannual climate variability strongly suggests that processing of bioactive materials in the river system will also respond to such forcing. In large rivers, however, this response will be modulated by the relative regional impacts, the influx of tributaries, and the



**Fig. 1.8** Hydrological and biogeochemical time series from Marchantaria, in the Solimões mainstem near Manaus (see Fig. 1.2). Data were collected at approximately monthly intervals from 1982 through 1993. The complete time series is shown for river discharge, alkalinity, and FSS. Annual composites for dissolved oxygen, nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ) are presented to illustrate the dominant seasonal variability patterns; these time series are created by plotting each value against the day in the year (1–366) when the sample was collected. Data from Devol *et al.* (1995).

relative timing of their hydrographs. Likewise, large episodic disturbance, such as earthquakes and mass wastings in steep Andean slopes, are likely to have substantial and long-lasting biogeochemical impacts on small and mesoscale rivers, as has been shown in small watersheds in Puerto Rico disturbed by hurricanes (Schaefer *et al.*, 2000).

**Table 1.1** Hydrological variables controlling seasonal biogeochemical variability at the Marchantaria sampling site, in the Solimões mainstem near Manaus. Biogeochemical parameters are grouped according to the dominant control variable resulting from multiple linear regression.

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**Andean group**

*Controlled by the relative contribution of river water from Vargem Grande, serving as a proxy of the Andean drainage of the Amazon mainstem.*

Fine suspended sediments (FSS), alkalinity (Alk), calcium ( $\text{Ca}^{2+}$ ), and sulphate ( $\text{SO}_4^{2-}$ )

**Stage height group**

*Controlled by the local stage height at Marchantaria.*

Dissolved oxygen ( $\text{O}_2$ ), dissolved carbon dioxide gas ( $\text{CO}_2$ ), nitrate ( $\text{NO}_3^-$ ), pH, sodium ( $\text{Na}^+$ ), chloride ( $\text{Cl}^-$ ), and % carbon by weight in coarse suspended sediments

**Local group**

*Controlled by the relative contribution of river water from small, local tributaries in the central lowlands and the flood plain.*

Silicate ( $\text{Si}(\text{OH})_4$ ), potassium ( $\text{K}^+$ ), and % carbon and nitrogen by weight in fine suspended sediments

**Surface slope group**

*Controlled by the river surface slope around Marchantaria, as a proxy of local turbulence.*

Coarse suspended sediments (CSS), fine particulate organic carbon (FPOC), coarse particulate organic carbon and nitrogen (CPOC and CPON), and total particulate phosphorus (TPP)

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## CONCLUSIONS

The Amazon River basin—from the Andean Cordillera to the Atlantic Ocean—contains within its border a large variety of river and basin types. Nevertheless, these rivers exhibit remarkable consistencies in the processes that control the fate and transport of bioactive elements. River-borne material resides in three compositionally distinct size fractions that have contrasting transport properties and reaction histories. Coarse particulates are the freshest, degrading to form the fine particulate and dissolved fractions, which continually interact with each other via sorption processes. Organic matter in these fractions contains most of the bioactive material in the river, yet inorganic material is of critical importance due to its ability to complex and protect organic matter from degradation.

Variability in the composition and dynamics of river-borne material from one river (or season) to another is often much less than differences between size fractions within a single river (or season). However, it is often this variability that offers the most insight regarding important processes. Understanding how these processes scale with basin size is of critical importance. The watersheds of streams and small rivers most often represent a single geological and climatic zone. Each small river thus exhibits the narrow range of characteristics typical of its limited basin, yet these rivers respond to episodic forcing (storms, landslides, fires, development) quite quickly and strongly. Large rivers can contain high sub-basin heterogeneity with respect to ecosystems, geology, climate, and timing of weather events. Material carried by these large rivers integrates this heterogeneity, yet the relative influence of each sub-basin is continually changing with time and with distance downstream. Thus the response of large rivers to environmental change is damped relative to its constituent drainages.

The cumulative understanding of natural undisturbed river systems sets the foundation for subsequent work to elucidate human impacts on rivers and to eventually develop sustainable management plans. For example, knowing which size fraction the material of interest (nutrients, pollutants, eroded sediments, etc.) can potentially reside in is a critical first step in evaluating its transport dynamics and bioavailability. The next step might be to evaluate issues of scale. How does the human flux of this material compare to the natural

riverine fluxes (transport, degradation, production, etc.) at that location? The answers to this question are likely to change across regions and with the time scale of interest. The evaluation of human impacts on river systems is rarely a simple and straightforward task—the natural world is too variable and complex for textbook solutions to every problem. However, systematic and well planned study of a natural system can yield the information necessary for sound management. Fortunately, a number of such studies are currently in place in the Amazon basin, including CAMREX (<http://boto.ocean.washington.edu/camrex/>), AARAM (Andean Amazon Rivers Analysis and Management; <http://amazonrivers.org/aaram/>), and HiBAm (<http://www.unb.br/ig/hibam/hibam.htm>).

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