

## Dissolved organic matter and terrestrial-lotic linkages in the central Amazon basin of Brazil

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**Abstract.** We evaluate the hypothesis that decomposition and adsorption reactions operating in upland soils of headwater catchments control the concentration and composition of dissolved and fine particulate organic matter in rivers of the Amazon basin. In two contrasting first-order catchments characteristic of the central Amazon basin, we analyzed plant, litter, soil, groundwater, and stream water chemistry. Our results indicate that clear and persistent differences exist in the concentration and elemental composition of dissolved organic matter (DOM) in stream waters and groundwaters from the two catchments, due mainly to corresponding differences in soil texture and chemistry. Within the more oxide and clay rich Oxisols underlying terra firme forest, groundwater DOM concentrations were uniformly low (120  $\mu\text{MC}$ ) and C/N ratios averaged 10. Conversely, within the oxide and clay deficient Spodosols underlying campinarana forest, groundwater DOM concentrations were greatly elevated (3000  $\mu\text{MC}$ ), and C/N ratios averaged near 60. We found that, in the terra firme/Oxisol terrain, the majority of DOM contributions to the stream derived from the riparian zone, while in the campinarana/Spodosol terrain, upland groundwater contributions could account for the concentration and composition of DOM in the stream. The implications of our findings are that in the terra firme terrains which dominate the region, upland soil profiles are not the site of definitive processes which impart compositional signatures to organic matter carried by the largest rivers of the Amazon basin, as was hypothesized. Instead, we suggest that definitive reactions are focused primarily in the river corridor.

### Introduction

Rivers form a critical link in the global carbon cycle by accumulating organic matter of terrestrial origin and transferring it to the coastal ocean. Of the world's rivers, none transfers more organic matter to the coastal ocean than the Amazon [Spitzky and Ittekkot, 1991]. At Obidos, 700 km upriver of the Atlantic Ocean, the river carries approximately 36 Tg of organic carbon each year, about 60% of which is dissolved [Richey *et al.*, 1990]. Within the main stem of the river, dissolved organic material (DOM) concentrations and compositions remain constant throughout the year but vary between tributaries. Dissolved organic carbon (DOC) concentrations in the main stem average 300-500  $\mu\text{M}$ . Similar concentrations are recorded in tributaries originating in Andean uplands and lowland rainforests, while higher concentrations characterize the Rio Negro (600-900  $\mu\text{M}$ ), which originates in the campina forests of the southwestern Guyana shield.

Present hypotheses to explain the composition and concentration of DOM in rivers of the Amazon basin hold that decomposition and adsorption processes operating in soils of upland forests exert primary controlling influences. As early as 1954, Sioli noted the relationship between stream DOM concentrations and catchment soil types [Sioli, 1954]. Sioli's hypothesis was subsequently supported in the Negro basin by Klinge [1966] and Ziechmann [1976], who identified Spodosols as the source of the river's black water. In a paper that remains influential among tropical biologists, Janzen [1974] proposed that high concentrations of dissolved organic material in black water streams were attributed to high component levels of plant-derived secondary ("toxic") compounds, which suppress the activity of decomposers and thus leave higher levels of organic molecules in solution. The effects of soils were thus secondary, in that their extremely low nutrient conditions forced the plant's adaptation of high levels of secondary compounds in its leaves [Janzen, 1974]. Leenheer [1980] clarified the hypothesis by fractionating the DOM of black, white, and clear-water rivers in the central Amazon into more and less physically reactive forms. He compared these fractions to humic substances in Spodosols and Oxisols of the region, concluding that a lack of DOM adsorption and low decomposition rates in Spodosols accounted for the high DOM concentrations of black waters, while abundant adsorption and relatively high decomposition rates in Oxisols accounted for the low DOM concentration of

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white and clear waters. Thus soils were shown to exert a primary control over DOM levels via sorption reactions within their profiles.

The hypothesis was advanced to its present state by researchers from the Carbon in the Amazon River Experiment (CAMREX) who employed isotopic, elemental, and molecular techniques to characterize the composition of DOM in the main stem and its major tributaries and thereby to further elucidate the strong control of decomposition and adsorption reactions [Ertel *et al.*, 1986; Hedges *et al.*, 1994]. Using elemental and lignin analyses, Ertel *et al.* [1986] showed the fulvic and humic acid fractions of DOM to be very degraded; fulvic acids were more oxidized and nitrogen-poor than humic acids. In view of the high degree of oxidation of dissolved riverine humic substances and similarities in the elemental composition of dissolved and soil humic substances, Ertel *et al.* [1986] speculated that all Amazon dissolved humic and fulvic acids may derive from the aerobic horizons of soils in the basin. Most recently, Hedges *et al.* [1994] isolated, through ultrafiltration, 65 to 85% of DOC from the main stem and several major tributaries. Elemental, carbohydrate, and amino acid analyses of the ultrafiltered fraction provided results consistent with those of Ertel *et al.* [1986], in that DOM was highly degraded and of apparent terrestrial origin. In addition, however, Hedges *et al.* [1994] found reduced ratios of basic to acidic amino acids in the DOM fraction when compared to the coexisting fine particulate organic matter (FPOM) fraction. This compositional pattern provides evidence of selective partitioning of more nitrogen-rich dissolved molecules onto cation exchange sites of mineral surfaces, leaving nitrogen-depleted organic molecules in the aqueous phase. Hedges *et al.* [1994] suggested that this partitioning occurred in the forest soil profile, with the DOM fraction entering the river via groundwater pathways and the FPOM fraction entering the river via soil erosion.

Inherent in the findings of these previous studies is the transport of soil-derived DOM to streams via groundwater flow. Moreover, this DOM is hypothesized to persist in the river system to eventually constitute the DOM fraction of the Amazon's main stem and largest tributaries. There has never been a systematic study of DOM in Amazonian groundwater or small streams, however, and existing hypotheses have involved inference and speculation. The present study was initiated to address this gap in our understanding by comparing soil organic matter (OM) to DOM in groundwater and nearby stream water, effectively tracing the transfer of terrestrial signals to the river system. Over the course of the study, we expanded our efforts to consider other sources of DOM to lotic ecosystems such as seepage from fringing wetlands and leaching of leaves input via direct litterfall. The basic question guiding our research may be summarized as follows: What are the important sources of terrestrially derived DOM to lotic ecosystems in the central Amazon basin, and what processes regulate the terrestrial to lotic transfers?

We based our fieldwork in two contrasting catchments of the central Amazon basin, one containing a black-water stream draining Spodosols and the other containing a clear-water stream draining Oxisols. These streams and their catchments are characteristic of the two principal landscape types that compose the central Amazon. Our results demonstrate that DOM concentrations and compositions vary in a predictable

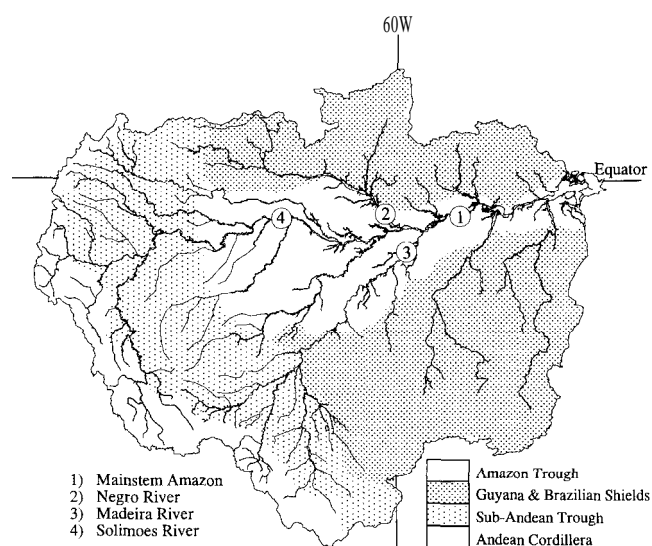
manner as a function of forest/soil type and position within the landscape. When combined with other available data, our results enhance our understanding of the sequence of processes controlling the concentration and composition of DOM carried by the smallest and largest rivers of the Amazon basin.

## Regional Setting

The central Amazon basin as defined here corresponds roughly to the Amazon trough, a large depositional basin covering slightly more than 1 million km<sup>2</sup> and extending eastward from the Sub-Andean trough to the Atlantic coast (Figure 1). The region is bounded to the north and south by the Guyana and Brazilian shields, respectively. Elevations generally do not exceed 300 m asl and are usually less than 200 m asl.

The geomorphology of the central Amazon basin is characterized by multiple generations of abandoned alluvial terraces and massive active floodplains. At least nine distinct terraces have been identified, the highest of which lies 180 m above the modern floodplain [Irion, 1989; Klammer, 1984]. The abandoned terraces have been subsequently incised by streams so that the resulting topography is one of plateaus dissected by a dendritic pattern of shallow, flat-bottomed valleys. The active floodplain of the main stem Amazon river is a prominent feature on the landscape, attaining widths in excess of 35 km. It is composed of a complicated assemblage of depositional features as well as abundant shallow lakes and side channels. Annual precipitation and temperatures are similar across the central Amazon region. Precipitation ranges from 2000 to 2500 mm/yr, with a pronounced rainy season from December through May. Mean annual temperatures range from 25° to 27°C [Superintend&ha do Desenvolvimento da Amazonia (SUDAM), 1984].

In general, different soil types of the central Amazon basin represent progressive phases of podzolization of a common parent material [Chauvel *et al.*, 1987; Lucas *et al.*, 1988] The



**Figure 1:** Principal morphotectonic regions of the Amazon basin, with superimposed river network and political boundaries. The results of this study apply most directly to the Amazon trough.

plateau surfaces are covered by deep, well-drained Oxisols, classified as Haplic Acrorthox by Lucas *et al.*, [1984] according to U.S. soil taxonomy [USDA, 1975]. Oxisols and Ultisols on the valley slopes become progressively more eluviated with increasing distance downslope and have been classified as Orthoxic Tropohumult or Palehumult [Lucas *et al.*, 1984]. Soils at the base of relatively short slopes (< 1 km), which dominate the region, have been termed sandy Oxisols [Brinkmann and dos Santos, 1973]. Soils covering the valley bottoms, where water table levels are shallow, are termed hydromorphic Oxisols [Brinkmann and dos Santos, 1973], however, Spodosols often develop at the base of valley slopes exceeding 1 km in length [Lucas *et al.*, 1984]. The Spodosols are composed predominantly of clean quartz sand, with the dark brown spodic horizon lying at depths greater than 2 m [Klinge, 1965]. For a more detailed description of soils of the region, the reader is referred to Sombroek [1966].

Four distinct forest types occur in the nonflooded portions of the central Amazon basin: upland terra firme forest, riverine forest, campina forest, and campinarana forest. The distribution of these forest types is closely associated with soil type, as upland terra firme forest occurs on Oxisols and Ultisols of the plateau surfaces and valley slopes, riverine forest occurs on hydromorphic Oxisols of the valley bottoms, and campina and campinarana forests occur on the dispersed Spodosols. Each forest type is compositionally, structurally, and functionally distinct from the others, but together they may be classified as “forest on terra firme” to distinguish them from the inundation forests (varzea and igapo) of the active floodplains [Prance, 1978].

Upland terra firme forest is the most widespread forest type in the central Amazon. It is the popularly envisioned dense Amazon forest consisting of a tall (25-40 m) multilayered canopy housing a diverse assemblage of trees, palms, shrubs, and saplings. In a single hectare of upland terra firme forest north of Manaus, Prance *et al.* [1976] identified 235 tree species, of which *Eschweilera odorata* and *Scleronemu micranthum* were most abundant. The phenology of most of these species is unknown, but of the 47 tree species with known phenology, 29 are evergreen, 16 are semideciduous (dropping most but not all foliage periodically), and 9 are fully deciduous [Alencar *et al.*, 1979; Anjo, 1970]. In addition, vast numbers of climbers, stranglers, epiphytes, and semi-parasites colonize the standing vegetation.

Riverine forest (also known as swamp forest by Guillaumet, [1987] and mata de várzea by Porto *et al.*, [1976]) is characterized by a shorter canopy (30 m maximum) and a greater abundance of palms than the surrounding upland terra firme forest [Guillaumet, 1987]. The abundance of palms increases with increased valley width and increased soil moisture; the dominant palm species are *Mauritia flexuosa*, *M. aculeata*, *Jessenia bataua*, *Inhira exorrhiza*, and *Euterpe precatoria* [Guillaumet, 1987]. Porto *et al.* [1976] identified 95 Dicotyledonous tree species distributed in 33 families. Four species (*Carapa procera*, *Vitex sprucei*, *Euterpe precatoria*, *Jessenia butuua*) made up 30% of the individuals surveyed. Good numbers are not available for the Monocotyledons, but they are thought to compose 12-31% of the species of flowering plants based on surveys from Surinam [Guillaumet, 1987]. Riverine and upland terra firme forests share only 13 known tree species in common [Guillaumet, 1987].

Campina forest is low (<10 m) and open, with vegetation concentrated in islands separated by areas of partially exposed white sands. The floral community is one specially adapted to extremely low nutrient soils (Spodosols). Other soil environmental factors such as elevated temperatures and low moisture storage capacity also require special adaptations [Lisboa, 1975]. Consequently, the species diversity of campina forest is less than that of other forests of the central Amazon [Prance, 1975]. The most common tree species is *Glycoxylon inophyllum*, but it, as well as the more than 40 other tree species identified, is irregularly distributed [Anderson *et al.*, 1975]. The campina forest shares no known tree species in common with upland terra firme or riverine forests [Guillaumet, 1987].

Campinarana forest is a low (10-20 m), relatively light forest, which occurs between upland terra firme and campina forests. Its understory is well developed in places, but it contains virtually no herbaceous layer [Guillaumet, 1987]. Because of its location and structure, campinarana forest may be thought of as transitional between upland terra firme and campina forests. However, it shares only three known tree species in common with upland terra firme forest and only 19 known tree species in common with campina forest [Guillaumet, 1987].

**Methods**

**Study Sites**

Our site investigations were centered in two small catchments located in protected forest reserves of the Brazilian Instituto Nacional de Pesquisas da Amazonia (Figure 2). These sites were selected both for their accessibility and because their features are characteristic of catchments in the region.

The Barro Branco catchment lies within the Ecological Forest Reserve “Aldolfo Duke,” located 26 km northwest of

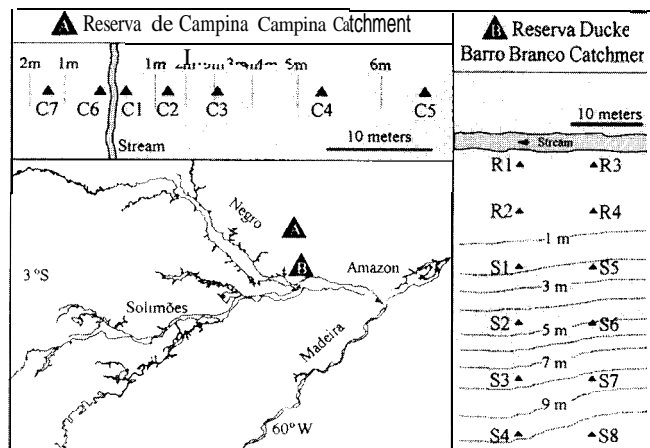


Figure 2: Site map showing regional and site specific views. Solid triangles mark the locations of soil cores and wells at the Campina and Barro Branco catchments. At Barro Branco, wells were not installed at S3, S4, S6, S7, or S8 because the water table was too deep to be reached using our augering equipment. Surface elevation contours are also shown.

the City of Manaus (2°60'S, 59°60'W); fieldwork was conducted between October 1992 and August 1993. The largely undisturbed catchment covers an area of approximately 1.5 km<sup>2</sup> and is drained by one perennial clear-water stream (Barro Branco) and several ephemeral streams. The geomorphology of the basin is remarkably consistent. A flat riparian zone up to 40 m in width forms a nearly complete border between the stream channel and surrounding hillslopes. Riverine forest occupies the valley bottom, in association with hydromorphic Oxisols. Hillslopes rise abruptly from the back of the riparian zone at slopes of 10° to 20°, reaching elevations of 10 to 20 m above the stream channel (-120 m asl); hillslope widths range from 50 m to more than 100 m. Terra firme forest covers the hillslopes, in association with Oxisols. At the section studied in detail, the riparian zone is 12 m wide, giving way to a hillslope rising at an approximate slope of 15° to an elevation of 11 m above the stream channel. The width of the hillslope is 50 m.

The Barro Branco stream follows a meandering course through the flat-bottomed valley and is bordered by several fringing wetlands. The stream channel averages roughly 1 m in width, is generally less than 50 cm deep, is sandy-bottomed, and is completely covered by the canopy of the riparian forest. The surface hydrology and water budget of the Barro Branco catchment was investigated by Franken and Leopoldo [1984] and Leopoldo *et al.* [1984]. Over the period of their study (1976-1977 and 1981-1982), mean monthly discharges ranged from 5 to 20 L/s. Discharge fell as low as 0.1 L/s during dry periods and reached upper extremes of 500 L/s during large storms [Leopoldo *et al.*, 1984]. Nortcliff and Thornes [1978; 1981; 1984] and Nortcliff *et al.* [1979] examined subsurface hydrologic flow paths linking the hillslope, riparian zone, and stream channel. Their findings indicate that flow within the unsaturated zone of the hillslope is dominantly vertical, with little lateral flow even during storms. Thus the principal linkage between hillslope and riparian zone is groundwater flow along the potentiometric gradient. Under base flow conditions, groundwater flow continues across the low gradient of the riparian zone to produce runoff in the stream channel. No information is currently available regarding the dimensions or hydrodynamics of the stream's hyporheic zone.

The Campina catchment lies within the Campina Biological Reserve, 60 km north of the City of Manaus (2°30'S, 60°00'W); fieldwork was conducted between July 1993 and July 1994. The catchment covers an area of less than 1 km<sup>2</sup> and contains a single black-water stream meandering beneath the closed canopy of the riparian forest. No detailed pedologic or botanical surveys have been published for the Campina catchment in particular, but the basic characteristics of the catchment are as follows. Both Spodosols and Oxisols occur, and forest types vary in accordance. Oxisols and associated terra firme and riverine forests are concentrated on the eastern side of the catchment near the stream's source, while Spodosols and associated campinarana forest cover the western hillslopes. Further to the west, campina forest covers the upland Spodosols. The stream's course along the valley bottom is somewhat irregular, with occasional branching into multiple channels and short reaches where flow is diverted through subterranean channels. The stream channel is less than 1 m wide and generally less than 30 cm deep, except

where pools have formed; the streambed is composed largely of plant litter and organic debris.

Neither groundwater nor surface water of the catchment have been studied previously, but Reichardt *et al.* [1975] examined groundwater flow in other Spodosols of the Campina Reserve. Using both tritium and calculations based on Darcy's law, they estimated horizontal flow rates within the saturated zone to be of the order of  $6 \times 10^{-6}$  cm/s, but this rate varied greatly, increasing by as much as 2 orders of magnitude during precipitation events [Reichardt *et al.*, 1975].

### Field Procedures

Samples collected as part of this study included water, soil, forest floor litter, stream channel and wetland litter, and live vegetation. Water samples included groundwater, soilwater, stream water, and water from fringing wetlands. Soil, soilwater, and groundwater were collected along transects oriented perpendicular to the stream channels of the two catchments. At Barro Branco, two parallel transects, including a total of 12 sampling points (Figure 2), were established on the left side of the stream. At Campina one continuous transect traversed the stream near its source, with five sampling points falling on the left side of the stream and two on the right (Figure 2). Litter and live vegetation samples were collected by hand from various points at the sites, with samples classified as either riparian or hillslope in the case of the Barro Branco catchment and simply as campina at the Campina catchment.

Soil samples were collected using a hand auger. After clearing away litter to expose the mineral soil, samples were collected at intervals of 10 or 20 cm in the upper meter of the cores and at intervals of 50 cm below 1 m depth. The maximum depth sampled was 5.5 m (core S2), but in general cores were less than 2 m in depth. Upon collection samples were composited by hand, subsampled, and sealed in plastic bags for transport to the laboratory in Manaus.

Wells were placed in holes left by the soil cores. Ceramic-cup lysimeters were installed using the same technique. Each well consisted of a 5 cm inside diameter (ID) polyvinyl chloride (PVC) tube sealed at the bottom and slotted over its lower 50 cm. Wells were developed by removing 10 casing volumes of water and were then allowed to equilibrate for 3 weeks with the surrounding groundwater. The relative elevation of each well was measured using a handheld level and staff. Water samples were collected at 1 to 2 week intervals over the course of 10-12 months. These time series samples were collected using a PVC bailer after evacuating three casing volumes of water or after bailing the well dry. The water level in each well was measured prior to bailing using a metal tape measure. At the Barro Branco site, lysimeters were sampled with the same frequency as wells. First, a vacuum of 6000 Pa was established and left for 5-7 days, after which samples were recovered using a small vacuum pump. Lysimeters were also installed at the Campina site, but no samples were obtained. Base flow stream water samples were collected by hand with the same frequency as groundwater samples. Wetland water samples were also collected by hand on selected occasions. Time series water samples were stored in 250 mL high-density polyethylene bottles and transported to the laboratory in Manaus for processing. Large volume water samples (20-100

L) were collected on selected occasions for ultrafiltration in the laboratory. Samples were stored in prerinsed 20 L plastic jerry cans.

### Laboratory Procedures

**Water sample processing and analyses.** Upon arrival at the laboratory in Manaus (usually within 2 hours of sampling), time series water samples were immediately filtered through precombusted Gelman A/E glass-fiber filters into precleaned sample bottles. Aliquots for determination of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were analyzed colorimetrically according to the methods of *Strickland and Parsons [1972]*. These values were summed to obtain a value for total dissolved inorganic nitrogen (TDIN). Aliquots for analysis of DOC and total dissolved nitrogen (TDN) were shipped via Federal Express® to the University of Washington. DOC samples were preserved with  $\text{HgCl}_2$ . Samples were refrigerated until analysis, which was usually within 1 week. DOC analyses were performed on a Shimadzu TOC-5000 Total Organic Carbon Analyzer. The procedure calls for acidifying the sample to pH 2 and sparging with air for 5-10 min to remove inorganic carbon. The sample is then analyzed for total carbon, which, within the method, translates to nonpurgeable DOC. Reproducibility of the analyses was 2-5%. TDN was analyzed by persulphate digestion according to the method of *Valderrama [1981]*. Values for TDIN were then subtracted from TDN to calculate dissolved organic nitrogen (DON).

Large-volume samples were processed using an Amicon DC-10L tangential flow system [*Benner, 1991*]. The advantage of tangential flow ultrafiltration is that material not passing through the membrane is concentrated in the process fluid rather than being retained on the membrane. Thus large volumes of sample (hundreds of liters) may be processed using a single membrane, which may be reused. By filtering in stages, different size classes of material may be recovered from a single sample, with the filtrate from one stage becoming the input to the subsequent stage. The overall filtration process that we used resulted in three size classes of recovered material, 63-0.1  $\mu\text{M}$  fine particulate organic material (FPOM; using hollow-fiber cartridges), 0.1  $\mu\text{M}$ -10,000 Dalton ultrafiltered dissolved organic material (UDOM; using spiral-wound cartridges), and 10,000-1,000 Dalton UDOM. Dissolved molecules smaller than the 1,000 Dalton cutoff were not recovered. The concentrates of both FPOM and UDOM were stored in 1 L polycarbonate bottles and preserved either by  $\text{HgCl}_2$  or freezing. Percent recovery for the FPOM fraction ranged from 50 to 60%, while percent recovery for UDOM was approximately 75%.

Stored samples of CPOM, FPOM, and UDOM were shipped to Seattle via Federal Express®, where they remained refrigerated or frozen until further processing. In the final stage of processing prior to analysis, CPOM, FPOM, and UDOM samples were dried at 65°C using either a rotoevaporation system or a standard drying oven. CPOM, FPOM, and UDOM samples were then analyzed for total C and N according to the same methods described in the next section.

**Soil sample processing and analyses.** Soil samples were air dried, resealed in plastic bags, and shipped to the University of Washington for further processing and

analysis. In Seattle, they were first passed through a 2 mm sieve to remove large organic debris and pebbles. Subsamples were then oven-dried at 100°C for 24 hours in order to determine moisture content. Bulk soil analyses included grain size distribution, surface area, oxalate extractable Fe and Al, total C, and total N. Grain-size distribution, surface area, and oxalate extractable Fe and Al were measured on a subsection of samples representing the three primary soil types (Oxisol, hydromorphic Oxisol, and Spodosol). Grain-size distribution was measured using a modified version of the settling technique of Day [1965]. Dispersion techniques were minimized so as to measure an effective grain size distribution which is more representative of conditions in the soil column. Grain sizes were broken into sand, silt, and clay fractions.  $\text{N}_2$ -specific surface area was measured on a Quantachrome monosorb 100 using the method described by *Keil et al. [1994]* and adhering to the guidelines in *Sing et al. [1984]*. Fe and Al were extracted according to the method of *McKeague and Day [1966]* and extract solutions were analyzed for Fe and Al using an inductively coupled plasma (ICP). Total C and N were measured simultaneously on a Carlo-Erba total elemental analyzer after the method of *Hedges and Stern [1984]*. The acidification step was omitted from the method, however, as carbonates do not occur in the highly leached soils of the region.

Selected soil samples were further processed to fractionate soil organic matter (SOM) into three functionally relevant fractions: (1) unbound SOM, (2) base-extractable SOM, and (3) water-extractable SOM. First, 100 g of air-dried soil is placed in a beaker filled with distilled water to the 1 L mark. The beaker is shaken for 16 hours at room temperature. The leachate is then filtered through a precombusted Gelman A/E glass fiber filter and a subsample is analyzed for DOC, TDIN, and TDN. The remaining leachate is evaporated at 65°C to produce a powder. This drying step did not always yield sufficient sample for further analyses, but when it did, samples were analyzed for total C and N. In the second stage of the fractionation, 15 g of air-dried sample is placed in 30 mL of a 2 g/cm<sup>3</sup> solution of sodium polytungstate and shaken by hand. The light and heavy phases are then separated by centrifugation at 3000 rpm for 30 min and subsequent filtration of the supernatant. This process is repeated three times for each sample. Material retained on the glass-fiber filter is rinsed with distilled water, dried, and analyzed for total C and N. In the final step of the fractionation, the rinsed heavy organic matter (OM) fraction from the density separation step is extracted with  $\text{NaOH-Na}_4\text{P}_2\text{O}_7$  according to the method of *Schnitzer [1982]* and analyzed for total C and N.

**Litter and live plant analyses.** Litter samples were air-dried, while live plant samples were oven-dried at 100°C for 12-24 hours. Samples were sealed in plastic bags and shipped to Seattle. Dried litter samples were then ground and homogenized, but live plant samples were subsampled individually. All litter and live plant samples were analyzed for total C and N according to the methods presented above.

**Statistical comparisons.** Statistical comparisons of mean values from the different data sets were performed at the 95% confidence level. Means were compared using a t test and assuming unequal variances.

Table 1. Well Information and Water Level Measurements

Site	Well	Depth, cm	Distance From Mean WT		Range in WT Level <sup>a</sup>	
			Stream	Level <sup>a</sup>	Maximum <sup>b</sup>	Minimum <sup>c</sup>
Campina Riparian	C1	150	1	-5	-14	+1
	C2	149.5	6	-16	-31	-9
	C6	150	1.5	-29	-37	-15
	C7	152	6.5	-30	-70	-16
Campina Hillslope	C3	99.5	11	-22	<-99.5	+5
	C4	241.5	21	-137	-177	-89
	C5	289	31	-183	<-289	-140
Barro Branco Riparian	R1	149	2	-35	-67	-18
	R2	149	10	-38	-80	-12
	R3	198	2	-28	-43	-11
	R4	200	10	-53	-104	-14
Barro Branco Hillslope	S1	496	20	-201	-236	-112
	s2	594	30	-405	-503	-85
	s3	450	20	-223	-272	-96

<sup>a</sup> WT, water table. Mean of measured values, where "level" is relative to the ground surface.

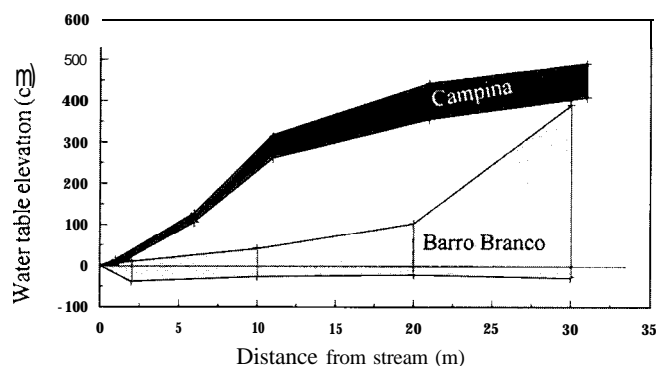
<sup>b</sup>C3 and C5 were dry on occasions, indicating that the WT level was below the depth.

<sup>c</sup>Positive values indicate exfiltration.

## Results

### Water Table Configurations

Water table levels varied greatly over the course of the study in response to seasonal patterns of precipitation, but overall the water tables at each site sloped toward the streams. At Campina, fluctuations in water table depths range from 15 cm in C1 to greater than 150 cm in C5, while at Barro Branco fluctuations range from 32 cm in R3 to 418 cm in S2 (Table 1). At both sites, the minimum fluctuation is recorded in wells adjacent to the stream, and the maximum fluctuation is recorded in the well farthest from the stream. Figure 3 illustrates the ranges in water table levels along transects perpendicular to stream channels. Levels along these transects reveal two very different water table configurations which reflect differences in topography between the sites. Additionally, the occurrence of levels beneath the 0 m value at Barro Branco indicates periods where the water table gradient slopes away from the stream.



**Figure 3:** Area plots showing the range of watertable elevations at the two sites. Elevation and distance are relative to the streams at each site. The water table configurations at the two sites generally reflect site topography, however, the Campina water table exhibits a narrower range of values.

### Water Chemistry

Mean DOC concentrations of groundwater and stream water at Campina are not significantly different from each other (2990 and 3170  $\mu\text{M}$ ), but they are 8 to 20 times the concentrations of DOC in groundwater and stream water at Barro Branco. The mean Barro Branco hillslope groundwater DOC concentration (127  $\mu\text{M}$ ) is significantly below that of riparian groundwater (291  $\mu\text{M}$ ). The mean DOC concentration of Barro Branco stream water (371  $\mu\text{M}$ ) is not significantly different from riparian groundwater but is significantly higher than hillslope groundwater. The consistency of DOC concentrations in groundwater and stream water is illustrated in Figure 4, where mean DOC concentrations are plotted versus month. The separation of Campina and Barro Branco waters is clear, along with the similarity of stream water and groundwater concentrations at Campina and stream water and riparian groundwater concentrations at Barro Branco. Although rainy season DOC concentrations in the streams appear higher than dry season concentrations, these differences are not significant at the 95% confidence level. There are no significant seasonal signals recorded in Barro Branco groundwater. Mean soilwater DOC concentrations at Barro Branco are significantly higher than for hillslope groundwater (Table 2).

The distribution of nitrogen between inorganic and organic forms differs greatly between the catchments. At Campina organic nitrogen is the dominant form, averaging 89% and 91% of TDN in groundwater and stream water, respectively. In contrast, at Barro Branco, organic nitrogen averages 34 to 75% of TDN in hillslope groundwater and stream water, respectively. A detailed treatment of dissolved nitrogen dynamics at Barro Branco is given by McClain et al. [1994] and Brandes et al. [1996]. Patterns of DON in Barro Branco water are the reverse of patterns for DOC. Mean DON concentrations in hillslope and riparian groundwater (18.7 and 20.5  $\mu\text{M}$  respectively) are significantly higher than that of stream water (13.3  $\mu\text{M}$ ). This reversal of concentration patterns is reflected in the C/N ratios of DOM at Barro Branco

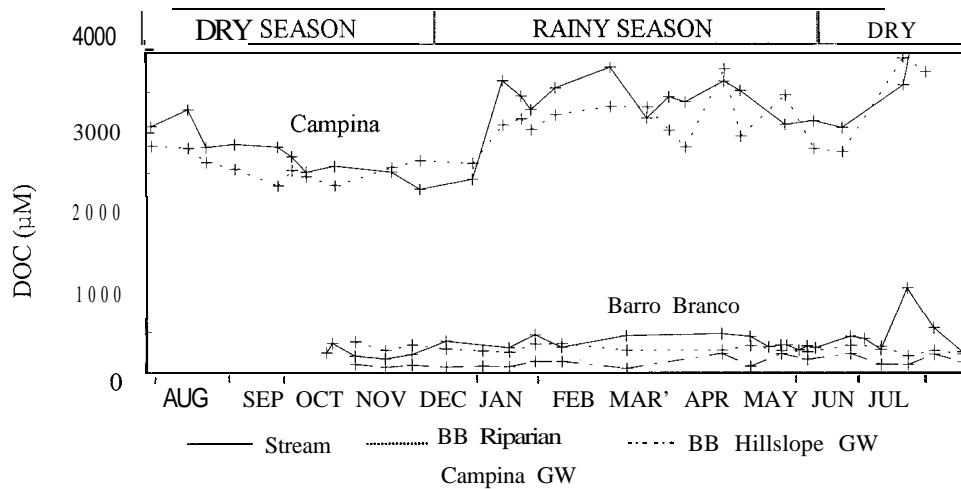


Figure 4: Time series plot of dissolved organic carbon (DOC) concentrations in different hydrologic compartments of the two sites. Results are plotted within the same 12 month period only for illustrative purposes. Campina waters were actually monitored during the year following monitoring at Barro Branco. The annual occurrence of rainy and dry seasons is shown. Crosses mark sample dates.

(Figure 5). Mean C/N ratios of DOM show a significant and progressive increase from hillslope groundwater (10) to riparian groundwater (15) to stream water (25). In contrast, mean C/N ratios of DOM in Campina groundwater and stream water are nearly identical (59 and 58, respectively).

Ultrafiltered water samples exhibited general compositional patterns similar to those of time series water samples (Table 3). Concentrates from the stream water and fringing wetland at Barro Branco were enriched in N (C/N = 21-31) relative to those of the stream water and distant groundwater at Campina (C/N = 39-63). Consistent differences in C/N ratios between size fractions were not observed in the two streams or the wetland sample. In the distant groundwater sample from Campina, the 1,000-10,000 Dalton fraction was depleted in

nitrogen (C/N ~ 50) relative to the 10,000D-0.1µM fraction (C/N ~39).

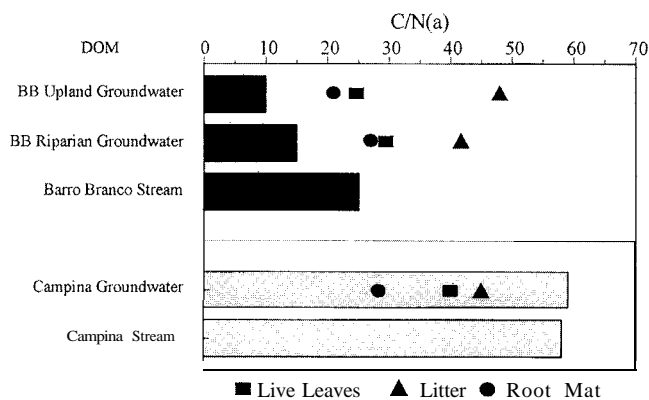
Soil Chemistry

Soils occurring in the study catchments exhibit distinct chemical and physical properties in relation to soil type and position in the catchment. Table 4 presents mean bulk soil data for Spodosols of the Campina riparian zone (< 5 m from the stream water margin) and hillslope (> 5 m from the stream water margin), hydromorphic Oxisols of the Barro Branco riparian zone, and Oxisols of the Barro Branco hillslope. Mean percent C decreases exponentially with depth in the hillslope Oxisols and Spodosols. The decrease is especially

Table 2. Summary of Time Series Water Chemistry

	Station I.D.	DOC, µM	s.d.	#	DIN, µM	s.d.	#	DON, µM	s.d.	#	C:N
Groundwater											
Spodosols	C1	2760	339	26	7.68	13.17	19	49.20	25.66	25	57
	C2	1940	918	26	5.41	4.87	19	33.60	19.08	24	57
	C3	3080	559	20	4.72	1.62	13	55.96	10.87	18	56
	C4	3380	1014	23	8.50	14.84	15	59.51	12.27	18	62
	C5	3590	674	17	5.62	1.67	10	57.11	10.12	13	67
	C6	3080	303	25	7.21	11.55	19	50.89	4.19	22	61
	c7	3390	424	26	5.46	3.34	19	57.10	9.42	23	60
	average/total	2990	826	163	644	9.16	14	5098	17.35	143	59
Hydromorphic											
Oxisols	R1	531	68	18	42.40	9.80	18	40.27	9.51	7	13
	R2	200	63	18	11.92	4.77	18	15.82	2.52	6	12
	R3	202	69	18	9.18	2.09	18	9.17	1.81	7	18
	R4	229	85	18	24.20	5.31	18	15.13	4.50	6	16
	average/total	291	157	72	1.93	14.51	72	0.45	13.61	26	15
Oxisols	S1	105	64	18	21.65	6.67	18	15.63	6.68	6	10
	s2	141	105	18	30.15	5.43	18	18.89	4.74	7	13
	s3	136	111	18	56.64	10.59	18	21.02	3.15	7	7
	average/total	127	95	54	36.15	16.91	54	18.66	5.19	20	10
Streamwater											
	Campina	3170	553	26	5.16	2.24	19	53.11	6.72	24	58
	Barro Branco	371	172	24	4.44	1.58	24	13.31	1.72	12	25

Concentrations are averages; sd, standard deviation; #, number of samples analyzed.



**Figure 5:** Plot of C/N ratios in different hydrologic compartments and in the different surface organic matter pools.

marked in the hillslope Spodosols, where 76% of C occurring in the first meter of the soil profile is found in the upper 20 cm. By comparison, in the hillslope Oxisols, only 33% of C in the upper meter is found in the 0-20 cm interval. Both riparian Spodosols and Oxisols have percent C minima in the 20-40 cm interval, followed by a second percent C maxima in the 60-100 cm range. In the riparian Oxisols, percent C then drops off exponentially with depth below the 1 m mark. The riparian Spodosols have the highest overall percent C in the upper meter. Mean percent N decreases with depth in all soil types. As with percent C, the highest overall percent N values are recorded in the riparian Spodosols. Nitrogen concentrations were below detection limits at depth in the hillslope Spodosols, riparian Oxisols, and hillslope Oxisols. Mean C/N ratios in the soils are variable with depth and across soil types. Values in the Spodosols range from 13 to 48, while in the Oxisols, the range is from 19 to 57. Ratios of C/N did not vary consistently with depth or soil type.

Mean levels of extractable Fe and Al are greatest in the hillslope Oxisols, with profiles for both elements showing maxima in the 40-60 cm interval. In the riparian Oxisols, extractable Al levels range from 1.14 to 3.87% with no obvious depth trends, but extractable Fe levels are uniformly

low, with a maximum of 0.49% in the 0-20 cm interval. Mean extractable Fe levels are even lower in the hillslope Spodosols where extractable Al was virtually undetected.

Coarse sand is the dominate effective particle size class in all soils analyzed (Table 4). Upon examination under a light microscope, the majority of coarse sand-sized particles in the hillslope and riparian Oxisols appear to be aggregates of finer particles, while in the Spodosols, individual quartz crystals dominate the coarse sand fraction. Only riparian Oxisols contained appreciable amounts of disaggregated silt and clay-sized particles. Hillslope Oxisols exhibited the largest surface areas, with a maximum of  $11.16 \text{ m}^2 \text{ g}^{-1}$  in the 81-100 cm interval. The lowest surface area measured ( $0.04 \text{ m}^2 \text{ g}^{-1}$ ) was in the 41-60 cm interval of the hillslope Spodosols. Surface areas did not appear to be severely reduced by aggregation processes.

The distribution of soil OM between unbound, base-extractable, and water-extractable fractions varied somewhat as a function of soil type and position in the landscape (Figure 6). Unbound SOM accounted for greater than 75% of the total SOM in all riparian Oxisol samples and greater than 85% of the total SOM in all near Spodosol samples. In the hillslope Oxisol and Spodosol, unbound SOM remained the dominant fraction, but base-extractable SOM also accounted for a sizable portion of the total, especially at depths greater than 20 cm. Water-extractable SOM accounted for less than 5% of total SOM in all samples but was relatively more abundant in the hillslope soil cores. The percent water-extractable SOM also tended to decrease with depth relative to the percent base-extractable SOM (Figure 7). No such relationship was observed for percent water-extractable SOM versus the unbound fraction.

Elemental concentrations within the SOM fractions showed few consistent patterns with depth or between fractions (Figure 8). In the Oxisols, the unbound fraction tended to be more nitrogen poor than the water- and base-extractable fractions. This is especially apparent in the hillslope Oxisol. In the Spodosols, the water-extractable fraction was consistently enriched in nitrogen relative to the other two fractions. In the riparian Oxisol, riparian Spodosol, and hillslope Spodosol (Figures 8b, 8c, and 8d), the C/N ratio of the base-extractable fraction generally increased with depth.

Table 3. Elemental Data for Concentrates of Ultrafiltration

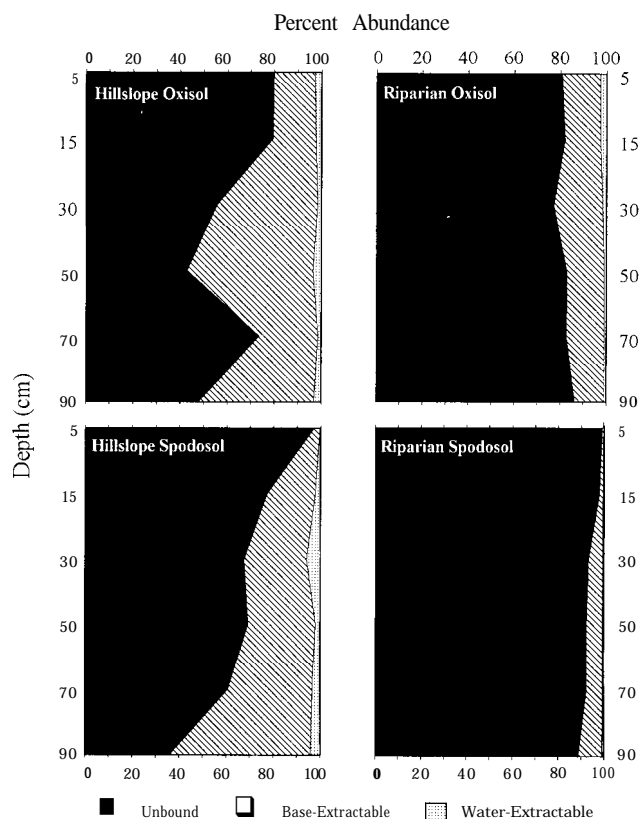
Sample	Minimum Size	Percent C	Percent N	CN	
Campina	stream	0.1 $\mu\text{M}$	46.3	0.9	59
		10,000 D	46.1	0.9	62
	groundwater	1,000 D	46.2	0.9	63
		10,000 D	41.5	1.2	39
Barro Branco	stream	1,000 D	45.4	1.1	50
		0.1 $\mu\text{M}$	32.8	1.3	28
		10,000 D	29.4	1.6	21
	fringing wetland	1,000 D	39.9	1.5	31
		0.1 $\mu\text{M}$	27.9	1.7	19
		10,000 D	27.2	1.3	24
	1,000 D				

Minimum size classes are shown. Dissolved OM concentrations in Barro Branco groundwater were so low, and yields from wells were so little, that we were not able to obtain ultrafiltration concentrates.

Table 4. Summary of Average Chemical and Physical Data for Soils in the Four Zones Investigated

Location	Depth Range, cm	Percent	C	s.d.	Percent	N	s.d.	C/N	s.d.	Ex.	Fe	s.d.	Ex. Al	s.d.	Surface Area, m <sup>2</sup> /g	Percent Coarse Sand	Percent Fine Sand	Percent Silt and Clay
Campina Riparian Spodosols	0-20	5.27	0.36	0.14	0.04	29	5											
	21-40	0.73	0.58	0.08	0.02	13	13											
	41-60	1.68	1.29	0.09	0.04	24	15											
	61-80	1.64	0.38	0.07	0.03	32	16											
	81-100	2.10	0.58	0.02			48											
Campina Riparian Spodosols	0-20	1.46	1.32	0.08	0.05	21	6			0.07			0.06		0.13	99	<1	<1
	21-40	0.29	0.24	0.04	0.05	24	21						ND			99	<1	<1
	41-60	0.06	0.07	10.01			16			0.02			ND		0.04	99	<1	<1
	61-80	0.05	0.05	<0.01						0.04			ND			96	<1	4
	81-100	0.05	0.03	<0.01						0.02			ND		4.36	99	<1	<1
	101-150	0.04	0.01	<0.01						0.06			ND			96	2	2
	151-200	0.04	0.03	co.01						0.40			ND		0.35	96	1	3
Ducke Riparian Hydromorphic Oxisols	0-20	1.15	0.61	0.06	0.03	24	3			0.49	0.18		3.37	1.14	1.94	95	4	1
	21-40	0.63	0.20	0.03	0.01	25	4			0.24	0.14		3.87	1.13		94	1	5
	41-60	0.75	0.33	0.03	0.02	33	10			0.15	0.06		3.36	1.67	2.96	98	0	2
	61-80	1.14	0.73	0.04	0.02	34	10			0.13	0.05		3.19	1.82		92	2	6
	81-100	0.97	0.79	0.03	0.01	57	14			0.14	0.14		3.26	1.66	2.14	95	2	3
	101-150	0.36	0.29	0.02		41	12			0.15			3.43			63	6	31
	151-200	0.13	0.04	<0.01						0.05			1.66		3.43	77	7	16
	201-250	0.11		<0.01						0.10			1.15			81	4	15
	251-300	0.09		<0.01						0.19			1.33			86	4	10
	301-350	0.08		<0.01						0.14			1.14			76	7	17
	351-400	0.11		<0.01						0.12			1.18			70	10	20
	0-20	0.99	0.48	0.05	0.03	25	6			4.18	1.54		4.09	1.56	5.89	98	1	1
	21-40	0.84	0.15	0.04	0.01	26	5			7.35	1.12		8.42	1.62		96	2	2
41-60	0.52	0.11	0.03	0.01	21	6			9.79	0.55		10.98	1.81	9.08	96	2	2	
61-80	0.35	0.13	0.02	0.02	27	9			8.59	0.82		8.74	0.32		96	1	3	
81-100	0.25	0.05	0.02	0.01	19	8			6.58	1.07		7.06	0.99	11.16	95	<1	5	
101-150	0.18	0.05	0.01	0.01	20	9			3.08	1.54		5.42	0.26		93	<1	7	
151-200	0.12	0.09	<0.01						1.38	1.32		3.59	1.48	10.84	93	<1	7	
201-250	0.11	0.06	<0.01						0.90	0.86		2.69	1.54		93	4	3	
251-300	0.06	0.01	<0.01						0.81	0.38		3.00	1.18		92	4	4	
301-350	0.05	0.02	<0.01						1.08	0.56		2.43	0.33		88	5	7	
351-400	0.05	0.04	<0.01						1.57	0.17		2.26	0.54		88	9	3	
401-450	0.06	0.01	<0.01							0.11		1.76						
451-500	0.07		<0.01															
501-550	0.03		<0.01															
>551	0.04		<0.01															

N.D. indicates result was below detection limits; sd, standard deviation; Ex., extractable.



**Figure 6:** Area plots of % soil organic matter fraction versus depth in the four zones investigated. Pronounced vertical trends appear only in hillslope zones where the water table lies below 1 m.

#### Live Leaf, Litter, and Root Mat Chemistry

Live leaves from the Campina site were depleted in percent N relative to those of Barro Branco (Table 5). In the root mat of the two sites, N was significantly enriched relative to

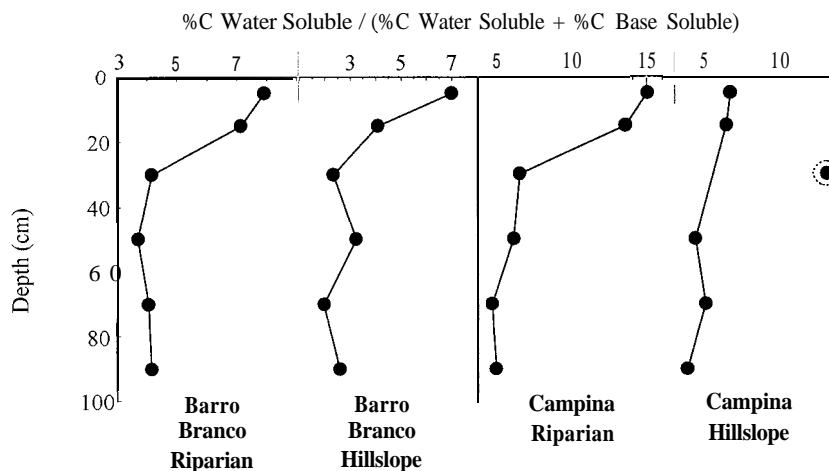
overlying litter, and at Barro Branco, root mat percent N returned to values near those of live leaves.

#### Discussion

Our results indicate that clear and persistent differences exist in the concentration and composition of DOM in waters from the Barro Branco and Campina catchments. Furthermore, these differences may be related to fundamental characteristics of the watersheds that are shared by other catchments in the region. The general pattern at Barro Branco of decreasing DOC concentrations between soilwater and groundwater beneath the hillslope and relatively elevated DOC concentrations in riparian groundwater is consistent with many previous studies from other regions [Cronan, 1990; Kaplan and Newbold, 1993], and measured concentrations are well within normally reported ranges [Thurman, 1985]. The consistently high DOC concentrations in Campina groundwater are less common but are not unlike those reported from sandy soils in other black-water regions [Meyer, 1986].

Remembering our general goal of examining terrestrial sources of OM to streams in the central Amazon, we will first discuss patterns in OM concentrations and compositions between upland, riparian, and channel zones of the two catchments. We then discuss the regional implications of these patterns by evaluating the hypothesis that the soil profile of upland forests exerts a primary control over terrestrial to lotic OM transfers and that processes operating there are largely responsible for the elemental composition of DOM and FPOM in the region's largest rivers.

The principal sources of OM in forested ecosystems are litterfall and root turnover. Litterfall deposits OM on the forest floor or directly into streams where trees overhang the channel. Litter deposited on the forest floor may be leached by infiltrating rainwater and move to streams via subsurface or surface hydrologic pathways, or, in riparian zones, litter may be blown into streams. During root turnover, dead roots decompose in the soil column or in the root mat, and root-



**Figure 7:** Plot of the ratio between % soil carbon (g/100 g soil) in the water soluble fraction and the sum of % soil carbon in the water soluble and base soluble fractions versus depth. The trend of decreasing ratios with increasing depth were observed in all four zones, while clear down-core trends were not visible when base soluble or unbound fractions were placed in the numerator. The circled point in the Campina hillslope plot is set apart because of its uniquely high ratio.

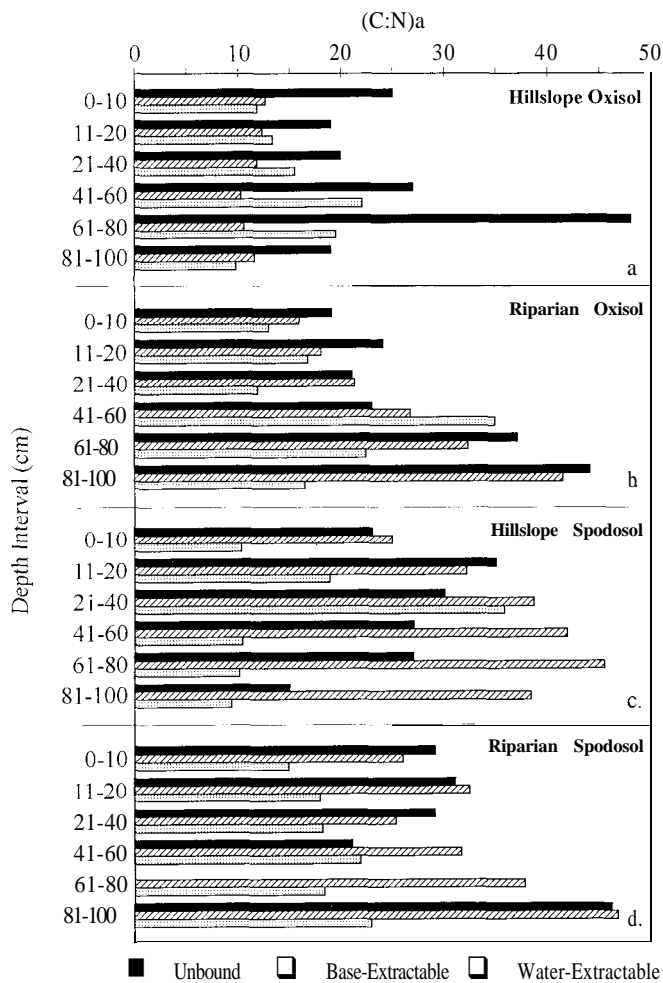


Figure 8: Bar plot of the atomic C/N ratio of soil OM fractions versus depth in the four zones investigated. Patterns and trends are discussed in the text. (a) Hillslope Oxisol; (b) Riparian Oxisol; (c) Hillslope Spodosol; and (d) Riparian Spodosol.

leached OM travels to streams only via subsurface or overland hydrologic pathways.

The majority of the landscape lies in upland areas where the only significant pathway linking forest and stream water is

rainwater infiltration and groundwater flow. In these areas, the important questions become; (1) What proportion of annual OM turnover in the forest is lost to groundwater? (2) What reactions control the concentration and composition of groundwater DOM? Furthermore, we are interested in how answers to these questions vary as a function of forest/soil type. In the riparian zone, terrestrial OM may enter the base flow of streams via groundwater, direct litterfall and litter blow in, and seepage from fringing wetlands. Because several transport pathways are active in addition to groundwater flow, terrestrial to lotic transfers of OM from riparian forests should be greater on a per area basis than are transfers from upland forests. Thus although the riparian zone represents a relatively small proportion of the central Amazonian landscape (~15%), it may contribute a disproportionately large amount of OM to streams. The relevant questions from a riverine perspective become; (1) What proportion of DOM input to the stream water derives from riparian sources? (2) How are riparian controls different from upland controls, and what are the consequences for the composition of OM input to the stream water? The following discussion addresses these questions in turn.

**Organic Matter Losses to Groundwater in Upland Forests**

Our findings, combined with data from other studies, enable us to estimate the magnitude of organic C and N losses from upland forests to groundwater at the two study sites. Upland groundwater DOC concentrations at Campina (~3000 uM) are consistently 20+ times greater than those at Barro Branco (~125 uM). Given the similarity in annual rainfall at the two sites and the lower water retention capacity of Campina soils, this difference in concentration likely translates to a similar magnitude more OM leaching loss from the campinarana forest ecosystem than from the terra firme forest ecosystem. Shuttleworth [1988] calculated that, on average, 50% of precipitation at Reserva Ducke (where Barro Branco is located) was reevaporated. If we assume a similar percent evaporation at Campina and take annual rainfall at both sites to be 2250 mm, an estimated 40 g m<sup>-2</sup> yr<sup>-1</sup> organic C is input to Campina upland groundwater, while 1.7 g m<sup>-2</sup> yr<sup>-1</sup> organic C is input to Barro Branco upland groundwater.

In order to estimate the percent loss to groundwater of organic C from Campina and Barro Branco forest ecosystems,

Table 5. Summary of Average Elemental Data for Certain Aboveground Fractions at the Two Sites

	Number of samples <sup>a</sup>	Percent C	sd	Percent N	sd	CN	sd
Live plant leaves							
Campina	11	49.7	2.5	1.6	0.5	40	12.5
BB Hillslope	1.5	47.9	3.0	2.4	0.8	25	6.7
BB Riparian	13	41.7	2.6	2.1	0.6	29	10.7
Leaf litter							
Campina	10	49.2	0.6	1.3	0.1	45	3.8
BB Hillslope	10	50.3	0.4	1.2	0.1	48	3.8
BB Riparian	10	48.6	0.4	1.4	0.1	42	1.8
Litter root mat							
Campina	11	33.4	4.5	1.3	0.2	29	1.5
BB Hillslope	--	22.1	--	1.2	--	22	--
BB Riparian	--	42.7	--	1.9	--	27	--

<sup>a</sup> a **Number** of samples applies only to elemental analyses; isotopes analyzed on selected samples. Values are averages with | standard deviation shown. Where standard deviation is not shown, it indicates that only 1 sample was analyzed. BB, Barro Branco.

we must estimate annual organic C inputs from litterfall and root turnover. Root exudates should also be considered, as they can amount to 40% of the total dry matter production of a plant [Lynch and Whipps, 1990], but we are aware of no relevant data from the Amazon or other regions of the tropics. **Franken et al. [1979]** reported annual litterfall rates averaging  $0.79 \text{ kg m}^{-2}$  in the upland terra firme forest of Barro Branco. This rate is similar to those determined in other terra firme forests of the region [Cuevas and Medina, 1986; Klinge and Rodrigues, 1968a; Luizdo, 1989]. Little information is available, however, concerning the annual turnover of roots in these forests. **Trumbore [1993]** estimated that fine root turnover in Oxisols at Reserva Ducke is equivalent to litterfall rates. She based her estimate on modeled turnover rates calculated from measurements of natural abundances of bomb  $^{14}\text{C}$  and litterfall rates taken from the study of **Klinge and Rodrigues [1968a]**. Trumbore's findings are consistent with those of **Luizdo et al. [1992]**, who also estimated rates of fine root turnover to be comparable with annual litterfall in a terra firme forest north of Barro Branco. **Luizdo et al. [1992]** based their estimates on differences between annual maximal and minimal values of fine root biomass. In consideration of these data, we estimate that the average annual input of nonliving organic matter to the soil system at Barro Branco is  $1.6 \text{ kg m}^{-2}$ , or  $0.8 \text{ kg C m}^{-2}$ . The  $1.7 \text{ g C m}^{-2}$  that arrives at the water table annually therefore represents only 0.2 % of C turnover in the forest, indicating that 99.8 % is remineralized (Figure 9).

Data for litterfall rates at the Campina reserve have not been published, but **Cuevas and Medina [1986]** measured an annual fine litterfall rate of  $0.56 \text{ kg m}^{-2}$  (standard error = .02) in a campinarana forest near San Carlos, Venezuela. Similarly, no studies have examined fine root turnover in Campina

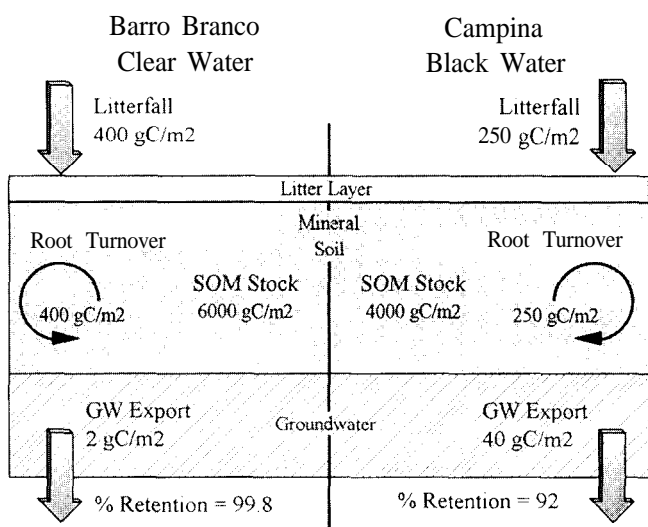
Spodosols, but **Klinge [1973]** reported 40 % less mass of fine roots in Spodosols as compared to Oxisols ( $2.8$  versus  $4.0 \text{ kg m}^{-2}$ ) in the region of our sites. If we assume that a comparable portion of fine roots turns over each year in the two soil types, fine root turnover rates in the Spodosols may be estimated as 60% of those in Oxisols, or  $0.5 \text{ kg m}^{-2} \text{ yr}^{-1}$  (which is again roughly equal to annual litterfall). By combining annual turnover rates from litterfall and fine roots, we estimate the average annual input of nonliving organic matter to the soil system at Campina to be  $1 \text{ kg m}^{-2}$ , or  $0.5 \text{ kg C m}^{-2}$ . The  $40 \text{ g C m}^{-2} \text{ yr}^{-1}$  input to Campina upland groundwater therefore represents roughly 8% of C turnover in the campinarana forest. Thus an estimated 92% of annual C turnover is remineralized (Figure 9).

Percent losses of DON in groundwater may be estimated in a similar manner. We found the N concentration of litter and roots to be approximately 1%, which is consistent with other studies from the region [Cuevas and Medina, 1986; Klinge, 1975; 1976; Klinge and Rodrigues, 1968b]. Applying this percent N to the OM input fluxes presented above, we estimate the average annual turnover of N in forest litter and roots is  $16 \text{ g N m}^{-2}$  at Barro Branco and  $10 \text{ g N m}^{-2}$  at Campina. The corresponding losses of DON to groundwater at the two sites are  $0.2 \text{ g N m}^{-2}$  and  $0.8 \text{ g N m}^{-2}$ , respectively. Thus DON losses amount to 1.2% of annual organic N turnover at Barro Branco and 8% of annual organic N turnover at Campina. Interestingly, while proportional losses of organic C from the campinarana forest at the Campina site are 40 times those of the terra firme forest at the Barro Branco site, corresponding losses of organic N differ by only a factor of 6.7. If inorganic N is considered, losses of total N to groundwater at Barro Branco and Campina are nearly identical ( $-0.85 \text{ g N m}^{-2} \text{ yr}^{-1}$ ).

Uncertainties in these estimates are not known, but clearly the vast majority of OM is remineralized, and thus the upper horizons of upland soils in both forest/soil types are a formidable barrier against OM transfers to streams. They are similar in that each conserves the majority of its OM stock within the actively cycling portion of the forest/soil terrain. However, from the perspective of inputs to stream water networks down gradient, the differences between these systems are striking.

### Controls on DOM Concentration and Composition in Upland Groundwater

The concentration of DOM in upland groundwater reflects the balance of DOM leached from the forest, forest floor, and upper soil horizons, DOM consumed by heterotrophic organisms, and DOM immobilized via sorption reactions within the soil column. The vastly different concentrations of DOM in Barro Branco and Campina upland groundwater suggest that balances of these processes differ between the sites. We have estimated that annual inputs of OM to the two catchments are similar, and we assume that leaching rates do not differ greatly between the sites (M.E. McClain unpublished data, 1993). Similarly, stores of soil organic matter at the two sites are comparable. Hillslope Oxisols at Barro Branco contain an average of  $6 \text{ kg C m}^{-2}$  in the upper meter of the soil profile, which is only 50% more than the  $4 \text{ kg C m}^{-2}$  contained in distant Spodosols at Campina. Even when considering only the water soluble fraction of organic matter



**Figure 9:** Schematic representation of estimated annual fluxes between the major organic pools of upland forests of the two catchments. Stocks of soil organic matter (SOM) are shown for the mineral soil horizons. The estimates make clear the formidable barrier imposed by the soil profile against transfers of dissolved organic matter between upland forests and stream systems.

in the upper meter of these soil types, hillslope Oxisols contain only 3 times as much organic carbon as do hillslope Spodosols (130 g C m<sup>-2</sup> versus 45 g C m<sup>-2</sup>). Thus the explanation for the factor of 20 imbalance in leaching losses between the systems most likely lies with processes removing DOM from downward percolating rainwater.

Adsorption to clay and oxide surfaces is an effective process for removing DOM from infiltrating waters. Although Oxisols and Spodosols at our study sites were dominated by sand-sized particulates, the Oxisols contained appreciably more clay, silt, Fe and Al oxides, and much greater surface areas. Even small amounts of clay (<10%) have been shown to strongly influence OM retention in soils [Oades, 1995; Christensen, 1996], and catchment soil clay content is frequently correlated with DOC levels in runoff waters [Nelson *et al.*, 1990]. Amorphous Fe and Al oxides are especially effective at binding DOM due to their variable charge characteristics [Davis, 1982; Tipping, 1981]. Thus based on soil physical and chemical data from our sites, adsorption reactions should be significantly enhanced in Oxisols of the Barro Branco catchment relative to the Spodosols of the Campina catchment.

The difference in DOM leaching losses between Barro Branco upland forests and those of Campina amounts to -40 g C m<sup>-2</sup> yr<sup>-1</sup>. Assuming that this OM is permanently removed from the dissolved phase via adsorption to soil surfaces, it should become incorporated into the base-extractable fraction of the soil OM. Hillslope Oxisols at Barro Branco contain roughly 2000 g C m<sup>-2</sup> more base-extractable OM in their upper meter than do hillslope Spodosols at Campina. This larger pool of soil OM would certainly accommodate the sorbed DOM. In fact, the enhanced DOM adsorption at Barro Branco would be scarcely detectable in the hillslope soils. Similarly, the upper meter of hillslope soils at Barro Branco contains 75 g C m<sup>-2</sup> more water-extractable soil OM than does the upper meter of distant Spodosols at Campina, so the additional DOM adsorption at Barro Branco could be accommodated in this fraction as well.

If DOM adsorption was the only process enhanced at Barro Branco, then over longer timescales, stocks of soil OM should increase, and proportional differences in soil organic matter between the two sites would approach those of groundwater DOM (i.e., 20+ times greater at Barro Branco). Assuming that soil OM stocks in the undisturbed forests of the central Amazon are at steady state, then increased DOM adsorption at Barro Branco must be accompanied by a similar magnitude of increased decomposition. Again, an additional 40 g C m<sup>-2</sup> yr<sup>-1</sup> decomposition at Barro Branco is only 5% of the estimated total annual decomposition of 800 g C m<sup>-2</sup>. Reduced levels of decomposition at Campina are consistent the hypothesis of Janzen [1974], where elevated concentrations of secondary organic compounds in trees growing on white sands were proposed to inhibit decomposition of leachate. An apparently crucial omission from Janzen's hypothesis, however, was the initial immobilization of leached organic matter by sorption onto soil clay and oxide surfaces.

Beyond the relatively large differences in upland groundwater DOM concentrations between the two catchments, notable differences in DOM nitrogen concentration were also measured. The elevated nitrogen concentrations in Barro

Branco upland groundwater (C/N ~ 10) relative to Campina upland groundwater (C/N ~ 60) run contrary to the hypothesis of Hedges *et al.* [1994], whereby DOM subjected to greater adsorptive partitioning is expected to become progressively depleted in nitrogen. Although C/N ratios of the various upland soil OM fractions at Barro Branco were quite variable, groundwater DOM appears to be generally more enriched in N. Conversely, at Campina, the upland groundwater is significantly depleted in nitrogen relative to soil OM, litter, and live vegetation.

The finding that N concentrations are lower in the DOM fraction subjected to the lesser amount of adsorptive partitioning may be partially explained by considering isotopic data from the sites in conjunction with growing evidence in the literature for direct DON uptake by plants growing on extremely leached soils [Kielland, 1994; Northrup *et al.*, 1995]. The <sup>15</sup>N (~0‰) of Campina vegetation and litter is significantly lighter than vegetation and litter from Barro Branco (~3‰) (M.E. McClain, unpublished data, 1995), suggesting that N assimilated by plants at Campina has bypassed, to some extent, nitrification and denitrification reactions which concentrate <sup>15</sup>N in the remaining NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> pools [Bards *et al.*, 1996]. Campina vegetation may take up N directly from the decomposing litter layer, most likely through associations with mycorrhizal fungi [Griffiths and Caldwell 1992]. Northrup *et al.* [1995] suggested that this bypass mechanism may be enhanced by the formation of insoluble protein-tannin complexes in the decomposing leaves. In addition to being resistant to leaching, these complexes are highly refractory to most microorganisms other than certain mycorrhizal fungi [Griffiths and Caldwell, 1992]. Although this mechanism has not been reported in the central Amazon, similarities in the edaphic conditions and plant chemistry of the campinarana forest at the Campina reserve and the pygmy pine forest studied by Northrup *et al.* [1995] support the comparison.

#### Riparian Influences and DOM Sources to Streams

The average base flow DOC concentration of the Barro Branco stream water is generally 2-5 times that of the upland groundwater that feeds it, indicating that the stream water receives significant amounts of OM from its riparian zone. Upland groundwater DOC could account for approximately 30% (100-150 μM) of stream water base flow DOC at Barro Branco if we assume it to be sufficiently soluble and refractory to pass conservatively through the riparian zone soils, which have lower surface areas and reduced levels of Fe and Al oxides. This is a conservative estimate considering that a proportion of base flow must derive from the riparian zone, thereby diluting upland groundwater inputs. By this measure, roughly 70% of DOM carried by the stream water would derive from only 15% of the catchment area.

Although riparian groundwater DOC concentrations at Barro Branco are greater than those of upland groundwater, they too are insufficient to account for DOC concentrations measured in the Barro Branco stream water base flow (Table 2). The average of the four riparian wells accounts for only 78% of stream water DOC concentrations, and when the uniquely high, average DOC concentration measured in well RI is excluded

from the riparian average, riparian groundwater accounts for only 57% of average stream water DOC concentrations. Thus it appears that an appreciable fraction of stream water DOM derives as seepage from fringing wetlands or from the leaching of particulate organic matter within the stream water channel. This condition is supported by differences in C/N between stream water base flow and adjoining groundwater. Whereas the C/N ratio of riparian groundwater DOM averaged 15, stream water DOM averaged 25, which lies between the measured C/N ratios of wetland DOM (~23) and riparian leaf litter (42). Abundances of  $^{15}\text{N}$  in stream water DOM likewise fall closer to litter and wetland sources than they do soil OM (M.E. McClain, unpublished data, 1995). No such differences were observed between groundwater and stream water DOM at the Campina site.

As in the upland forest, estimated losses of DOM from the riparian forest would amount to only a small fraction of annual C and N turnover. However, differences in the transfer pathways followed by riparian OM result in a very different quality of OM input to the stream water. Organic matter input via wetland seepage and leaf litter leaching is potentially more hydrophobic and surface reactive than DOM input via groundwater. Similarly, it is likely to be more labile and thus a more important source of energy for heterotrophic organisms in the stream water.

### Regional Implications

Our findings from Barro Branco and Campina hold several implications for interpreting the regional biogeochemical signals integrated into larger rivers of the region. Many questions surround the generalization of results from small basin studies to regional areas, and our discussion of the regional implications of our results cannot be entirely free of these concerns. However, in the central Amazon, catchments do fall into two predominant terrain types based on distinct associations of soil, vegetation, and resulting hydrochemistry. Furthermore, internal variability of these terrain types appears minimal in relation to variability between terrain types. Thus we judge our site data useful and appropriate for the following discussion.

Hedges *et al.* [1986a; 1994] proposed what is currently the most comprehensive and thoroughly developed model of processes regulating terrestrial to lotic transfers of organic matter in the Amazon basin. This "regional chromatography model" holds that compositional differences between dissolved and particulate organic matter in the Amazon's largest rivers are primarily explained by the simultaneous action of decomposition and sorption reactions in headwater soil systems. In the model, riverine dissolved and particulate OM each originate as leaf leachate at the forest floor, but selective adsorption of hydrophobic, nitrogen-rich molecules onto soil minerals during downward transport partitions the leachate into dissolved and mineral-bound fractions. The fractions are then subjected to different decompositional histories due partly to the protection afforded adsorbed molecules [Theng, 1979]. Partitioning also results in very different modes and timescales of OM mobilization into the river network, as DOM is expected to reach the river relatively quickly via groundwater base flow, while POM must be physically eroded into the system [Hedges *et al.*, 1986b].

Our results shed light on two notable components of the regional chromatography model. First is its assertion that nitrogen content is a fundamental modulating factor in partitioning leaf leachate in upland soil systems, and second is its suggestion that OM signatures are set prior to entering the river corridor. The model predicts that nitrogen concentrations should be enriched in mineral-bound soil OM relative to coexisting groundwater DOM. This is not the case at Barro Branco where the nitrogen concentrations of groundwater DOM are not significantly different from those of base-extractable soil OM (Figure 8 and Table 2). It should also be noted that the C/N ratio of groundwater DOM at Barro Branco is generally only one fifth to one third that of DOM in the region's rivers, where ratios range from 30 to 50 [Hedges *et al.*, 1994]. In the campinarana terrain, groundwater DOM is depleted in nitrogen relative to coexisting base-extractable OM, but uncertainty remains as to whether the difference is attributable to adsorptive partitioning following leaching (as called for in the model), sequestration of organic nitrogen, prior to any leaching, in highly insoluble protein-tannin complexes, or some other process not yet considered.

The regional chromatography model also predicts that the fraction of strongly bound (i.e. base-extractable) OM should decrease along soilwater flow paths, while the fraction of reversibly bound OM (i.e., water extractable) should increase [Hedges *et al.*, 1994]. Although concentrations of base-extractable soil OM did decrease exponentially with depth at Campina and Barro Branco, so did concentrations of water-extractable OM. In fact, concentrations of water-extractable OM decreased relative to those of base-extractable OM within the upper meter of all soil profiles analyzed (Figure 7). If the nitrogen-modulated partitioning reactions detailed in the regional chromatography model are operating in the upland soil systems of Campina and Barro Branco, our results suggest that they are effectively masked by more intense processes driven by microbial decomposition, direct nutrient recycling, and/or other surface processes such as ligand exchange and hydrophobic sorption. Nitrogen-modulated partitioning reactions do not appear to control OM retention in upland soil systems as hypothesized in the regional chromatography model. Furthermore, they do not appear to influence significantly the determination of which organic molecules will be lost from the system via groundwater base flow.

Our findings suggest that definitive reactions controlling compositional differences in organic matter fractions from the largest rivers of the Amazon basin do not take place in upland soil systems. This suggestion is further supported by mass balance considerations. Oxisols, and pedologically similar Ultisols, are by far the most widespread soil types in the central Amazon. In fact, these soil types cover an estimated 72% of the entire Amazon basin [Centro Internacional de Agricultura Tropical (CIAT), 1985]. Our findings demonstrate that DOC concentrations in groundwater from upland Oxisols at Barro Branco average near 100  $\mu\text{M}$ , and Williams and Melack [1997] reported equally low DOC concentrations in groundwater from Oxisols 100 km west of Barro Branco (near Lago Calado). These values are characteristic of DOC concentrations reported in groundwater from many other regions of the world [Thurman, 1985], and they are likely representative of much of Amazonia. In contrast, concentrations of DOC average between 300 and 500  $\mu\text{M}$  in

large rivers draining Oxisol/terra firme terrains [Hedges *et al.*, 1994]. Clearly, upland groundwater DOC levels are incapable of supporting large river concentrations, just as they are incapable of supporting DOC concentrations in the Barro Branco stream water. This is especially true when riverine decomposition is considered.

Consequently, a significant proportion of riverine DOM must derive from within the river corridor either via inchannel leaching of particulate OM or influxes of DOM from adjoining wetlands and floodplain groundwater. Low DOC concentrations (average 180  $\mu\text{M}$ ) in Andean Amazon rivers, where wetlands are rare, suggest that the presence or absence of wetlands is a crucial determinant in the magnitude of DOM input to streams and rivers [Guyot and Wasson, 1994; McClain and Richey, 1996]. High concentrations of DOM are input via groundwater draining Spodosol terrains, but these cover only 1.5% of the Amazon basin [CIAT, 1985] and are significant only in the Negro subbasin. Assuming that the majority of DOM carried by Amazonian rivers is derived within the corridors of lowland Amazon rivers, and given that the vast majority of suspended sediments derive from low-DOM Andean tributaries [Meade, 1985; 1994], partitioning processes detailed in the regional chromatography model should be concentrated in lowland river corridors and not in upland soil systems.

A final regional implication of our findings relates to the utility of rivers in providing integrated signals of processes occurring in their catchments. A river's organic solute and particulate loads carry detailed information about catchment processes such as photosynthesis and decomposition, nutrient cycling, and OM storage. By further illuminating the relationships between river signals and catchment processes, there is promise of one day monitoring integrated regional processes "remotely" by monitoring the biogeochemistry of rivers draining the region. Our findings suggest, however, that for streams and rivers draining terra firme forest/Oxisol terrains in Amazonia, OM biogeochemistry is biased toward riparian sources and processes, even though riparian zones compose a relatively small proportion of the landscape. This bias is not so marked in campinarana terrains where upland groundwater contributes a larger proportion of stream water DOM. Nevertheless, great care must be taken in recognizing the limits, as well as the potential, of riverborne signals as geochemical indicators of catchment processes.

## Conclusions

The investigation described here sheds considerable new light on the earliest stages in the sequence of processes leading to the production of organic matter concentrations and compositional signatures in the largest rivers of the Amazon basin. It is the first study to examine the terrestrial-lotic interface of small Amazon catchments with the expressed goal of relating processes there to biogeochemical signals integrated into larger rivers. We have delineated two very different systems, which together reflect the variability of conditions that may be encountered in the central Amazon. Our major findings are as follows.

1. Clear and persistent differences exist in the concentration and composition of DOM in the two catchments studied, and

by association, in the two principle landscape types composing the central Amazon basin. In terra firme forest/Oxisol terrains, upland groundwater DOM concentrations are uniformly low ( $\sim 100 \mu\text{M}$ ), and C/N ratios average near 10. Conversely, in campinarana forest/Spodosol terrains, groundwater DOM concentrations are greatly elevated ( $\sim 3000 \mu\text{M}$ ) and C/N ratios average near 60. Groundwater DOM inputs in the campinarana terrain can account for virtually all DOM exported in stream water base flow, while, in the terra firme terrain, upland groundwater DOM inputs are insufficient to maintain stream water DOM levels ( $\sim 350 \mu\text{M}$ ). Concentration and compositional data from the terra firme terrain suggest that between 20 and 40% of stream water DOM derives from a combination of wetland seepage and inchannel leaching of particulate organic matter.

2. Losses of OM from upland forests in groundwater represent only a small portion of total annual turnover of organic C and N in the systems. In the terra firme terrain, we estimate that groundwater losses account for roughly 0.2 and 1.2% of annual C and N turnover, respectively, while in the campinarana terrain, groundwater losses account for an estimated 8% of annual C and N turnover. When inorganic N species are considered, estimated N losses from the two terrains are nearly equal.

3. We attribute the lower percent losses of organic C and N from the terra firme terrain to coupled sorption and decomposition reactions in the Oxisol profile. Assuming that OM stocks in the two soil types are at steady state over long timescales, then the enhanced sorption and decomposition rates in the Oxisols are roughly equivalent.

4. In the terra firme terrain, of the order of 70% of DOM in stream base flow derives from the riparian zone. Riparian groundwater inputs account for between 20 and 50% of this value, with seepage from fringing wetlands and leaching of inchannel particulate OM accounting for the remainder. As a consequence, the majority of DOM exported in the stream water draining the terra firme terrain derives from a relatively small proportion of the landscape. In the stream water draining the campinarana terrain, upland groundwater transports sufficient quantities of DOM to account for the DOC concentration of base streamflow. Thus DOM in the campinarana stream water likely derives from a significantly greater proportion of the landscape.

These findings, and the detailed data incorporated into them, revise two aspects of our current hypothesis to explain the biogeochemistry of OM in the main stem Amazon and its principal tributaries (as articulated by Hedges *et al.*, 1986a; 1994). First, N had been hypothesized to directly influence the partitioning of leaf leachate between sorbed and aqueous forms in the upland soils of the basin, with elevated N concentrations favoring sorption. Our data did not support this hypothesis. Second, our findings did not support the hypothesis that DOM and particulate OM compositions are established in upland soils prior to entering the river corridor. Instead, we conclude that processes operating within the river corridor are more important in producing downstream signals. We suggest that rivers hold real promise of providing integrated signals of processes operating in their catchments, but certain aspects of our understanding must be improved in order to accurately interpret such signals.

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