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Contributions of carbon and nitrogen from the Andes Mountains to the Amazon River: Evidence from an elevational gradient of soils, plants, and river material

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Abstract

We determined the carbon (C) and nitrogen (N) elemental and stable isotopic composition of riverine and terrestrial organic matter (OM), as well as the concentration of dissolved organic C (DOC), $\delta^{15}NO_3^-$ and $\delta^{18}O$ of river water along an altitudinal (4,043–720 m above sea level [masl]) transect in the Andes of Peru. Plant $\delta^{13}C$ increased with increasing elevation, but unlike previous studies, foliar ^{13}C and %N were negatively correlated. Soil $\delta^{13}C$ values did not exhibit similar trends and were enriched by 1–3‰ over plants. Isotopically, riverine fine particulate OM (FPOM, $<60\ \mu m$) resembled soils, and coarse particulate OM (CPOM, $>60\ \mu m$) resembled leaves. Both FPOM and CPOM exhibited OM levels beyond those attributable to sorption. Percentage OC and N of soils and FPOM were positively correlated with altitude and highlight a trend of sequential downstream dilution of OM with inorganic material. FPOM began to resemble plant OM isotopically at lower altitudes, perhaps due to increased plant and surface soil inputs to lower rivers. The compositional similarity of particulate organic matter to terrestrial plants and soils indicates that the dominant processes affecting riverine OM are occurring on the landscape, not within the river. Dissolved OC ($<0.2\ \mu m$) concentration, $\delta^{15}NO_3^-$, and $\delta^{18}O$ of H_2O are variable in high-altitude tributaries but approach constant values downstream. Elemental and isotopic analyses of riverine OM suggest compositional differences between size fractions, similar to the lower Amazon; however, unlike previous studies, we have found significant within-stream changes with altitude in OM composition.

Rivers are the main means of transport of terrestrial organic carbon (OC) to the world's oceans, so an understanding of riverine C dynamics is critical to global C budgets. The Amazon River contributes about 36×10^9 kg yr^{-1} of OC to the oceans, of which about 62% is dissolved, 34% is fine particulate OC (FPOC, $<63\ \mu m$), and 4% is coarse particulate OC (CPOC, $>63\ \mu m$; Richey et al. 1990). Most of this flux is thought to be allochthonous (McClain and Richey 1996). Isotopic and biomarker OC studies in the lower Amazon have shown that coarse particulate organic matter (CPOM) is dominated by fresh plant material, and that fine particulate organic matter (FPOM) and dissolved organic matter (DOM) are more degraded (Hedges et al. 1986*a*, 2000). The organic composition of FPOM and DOM in the Amazon differs despite their presumed close interaction (Hedges et al. 1986*a*, 1994), implying different diagenetic histories. Biodegradation of fresh plant material leads to chemical alteration of OM into progressively smaller molecules, and isotopic, biochemical, and/or size fractionation of various molecules during degradation and transport is likely one control on OM distribution (Hedges et al. 2000).

The regional chromatography model was developed to explain the compositional differences in FPOM and DOM in the Amazon (Hedges et al. 1994; Devol and Hedges 2001). This model is based on observations that N-rich, hydrophobic organic molecules are more likely to be sorbed to terrestrial and riverine fine mineral particles than their N-poor, hydrophilic counterparts, which remain dissolved and are washed out of soils (Hedges et al. 1994). A laboratory study confirmed this partitioning of N during sorption (Aufdenkampe et al. 2001), and sorbed material is the majority of FPOM in the lower Amazon (Mayorga and Aufdenkampe

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2002). Evidence for the regional chromatography model suggests spatial and temporal variability in OM distribution in the Amazon, but sampling of the mainstem has failed to catch any major variations (Hedges et al. 2000; Devol and Hedges 2001). Past studies (Richey et al. 1980, 1990; Hedges et al. 1986*a*, 1994, 2000) have been modeled on the river continuum concept, which emphasizes longitudinal patterns in rivers from source to delta (Vannote et al. 1980). In contrast, small headwater streams often exhibit variable chemical characteristics because they reflect geomorphology and ecology in individual watersheds, consistent with a river discontinuum theory, recognizing the uniqueness of small streams draining dramatically different catchments and gaps in downstream patterns that occur as tributaries merge (Poole 2002). Mountain rivers are especially likely to exhibit variable biogeochemical characteristics when altitudinal changes in terrestrial ecosystems are reflected in streams.

It has been proposed that Andean headwater streams partially control OM distribution and composition in the Amazon (Richey et al. 1990; Quay et al. 1992; Hedges et al. 1994, 2000), although the Andes remain largely unstudied (McClain et al. 1995). Headwater streams may exert significant influence over C and N cycling in large rivers (Peterson et al. 2001). Consistent longitudinal patterns in mainstem OM led Hedges et al. (2000) to conclude that patterns were set in low-order headwater streams, whose variable chemical characteristics are integrated as water flows downstream. Andean tributaries are implicated as C, N, and phosphorus (P) sources because concentrations in the mainstem are often higher than in lowland tributaries (Devol and Hedges 2001). Enriched δ^{13}C values of FPOM in the mainstem, relative to local sources, have been attributed to the Andes (Quay et al. 1992). The Andes are also implicated because they are the source of the vast majority of sediments to the Amazon (Meade et al. 1985), which may carry sorbed OM and nutrients (Aufdenkampe et al. 2001).

However, many questions remain about Andean river OM sources and factors influencing its transport and eventual deposition into the ocean because no comprehensive study has been conducted to answer them. Cai et al. (1988) analyzed the δ^{13}C of Andean river particulate organic matter (POM) but not that of its potential sources. Guyot and Wasson (1994) studied DOC concentrations along an altitudinal gradient, but the highest samples were taken at 2,500 m above sea level (masl), well below the highest reaches of the Amazon. Hedges et al. (2000) studied C and N cycling in Bolivian tributaries of the Amazon, but only one high-altitude sample was taken at 3,900 masl; the next highest sample was at 430 masl. These previous sampling efforts were insufficient to capture spatial or temporal variability in concentrations and compositions of OM size fractions, which is critical to understanding how OM is transported from headwater streams to the Amazon mainstem and eventually to the ocean.

Stable isotopes are natural indicators of geochemical and ecological processes and are useful in studies requiring small sample volumes and a time lapse between sampling and analysis. Carbon-13 (^{13}C) shows an altitude effect in plants, with increasing δ^{13}C values at higher altitudes (Körner et al. 1991). Plant ^{13}C content also reflects its C source and its water-use efficiency; water stress increases δ^{13}C values (Körner et al. 1991) and its photosynthetic pathway, either the Calvin cycle (C_3), the Hatch–Slack cycle (C_4), or Crassulacean acid metabolism (CAM; Lajtha and Marshall 1994). Nitrogen-15 (^{15}N) has not been shown to vary with altitude, but the δ^{15}N of soil OM does vary with precipitation and temperature (Amundson et al. 2003), both of which may vary with altitude. δ^{15}N and δ^{13}C can also be used to assess the diagenetic history of OM (Nadelhoffer and Fry 1988). In addition, oxygen-18 (^{18}O) in river water generally becomes depleted at increasing altitude (Seigenthaler and Oescheger 1980).

In order to investigate these concepts, we conducted a field study of the Pachitea River basin in the Andean Amazon of Peru in July of 2002. The purpose of this study was to determine OM inputs into Andean streams, identify OM sources and factors controlling its transport, and survey trends in C and N concentrations and δ^{13}C and δ^{15}N of plants, soils, and suspended and dissolved OM. More specifically, this study addresses the question of how the composition and concentration of different OM reservoirs vary in the rivers of the Peruvian Amazon and whether these patterns are variable or conservative as streams flow into larger rivers downstream.

Study area

All samples were collected during July 2002. Samples were taken in the Huancabamba, Chontabamba, and Santa Cruz River watersheds in the central Andes of Peru (Fig. 1). Sampling began just east of the Huagaruncho range (5,879 masl) in the Amazon drainage. Site elevations ranged from 4,043 masl to 720 masl (Table 1). Highest elevation sampling was conducted above the tree line in the Santa Cruz and Huancabamba valleys. Samples were collected at midelevations on the Chontabamba River, and lowest elevation samples were taken from the Santa Cruz and Huancabamba Rivers near the town of Pozuzo (Fig. 1).

Methods

Sampling—River water for particulate analysis was collected from the edge of the stream in a 1-liter polycarbonate bottle and filtered immediately, taking care to agitate the bottle before pouring to ensure particulate resuspension. Water for CPOM collection was filtered through preweighed, 47-mm-diameter, 60-μm-pore–size Millipore™ nylon filters. The filtrate was then filtered through precombusted, preweighed, 50-mm-diameter, 0.7-μm-pore–size Whatman™ glass-fiber filters using a hand-operated vacuum pump to isolate FPOM. Filters were kept in 50-mm-diameter Petri dishes. At the end of sampling, filters were dried at 40°C at the Andean Amazon Research Station in Oxapampa (Fig. 1). Unfiltered water for δ^{18}O analysis was collected in 20-ml glass vials with polycarbonate cone tops. This water was carefully contained without headspace gas by filling and capping the bottles underwater. Water for DOC analysis was filtered on site through 0.2-μm nylon syringe filters into precleaned, precombusted 20-ml glass vials containing 20 μl

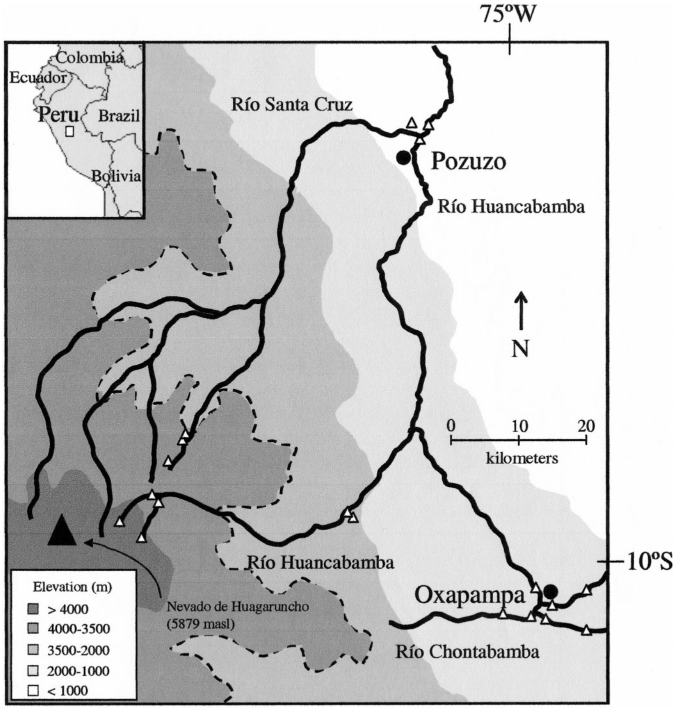

Fig. 1. Map of the study area, including areas of intense sampling (white triangles) and names of major rivers and towns. The dotted line indicates the position of the tree line. Large black triangle indicates the location of the highest mountain in the range (5,879 masl). Inset shows location within northwestern South America.

H_2SO_4. Water for $\delta^{15}NO_3^-$ analysis was syringe filtered into precleaned, precombusted, 40-ml amber borosilicate vials containing 40 μl of H_2SO_4. The first 10 ml of all syringe-filtered water was discarded to prevent contamination from the syringe filter. All bottles were capped and sealed on the outside with Parafilm™.

Six soil samples were collected at each location, three at the riparian zone, not more than 1 m from the stream, and three about 100 m uphill, perpendicular to the stream. Soils were collected from three approximate depths: the surface below vegetation, 10 cm, and 20 cm. Soils were placed in precombusted, 40-ml amber borosilicate vials. Leaves from the most abundant (by visual inspection) plants were also collected from each subsite at each sampling location. Small pieces of living, not visibly diseased or damaged leaves, were removed and placed in precleaned, precombusted, 40-ml amber borosilicate vials. Because most sampling sites were remote, it was impossible to dry all plants, soils, and filters immediately, but all were kept dark and cool until arrival at the field station, when they were placed into an oven at 40°C.

Sample analyses—Dried particulate samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ and mass %C and %N on a Carlo Erba NC 1500 elemental analyzer coupled to a Finnigan MAT DELTA plus continuous-flow isotope ratio mass spectrometer. Carbonates were removed from soils and river particulates prior to $\delta^{13}C$ analysis by vapor-phase acidification with HCl for 24 h followed by drying at 40°C for 24 h (Hedges and Stern 1984). Inorganic C was, on average, 2.5% of soil C, based on %C measurements before and after acidification. Neither particulate samples for $\delta^{15}N$ analysis nor plants were acidified. Fine particulates on glass-fiber filters were analyzed directly on the elemental analyzer; coarse particulates were washed onto glass filters. Glass–fiber-filter results were corrected for the filter blank.

Acidified water samples were neutralized with NaOH prior to $\delta^{15}NO_3^-$ analysis with the denitrifier method (Sigman et al. 2001). Nitrous oxide produced by this method was analyzed on a Finnegan MAT DELTA plus with a ThermoFinnegan Trace GC and a PreCon interface. DOC was analyzed on a Shimadzu TOC Vcsh analyzer. The $\delta^{18}O$ of H_2O was measured by CO_2 equilibration at the Jackson School of Geological Sciences at the University of Texas at Austin. C, N, and O stable isotope ratios are reported as $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$ relative to the Vienna Pee Dee Belemnite, atmospheric N_2, and Vienna Standard Mean Ocean Water standards, respectively.

Data analysis—Location and elevation at each sampling location were recorded using hand-held global positioning satellite units. Results for plants and soils were averaged for each site; all trends shown are representative of the full data set. Plant data shown are for C_3 plants only; plants for which $\delta^{13}C$ indicated a C_4 pathway ($\sim -10‰$) were not included in our calculations. C_4 plants were scarce (5 out of 68) and were found only at sites below 2,400 masl. Statistical significance of correlations was determined using critical values of r^2. A correlation was considered significant after a two-way regression analysis if the p value was 0.05 or below. Averages are expressed as plus or minus the standard deviation (±SD).

Results

Plants—Plant $\delta^{13}C$ values were positively correlated with altitude ($r^2 = 0.3029$, $p < 0.02$, $n = 20$; Fig. 2A); the average $\delta^{13}C$ of leaves from all sites was $-28.2‰ \pm 1.8‰$. $\delta^{15}N$ of plants showed no significant trend with altitude ($r^2 = 0.0007$), with an average $\delta^{15}N$ of $1.1‰ \pm 2.1‰$ (Fig. 2B). Percentage N of leaves was negatively correlated with altitude ($r^2 = 0.4477$, $p < 0.002$, $n = 20$; Fig. 2D). Percentage C was not correlated with altitude ($r^2 = 0.0007$; Fig. 2C). $C:N_{molar}$ of plant leaves was negatively correlated with altitude ($r^2 = 0.4568$, $p < 0.002$, $n = 20$; Fig. 2E). Mean $C:N_{molar}$ of plants was 24.7 ± 8.7.

Soils—Stable isotope content of soils did not vary with altitude: neither $\delta^{13}C$ ($r^2 = 0.0581$) nor $\delta^{15}N$ ($r^2 = 0.0577$) of soils is correlated with altitude (Fig. 3A,B). Soils were more enriched than plants in both ^{13}C and ^{15}N. The average $\delta^{13}C$ of all soils sampled was $-24.4‰ \pm 1.9‰$ and the average $\delta^{15}N$ was $4.3‰ \pm 1.6‰$. Soils had greater OM content at higher altitudes. Percentage C in soils was positively correlated with altitude ($r^2 = 0.5477$, $p < 0.001$, $n = 20$), as was %N ($r^2 = 0.3951$, $p < 0.005$, $n = 20$; Fig. 3C,D). $C:N_{molar}$ was positively correlated with altitude ($r^2 = 0.2616$, $p < 0.05$, $n = 20$; Fig. 3E). $C:N_{molar}$ of soils was markedly

Table 1. Locations, names, and elevations of sampling sites in this study, with water characteristics as determined for each site.

Site	Altitude (masl)	Latitude (°S)	Longitude (°W)	DOC (mg L^{-1})	δ^{15}N of NO_3^- (‰)	δ^{18}O of H_2O (‰)
Río Lecma, near lake source	4,043	10°27′52.4″	76°6′39.4″	1.3	5.6	−14.2
Río Muñapampa, lake source	4,016	10°30′0.7″	76°8′1.6″	1.3	2.6	−13.7
Río Muñapampa, 5 July 02	3,797	10°27′52.4″	76°9′15.5″	1.6	5.1	−13.2
Río Muñapampa, 9 July 02*	3,797	10°27′52.4″	76°9′15.5″	2.6	2.4	−12.7
Río Lecma, high altitude	3,780	10°27′37.0″	76°9′13.6″	1.3	6.3	−13.2
Río Galvez, near source*	3,749	10°25′59.1″	76°11′15.0″	4.7	n/d	−10.8
Río Lecma, midaltitude	3,562	10°28′6.2″	76°11′11.9″	3.2	3.8	−12.0
Río Ramos*	3,500†	n/d‡	n/d	2.4	2.0	−11.3
Stream entering Río Ramos*	3,488	10°24′15.2″	76°10′47.0″	1.3	4.4	−12.2
Bog draining into Río Galvez*	3,433	10°23′54.7″	76°11′28.4″	0.7	3.6	−12.4
Río Galvez at treeline*	3,433	10°23′54.7″	76°11′28.4″	2.8	2.9	−11.6
Confluence of Ríos Galvez and Ramos	3,400†	n/d	n/d	2.8	1.4	−11.5
Río Galvez during storm*	3,360	10°23′37.8″	76°11′10.5″	6.1	4.0	−10.6
Río Lecma, low altitude*	2,760	10°29′39.9″	76°14′57.5″	3.8	3.6	−12.5
Río Muspes*	2,422	10°31′6.1″	76°16′36.4″	3.8	4.3	−12.1
Río Llamaquizu	2,394	10°37′26.3″	76°42′16.0″	4.6	n/d	−10.5
Río Huaylamayo*	2,387	10°30′55.4″	76°16′49.3″	1.1	5.2	−12.0
Río Churumazu, high altitude	2,200	10°38′11.8″	76°32′24.2″	n/d	n/d	−10.2
Río Churumazu, low altitude	1,908	10°36′43.8″	76°33′4.2″	n/d	4.2	−9.7
Río San Alberto	1,867	10°34′38.8″	76°36′27.8″	2.2	n/d	−10.8
Río Chontabamba, high altitude	1,854	10°36′1.8″	76°33′25.5″	n/d	3.5	n/d
Río Chontabamba, midaltitude	1,830	10°34′4.9″	76°35′12.4″	1.8	n/d	−10.5
Río Huancabamba, upstream of Pozuzo	1,756	n/d	n/d	n/d	3.8	−10.4
Río Chontabamba, low altitude	1,752	10°26′1.4″	76°28′55.4″	1.9	4.7	−10.6
Río Huancabamba, above Chontabamba	1,715	10°24′0.5″	76°26′36.0″	1.4	n/d	−11.6
Río Huancabamba, below Pozuzo	764	10°6′4.9″	76°27′28.7″	1.1	n/d	−10.3
Río Santa Cruz, above Huancabamba	720	10°2′32.0″	76°27′33.4	n/d	3.8	−10.8

* Sample was collected during a storm event.
† estimated altitude, GPS not available.
‡ n/d, not determined.

different from that of aboveground biomass, averaging 11.8 ± 3.7 (Fig. 2E). Percentage C and N in soils were well correlated with each other ($r^2 = 0.8107$, $p < 0.001$, n = 20; Fig. 3F), but with a positive y-intercept at 0.04 %N. The slope-derived C : N of soils was 15.3 (Fig. 3F).

Suspended particulates—δ^{13}C and δ^{15}N show that FPOM more closely resembled soils than plants. The δ^{13}C of FPOM was positively correlated with altitude ($r^2 = 0.2687$, $p < 0.02$, $n = 20$; Fig. 4A), with the average for all sites being −25.3‰ ± 2.3‰. δ^{15}N of FPOM was not correlated with altitude ($r^2 = 0.1189$; Fig. 4B), and the average was 3.6‰ ± 0.9‰. Percentage C of fine suspended sediments (FSS) was positively correlated with altitude ($r^2 = 0.4017$, $p < 0.01$, $n = 17$; Fig. 4C), as was %N ($r^2 = 0.5585$, $p < 0.001$, $n = 18$; Fig. 4D). There was no correlation of $C : N_{molar}$ of FPOM with altitude ($r^2 = 0.0256$; Fig. 4E), with an average value of 10.6 ± 5.7. Percentage C and N of FSS were well correlated with each other ($r^2 = 0.8127$, $p < 0.001$, $n = 17$; Fig. 4F), but with a positive y-intercept at 0.12 %N. The slope-derived C : N of FPOM was 12.5 (Fig. 4F). There was a significant inverse logarithmic relationship (as initially expressed in Meybeck 1982) between %OC in fine sediments and the total fine-sediment load ($r^2 = 0.5962$, $p < 0.02$, $n = 15$).

On the other hand, the elemental and isotopic composition of CPOM more closely resembled that of fresh leaves than soils. Some trends are not statistically significant for CPOM because the sample number was reduced by a lab accident. δ^{13}C of CPOM had a positive, although statistically insignificant, relationship with altitude ($r^2 = 0.1191$), and the average was −26.6‰ ± 1.1‰ (Fig. 5A). The δ^{15}N of CPOM is positively correlated with altitude ($r^2 = 0.7548$, $p < 0.05$, $n = 6$), with an average value of 1.9‰ ± 2.1‰ (Fig. 5B). Percentage C of coarse suspended sediments (CSS) is positively correlated with altitude ($r^2 = 0.4157$, $p < 0.05$, $n = 12$), although %N is not (Fig. 5C,D). $C : N_{molar}$ was not correlated with altitude. The average $C : N_{molar}$ of CPOM was 16.7 ± 7.6 (Fig. 5E). Percentage C and N of CSS were more poorly correlated ($r^2 = 0.5485$) than those of soils and FSS. There was no significant logarithmic relationship between %OC in coarse particulates and total CSS ($r^2 = 0.0933$), to be expected in a size class strongly influenced by plant litter, not mineral grains.

Dissolved components—Dissolved OC concentrations in rivers were not correlated with altitude ($r^2 = 0.0124$; Table 1). The overall average DOC concentration was 2.4 ± 1.4 mg L^{-1}. DOC concentrations were more variable in streams above 3,000 masl (average 2.5 ± 1.5 mg L^{-1}) and approached the average value in lower altitude rivers (average 2.3 ± 1.1 mg L^{-1}). δ^{18}O of H_2O was negatively correlated with altitude ($r^2 = 0.482$, $p < 0.001$, $n = 22$; Table 1). River δ^{18}O was more scattered above 3,000 masl (average −12.3‰

± 1.2‰) than below (average −10.9‰ ± 0.8‰). The $\delta^{15}NO_3^-$ varied between 1.4‰ and 6.3‰ and was not correlated with altitude ($r^2 = 0.0007$; Table 1). The average $\delta^{15}NO_3^-$ was 3.8‰ ± 1.2‰, which was closer to that of FPOM (3.6‰) and soils (4.3‰) than plants (1.1‰). $\delta^{15}NO_3^-$ was more scattered above 3,000 masl (average 3.7‰ ± 1.4‰) than below (average 4.1‰ ± 0.5‰).

Discussion

Our results reveal distinct shifts in the biogeochemistry of riverine organic matter between 4,000 and 700 masl, indicating that processes operating in this zone of the Andean Amazon are instrumental in determining the biogeochemistry of organic matter observed in lower reaches of the river system. The following discussion is divided into three sections. The first identifies and discusses downstream or altitudinal patterns in the data. The second considers whether these patterns are useful in tracing sources of organic matter to Andean rivers and, ultimately, to the Amazon River as a whole. These are pertinent questions to the study of the organic geochemistry of the Amazon, and in answering them, this discussion incorporates patterns seen and questions raised in the past 40+ years of research in the Amazon. The final section attempts to place the results of this study within an appropriate conceptual framework.

Altitudinal distributions—Previous montane plant studies have shown increasing $\delta^{13}C$ with increasing altitude, attributed to an increase in carboxylation efficiency at altitude that decreases the ratio of internal to atmospheric CO_2 (p_i/p_a) (Körner et al. 1991). Plants in this study follow this trend (Fig. 2A). Several studies report a concurrent increase in leaf N with altitudinal $\delta^{13}C$ increases (Morecroft et al. 1992; Sparks and Ehleringer 1997), attributed to an increase in N-rich, C-fixing enzymes, such as ribulose 1,5-biphosphate carboxylase (RuBP carboxylase) at altitude (Hultine and Marshall 2000). However, the plant data in the current study do not have the same relationship (Fig. 2D), and, in fact, $\delta^{13}C$ of plants is significantly negatively correlated with leaf %N ($r^2 = 0.4371$, $p < 0.002$, $n = 20$), suggesting that different processes may control plant C and N in this region.

Besides enzyme content, other factors may influence leaf %N, such as soil N availability and species composition. Venezuelan trees showed no change in %N with increasing altitude, attributed to lower N availability in upland soils (Diaz et al. 1996). Alternate explanations for the variation in $\delta^{13}C$ of plants include water stress, variations in atmospheric CO_2 content, and species composition. Water stress can increase $\delta^{13}C$ (Körner et al. 1991), and precipitation decreases at altitude in the Andes (Mayorga and Aufdenkampe 2002). It is possible that ambient CO_2 does not vary conservatively with atmospheric pressure because CO_2 levels in forested areas are higher than in watersheds above the tree line; this may be an alternate explanation for our trend of increasing foliar $\delta^{13}C$ with altitude. Furthermore, foliar $\delta^{13}C$ does not always increase with altitude: Diaz et al. (1996) found that C_3 trees in the Venezuelan Andes were not ^{13}C enriched at altitude. Species composition can also affect $\delta^{13}C$: Functional grouping of life forms is often a better predictor of altitudinal patterns of $\delta^{13}C$ than p_i/p_a (Brooks et al. 1997). This is likely to be the case in this study because a visible transition in plant ecosystems was observed down the mountain. If a change in plant functional groups, not an increase in RuBP carboxylase content, is the cause of the altitudinal $\delta^{13}C$ trend, this may explain why leaf $\delta^{13}C$ is negatively correlated with leaf N.

Neither $\delta^{13}C$ nor $\delta^{15}N$ of soils exhibited an altitudinal gradient (Fig. 3A,B). Previous studies of altitudinal trends in soil $\delta^{13}C$ have found patterns mirroring those of plants (Bird et al. 1994). In natural terrestrial ecosystems, soil OM typically is either derived from plants growing above or from root, microbial, and/or fungal biomass growing in the soils (Ehleringer et al. 2000). Plant degradation, root inputs, and microbial growth can lead to ^{13}C- and ^{15}N-enriched soils, and the dominant mechanism controlling soil isotope ratios is uncertain (Lehmann et al. 2002). Sorption can also influence the isotopic composition of POM (Aufdenkampe et al. 2001). Studies have shown that fine roots are often enriched in ^{13}C and ^{15}N with respect to leaves (Kitayama and Iwamoto 2001; Hobbie et al. 2002), and preliminary data from another study site in the region confirm this (data not shown). Soils collected for this study are 1–3‰ more enriched in ^{13}C and ^{15}N than leaves. Also, the C : N of soils (11.3) indicates that they are a mixture of plant and microbial sources because microbial biomass has a C : N from about 5–8 and plant material C : N is ~24. Unlike plant leaves, soil C : N decreased at lower altitudes (Fig. 3E), possibly indicating a greater microbial component in low-altitude soils or faster decomposition rates at lower altitudes. Regardless of mechanism, the isotope shift between plants and soils is a potential indicator of riverine OM sources.

Past changes in plant populations and soil contributions from mass-movement processes can potentially complicate the interpretation of soil patterns. Although soils are often derived from past plant populations, there is no evidence (isotopic or otherwise) that there has been a major shift in vegetation coverage in this area. Alluvial soil contributions are often important to riparian ecosystems, but no isotopic or elemental differences were found between riverbank soils and those located 100 m away from the river. Belowground recycling of root biomass may also be a significant source of OM in these soils. Soil formation is also dependent on underlying geology. Rocks underlying the study area are mostly late Permian granites and granodiorites (Instituto Geologico, Minero y Metalurgico 1996). Old sedimentary rocks containing kerogen can be a source of OC in soil formation (Hedges and Oades 1997), but the igneous rocks found in this study area are unlikely to be a significant OC source. However, geology and sediment transport are very poorly studied in this area, and a better understanding of these processes will be necessary in the future to better constrain Andean sources of OM to the Amazon.

Unlike plants, %C and %N of soils sampled in this study are both significantly positively correlated with altitude (Fig. 3C,D), indicating higher organic : mineral ratios with increasing altitude. Increases in soil OM degradation are usually accompanied by a decrease in %OC and %N (Nadelhoffer and Fry 1988). Soil stable-isotope signatures also support this hypothesis. Our data indicate that soil OM at

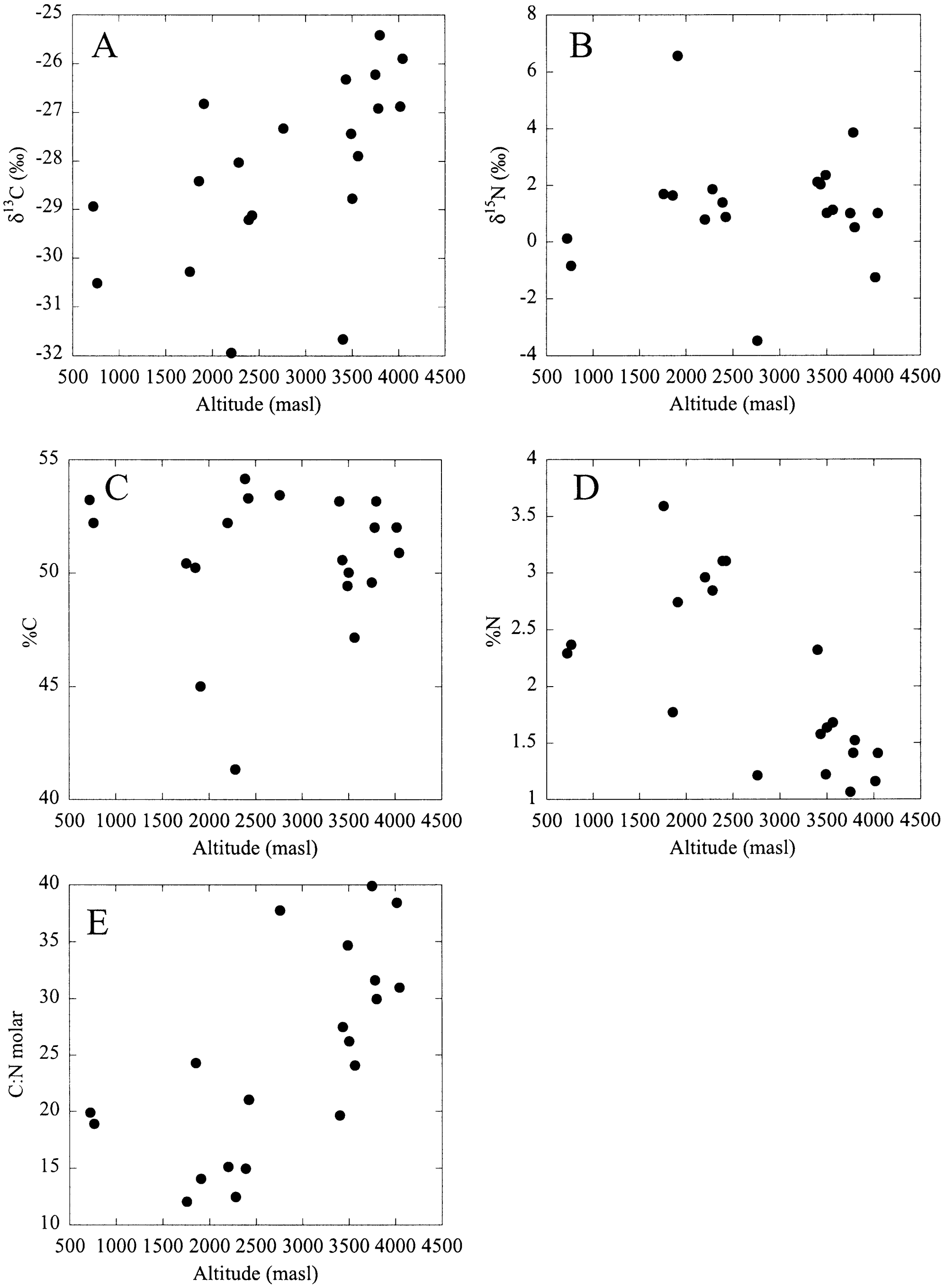

Fig. 2. Elevational trends of (A) $\delta^{13}C$, (B)$\delta^{15}N$, (C) %C, (D) %N, and (E) molar C : N of plant leaves collected during this study. Each point represents an average value for all plants (riparian and upland) sampled at that station.

higher altitudes was closer in isotopic composition to plants and thus less degraded than soils at lower altitudes. Increasing dampness and lower temperatures at higher altitudes likely slow decomposition rates (Batjes 1996; Coûteaux et al. 2002). Peat soils (found at our highest altitude sites) are often OC rich and minimally degraded (Batjes 1996). Thus, the combination of elemental and isotopic comparisons between soils and plant leaves supports the hypothesis of a soil decomposition gradient in the Peruvian Andean Amazon.

All the dissolved parameters measured in this study have more scattered distributions at higher altitudes and approach averages at lower altitudes, demonstrating the integrating effect of rivers and indicating that adjacent headwater streams can have dramatically different geochemical characteristics. The same trend can be seen in isotopic and elemental composition of FSS (Fig. 4). Because high altitude samples represent smaller catchments, small differences in ecosystem C, N, and H_2O cycling can lead to large differences in the

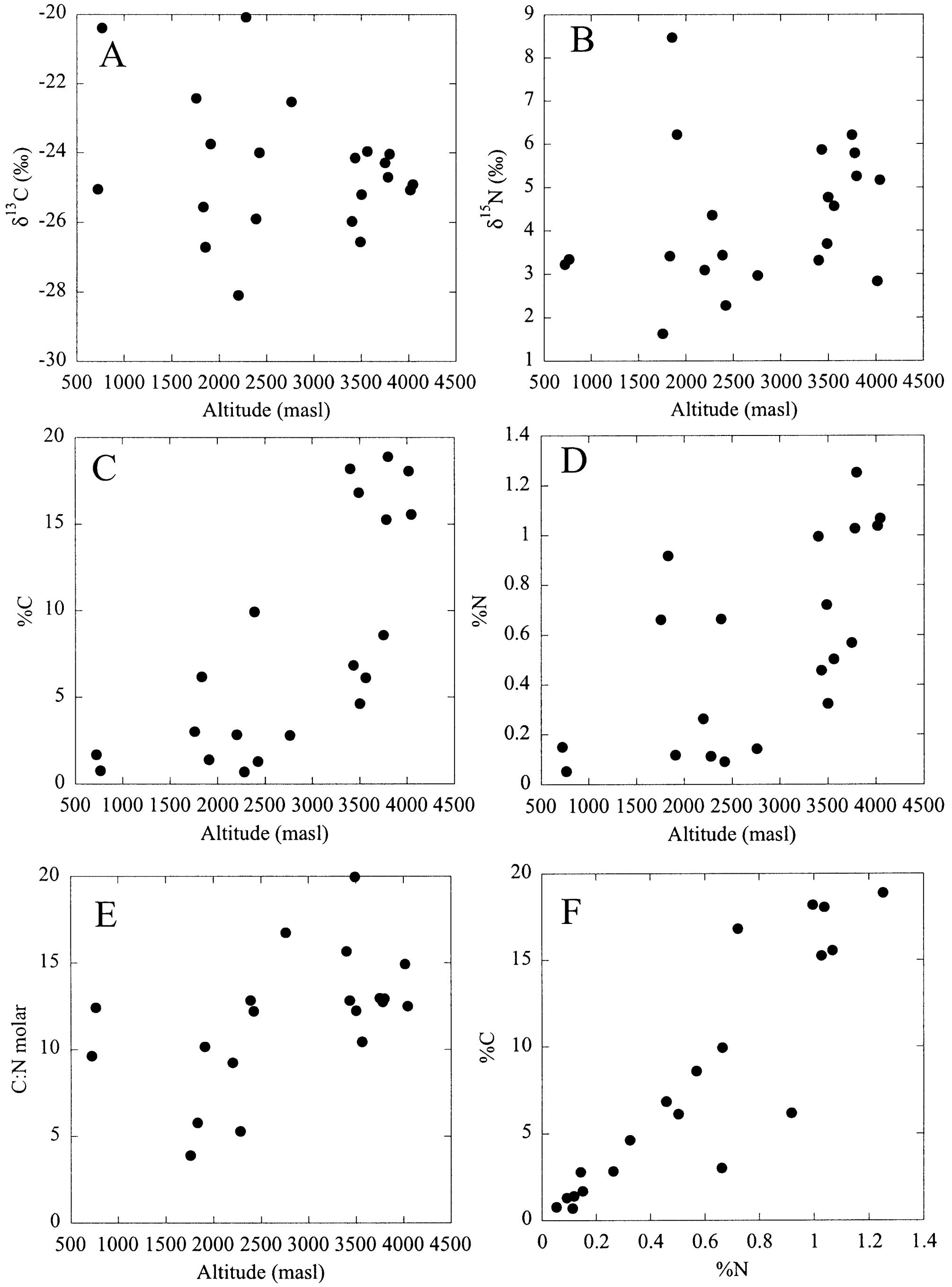

Fig. 3. Elevational trends of (A) δ^{13}C, (B) δ^{15}N, (C) %C, (D) %N, and (E) molar C : N of soils collected during this study. Each point represents an average value for all soil horizons sampled at that station. Weight percent of carbon versus weight percent of nitrogen of soil samples is shown in (F).

chemical composition of exported water. Dissolved organic carbon concentrations in this study ranged from 0.7 to 6.1 mg L^{-1} (Table 1). Previous studies found concentrations in the Andes to range from ~1 to 2 mg L^{-1} (Guyot and Wasson 1994; Hedges et al. 2000), although one of these studies did not sample above 2,500 masl (Guyot and Wasson 1994) and the other had only one sample above 450 masl, at 3,900 masl (Hedges et al. 2000). And Guyot and Wasson (1994) found that DOC concentration increased at approximately 200 masl, where the topography flattened and wetlands appeared along the channels to a mainstem average of 5 mg L^{-1} (Richey et al. 1980, 1990). In contrast, the current study shows no significant trend of downstream DOC enrichment (Table 1), and the highest concentrations are found in high-altitude streams draining peat soils. This is in sharp contrast with other high-mountain river studies, where DOC is usually

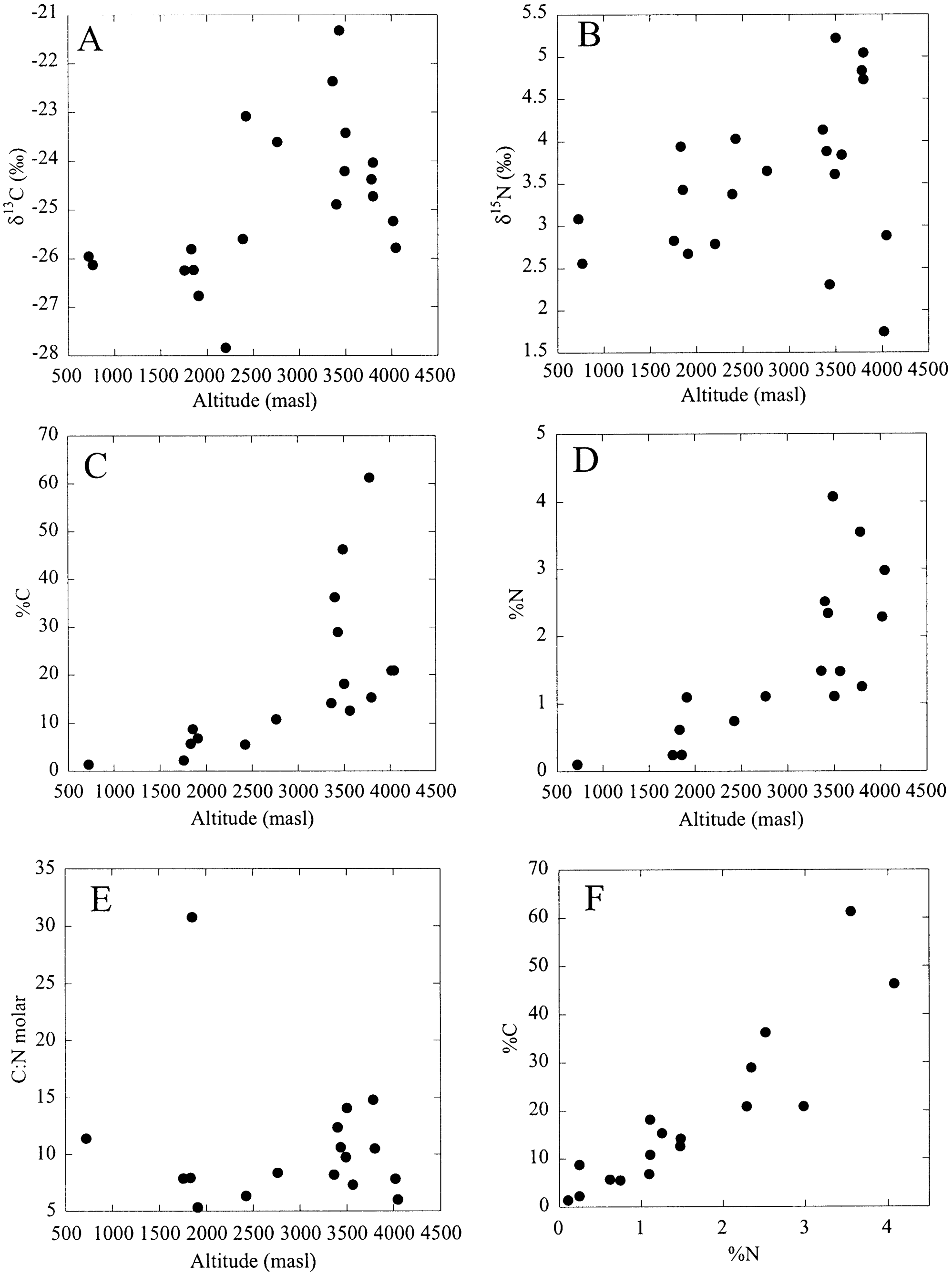

Fig. 4. Elevational trends of (A) $\delta^{13}C$, (B) $\delta^{15}N$, (C) %C, (D) %N, and (E) molar C : N of fine POM (>0.2 μm, <60 μm) collected from rivers on glass-fiber filters during this study. Weight percent of carbon versus weight percent of nitrogen of fine particulate samples is shown in (F).

among the lowest concentrations in the world (Meybeck 1982; Hedges et al. 2000), but most of these studies were conducted at higher latitudes, where organic-rich peat soils do not occur at very high altitudes. Also, our high-altitude samples were taken from small headwater streams, where the importance of stream order on riverine biogeochemistry is magnified during storm events, when runoff is generated rapidly in small streams but delayed in larger rivers (McGlynn and McDonnell 2003). DOC concentrations in this study were affected by the amount of precipitation (Table 1) as well as ecological and topographical differences between watersheds.

River water $\delta^{18}O$ values become enriched downstream, as expected, except that isotopically heavy rains during sample collection weaken the correlation. In general, the highest $\delta^{18}O$ values occurred when rainfall was heaviest, due to an enriched rain or runoff source. Stream ^{18}O is positively correlated (although insignificantly) to DOC concentration (r^2

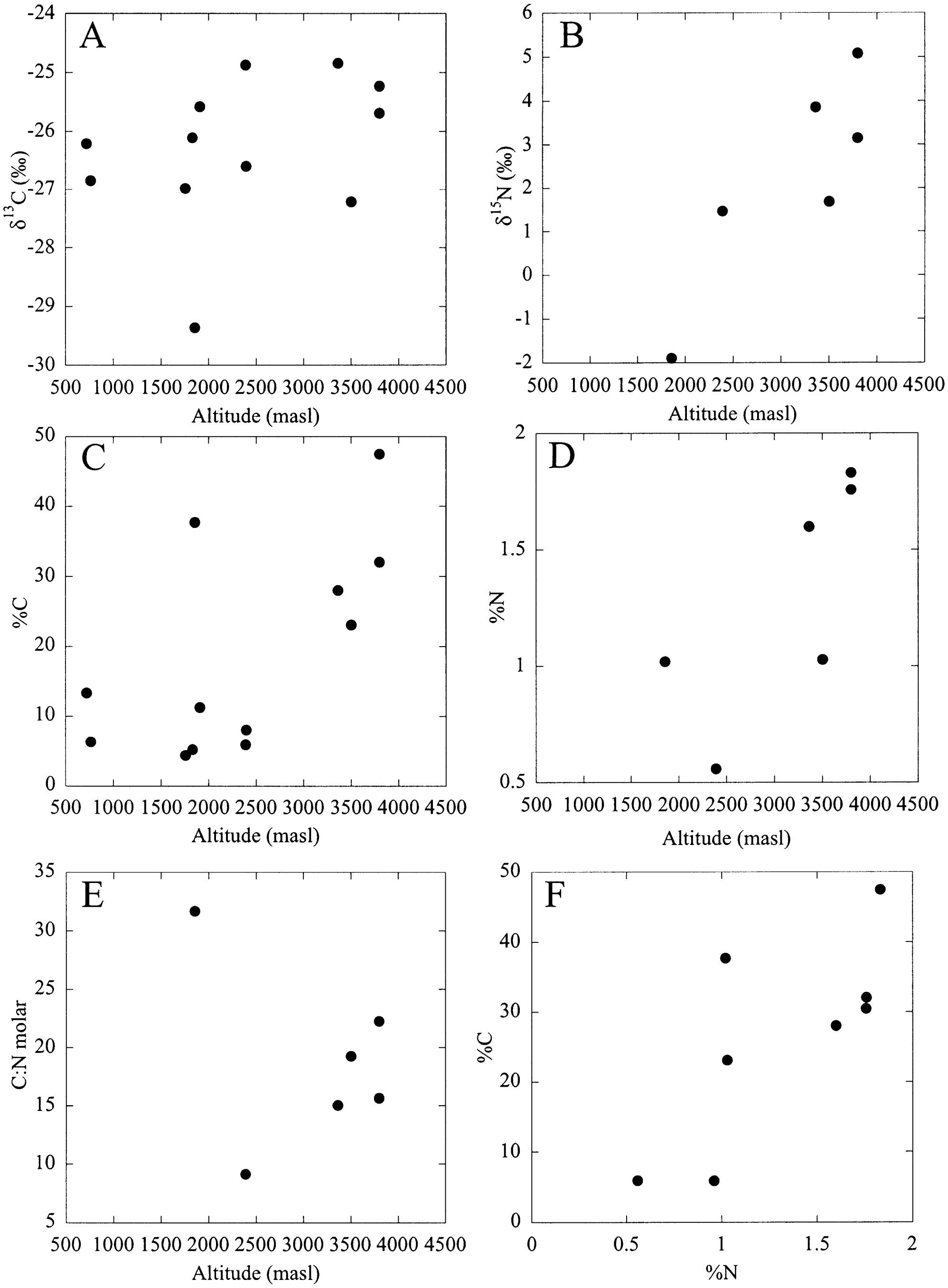

Fig. 5. Elevational trends of (A) δ^{13}C, (B) δ^{15}N, (C) %C, (D) %N, and (E) molar C : N of coarse POM (>60 μm) collected from rivers on nylon filters during this study. Weight percent of carbon versus weight percent of nitrogen of coarse particulate samples is shown in (F).

= 0.1687), raising the possibility that storm events contribute to loading of OC-rich, isotopically heavy soil waters, especially in small, low-order streams.

The average $\delta^{15}NO_3^-$ in this study is 3.8‰ ± 1.2‰, close to that measured in the Amazon mainstem at Manaus (4.1‰ ± 0.3‰; Brandes and Devol 2002). Nitrate concentrations in the mainstem are controlled by river-floodplain interactions and in-channel processes (Devol et al. 1995; McClain et al. 1997). However, mechanisms controlling NO_3^- concentrations in upstream tributaries are unknown. However, remineralization of organic N and uptake of dissolved inorganic nitrogen by heterotrophic microbes is likely significant; in fact, Brandes et al. (1996) found that in-stream remineralization of organic N was the most likely source of NO_3^- to a small stream in the lower Amazon. Overall $\delta^{15}NO_3^-$ values in this study are also consistent with a soil or POM (~4%) mineralization source, although values are not significantly correlated with each other (δ^{15}N of FSS vs.

NO_3^- $r^2 = 0.0077$; $\delta^{15}N$ of soil N vs. NO_3^- $r^2 = 0.0367$). Nitrate may be isotopically lighter than POM at a site due to incomplete oxidation, a rainwater NO_3^- source, or the presence of N_2 fixation, whereas an enriched NO_3^- pool may have been subjected to fractionation such as during denitrification or uptake (Brandes et al. 1996).

Tracers of riverine OM sources—$\delta^{13}C$, $\delta^{15}N$, and $C:N_{molar}$ of FPOM (Fig. 4) are similar to those of soils (Fig. 3), supporting the hypothesis that soils are the predominant source of C in these rivers. Phytoplankton growing in the Andean Amazon have an estimated $\delta^{13}C$ of −33‰ to −55‰ (Cai et al. 1988), which, when compared with the average $\delta^{13}C$ for both FPOM (−25.3‰) and CPOM (−26.3‰), indicate that algae is a minor component in these rivers. Also, undisturbed lowland Amazonian streams are thought to have virtually no in situ photosynthesis (McClain and Elsenbeer 2001). FPOM $\delta^{13}C$ and $\delta^{15}N$ are more enriched than plants but are similar to soils. Isotopic analyses as well as relatively high %C compositions at lower altitudes indicate that CPOM may be less degraded or altered from plant sources as compared with FPOM (Fig. 5). $\delta^{13}C$ values of CPOM are intermediate between plants and soils, and the low average $\delta^{15}N$ of CPOM strongly resembles a plant source. In the lower Amazon, CPOM has chemical characteristics between those of plants and soils, and the original OM source is mainly leaves (Hedges et al. 1986*a,b*, 2000). Previous studies of the Amazon using biochemical indicators of decomposition found that FPOM was more degraded than CPOM (Hedges et al. 1986*a*, 1994). In this study, FPOM is more enriched in $\delta^{13}C$ and $\delta^{15}N$ than CPOM, which may indicate that FPOM comes from a more degraded source than CPOM in the Andes as well as in the Amazon mainstem. This study shows that sources of riverine fine and coarse particulate OM in the Andean Amazon are probably similar, at first approximation, to those determined for the lower Amazon, but, unlike the lower Amazon, chemical composition of those sources and fractions differs with altitude.

Despite their relatively distinct C and N isotopic signatures, elemental compositions of FSS and CSS exhibit similar patterns (Figs. 4C,D, 5C,D). Both FSS and CSS are enriched in OC with respect to soils (Fig. 3C), with CSS more so and approaching plant values at high altitude (Fig. 4C). FSS and CSS have similar N content as compared with plants (Fig. 2C) but are slightly less N rich than soils (Fig. 3C). Both size classes of suspended sediment collected in this study are more enriched in OC than those found in the mainstem. FSS in the Amazon has from 0.9% to 1.5% OC by weight and CSS from 0.5% to 3.4% OC, with no downstream trend in %C of FSS (Richey et al. 1990). In contrast, OM contents of both FSS and CSS in the current study are positively correlated with altitude.

While $\delta^{13}C$ and $\delta^{15}N$ seem to indicate that FPOM is soil derived, in general, OC and N are higher in FSS than in soils (Figs. 3C,D, 4C,D). In some cases, %C and %N of FSS are nearly twice those of soils, indicating some type of in-stream process affecting the composition of FSS. Previously, Aufdenkampe et al. (2001) determined that sorption of DOM could increase the OM content of suspended kaolinite in simulated Amazonian rivers, but only from 0% to 3%. There are two possible reasons for the observed enrichment in OC and N in FPOM in this study over the probable soil source. The first possibility is that sorption of dissolved OM to riverine particles is greater than indicated by laboratory studies (Aufdenkampe et al. 2001), thus supporting the regional chromatography model of organic matter transport in the Amazon (Hedges et al. 1994; Devol and Hedges 2001). During a recent study of OM dynamics in the Andean Amazon, Hedges et al. (2000) found a similar offset in N content of FSS and soils and attributed it to the sorption of ^{15}N-rich DOM to suspended soil minerals. The current study indicates a similar offset. Although the isotopic composition of DOM was not measured in this study, FPOM does have consistently lower $\delta^{15}N$ values (~0.5‰) overall than soil OM (Figs. 3B, 4B), indicating that sorbed DOM is isotopically light, consistent with a possible leaf leachate source. The second possibility is that FPOM in the Andes consists at least partially of small pieces of plant material and more OM-rich surface litter as opposed to deeper OM-poor soil minerals, which is supported by altitudinal trends in isotopic composition of FPOM (see further discussion below). These ideas will be further investigated in future studies using compound-specific analyses and/or radiocarbon measurements of soils and particulates.

Results from this study show a significant increase in $\delta^{13}C$ of FPOM at higher altitudes (Fig. 4A), consistent with Cai et al. (1988), whose highest $\delta^{13}C$ values (−24.6‰) in bulk POM were found in the high Andes. However, while Cai et al. (1988) attributed altitudinal patterns in POM $\delta^{13}C$ values directly to changes in plant ^{13}C, the results of this study indicate that FPOM is mainly soil, not plant, derived. We attribute elevational patterns in POM $\delta^{13}C$ values to changes in the relative contribution of sources rather than to changes in $\delta^{13}C$ of a single source. Decreasing POM $\delta^{13}C$ values at lower altitudes support an increased contribution of plant material to FPOM at lower altitudes, where riparian forests appear and litterfall inputs are greater (McClain and Richey 1996). At high altitudes (~4,000 masl), cold temperatures and relatively low rainfall levels lead to the production of OM-rich soils, which are transported to the river by shallow runoff during rain events. On the other hand, OM inputs at lower altitudes are likely to be a mixture of fresh leaf litter and OM-poor soils added during frequent landslides or other disturbances as well as material exported from upstream. The OM-poor nature of lower altitude soils will make any leaf-litter contributions to rivers more important, as compared with higher altitudes, where more OM-rich soils dominate riverine OM sources. These hypotheses are supported by elemental data (discussed below), as well as isotopic analyses: FPOM $\delta^{13}C$ values approach those recorded for CPOM and plants at low-altitude sampling sites (Figs. 4A, 5A). There is no significant trend of $\delta^{15}N$ of FPOM with altitude in this study (Fig. 4B), consistent with both soils and plants (Figs. 2B, 3B). Unlike the $\delta^{13}C$ trend, $\delta^{15}N$ of FPOM and CPOM seem to converge upstream, indicating that CPOM at sites above the tree line is derived from soils rather than plants, a logical conclusion for streams draining basins where more biomass is below ground than above. However, these hypotheses will need to be tested in other, more detailed studies.

Percentage of C and N in FPOM and CPOM are positively correlated with altitude (Figs. 4C,D, 5C,D). This may be attributed to in-stream processing of POM, but as the same trend is apparent for soils (Fig. 3C,D), the loss of C and N mass in particulates is a likely indicator of the downstream addition of low-OM mineral soils. Previous river studies have shown that %OC of suspended particulates decreases when sediment load and discharge increase (Meybeck 1982), either because of dilution of suspended OM with mineral soils or because of differences in source and processing of OM at different locations along the river. In this study, %OC of FSS decreases with increasing total FSS load, but this relationship is not true for CSS, perhaps due to either low overall suspended sediment loads (<10 mg L^{-1}) or low number of samples. Similarly, in the lower Amazon, TSS controls FPOM concentrations while CPOM concentrations are relatively independent of total CSS concentration (Hedges et al. 2000). However, unlike the present study, in the lower Amazon, FPOM concentrations increase as FSS increases (Hedges et al. 2000) because high-topography Andean rivers are dominated by erosion as opposed to deposition and sorption. Because samples in this study were taken along a known altitudinal gradient, we can infer a decreased input of mineral soils at the highest altitudes.

The Andes have been proposed as a significant particulate inorganic N source to the Amazon based on C : N of FPOM and CPOM with positive N intercepts, indicating that an average of 50% of N was inorganic (Hedges et al. 2000). FPOM, CPOM, and soils (Figs. 3F, 4F, 5F) in the current study show evidence for only a small percentage at most ($<10\%$ on average) of inorganic N in Andean particulates. In addition, unlike Hedges et al. (2000), we do not see a significant downstream increase in $\delta^{15}N$ in any particulate fraction. Samples collected in this study were from higher altitudes than most of those in Hedges et al. (2000), and due to a combination of factors (different regions of the basin, different number of samples), our study indicates that the central Peruvian Andes are not a significant source of particulate inorganic N to lower altitude tributaries. In fact, the Andes are likely a greater source of dissolved than particulate inorganic N. Given an average FSS concentration of 5.3 mg L^{-1}, an average %N of FSS of 1.9%, and assuming that a maximum 10% of that N is inorganic, the approximate concentration of fine particulate inorganic N in these rivers is 0.7 μmol L^{-1}. This is more than an order of magnitude lower than the approximate maximum NO_3^- concentration of 5 μmol L^{-1}.

One goal of this and other studies has been to determine the extent to which Andean organic matter persists in the Amazon mainstem and estuary. Andean POM derived from high-altitude plants was thought to be the source of the enriched $\delta^{13}C$ value of POM at Obidos (Quay et al. 1992). Quay et al. (1992) used the $\delta^{13}C$ of POM from Cai et al. (1988) to calculate that approximately 65% of POC in the Amazon mainstem was Andean. More recently, this figure was revised based on other $\delta^{13}C$ of FPOM data from the Andes, to less than 40% (Hedges et al. 2000). Using the average $\delta^{13}C$ of FPOM from all Andean rivers sampled in this study (-25.3‰) and the lowland end member of -28.5‰ (Quay et al. 1992), 35% (by isotope balance) of FPOM in the Amazon mainstem at Obidos (-27.4‰; Hedges et al. 2000) is derived from Andean rivers above 700 masl. This is very close to the estimate of Andean FPOM loading by Hedges et al. (2000). This mass balance calculation for CPOM also yields the same results as Hedges et al. (2000): Less than 40% of CPOM in the mainstem is derived from the Andes. Because the Andes supply ~85% of suspended sediment to the Amazon River (Meade et al. 1985), our results imply that OM transported with suspended particles is remineralized, replaced, and/or amended during transport through lowland portions of the river basin, in agreement with previous studies (Hedges et al. 2000). However, in contrast with previous work (e.g., Hedges et al. 2000), the present study shows that highly degraded soil C, as opposed to plant leaves, is the dominant source of POM in the Andes; indeed, if Andean riverine OC consisted of plants in the 1,000–3,000 masl region, where most sediment loading occurs, it would be much lighter in $\delta^{13}C$ and $\delta^{15}N$ than what we find. Therefore, it seems that the dominant processes affecting OM composition in the Andean Amazon take place prior to entering the river, not within it.

The existing conceptual model of organic matter dynamics in the Amazon River system is the regional chromatography model (Hedges et al. 1986*b*, 1994; Devol and Hedges 2001), based on years of work in the mainstem Amazon. This model was developed to explain the different compositions and concentrations of various OM size classes. In the mainstem Amazon, leaves are the ultimate source of riverine organic matter. According to the regional chromatography model, leaf litter decays rapidly on the forest floor, where it is either exported as relatively intact CPOM or further decomposed into dissolved organic molecules. Depending on its hydrophobicity, this DOM either remains dissolved or sorbs to soil minerals, producing FPOM. These patterns, as reflected in the chemical composition of these OM size classes, were found to be remarkably consistent along the entire ~1,800 km of the Amazon mainstem. Although the current study does not include all the analytical techniques used to describe the above patterns, a preliminary comparison can be made between OM dynamics in the Peruvian Andes and those explained by regional chromatography. First, similar to the lowland Amazon, our data indicate that terrestrial plants are the ultimate source of riverine OM, although more specific evidence would strengthen this argument. In addition, stable isotopic evidence indicates that CPOM is derived from minimally degraded terrestrial plants and that FPOM is more degraded, just as has been found in the mainstem. We also show preliminary evidence for sorption of dissolved organic N to FSS, but the levels of organic C and N in fine particulates are too high for sorption of DOM to be the main source of FPOM, as the regional chromatography model predicts (Hedges et al. 2000; Aufdenkampe et al. 2001), unless sorption is occurring at a much higher proportion in Andean rivers. We propose that soil OM consisting of highly degraded plant material, as opposed to mineral-sorbed DOM, is the primary source of FPOM in the Andean Amazon. As predicted by the regional chromatography concept, results presented here indicate that processes operating outside the river are the most important control on riverine organic matter composition, and downstream changes in in-stream com-

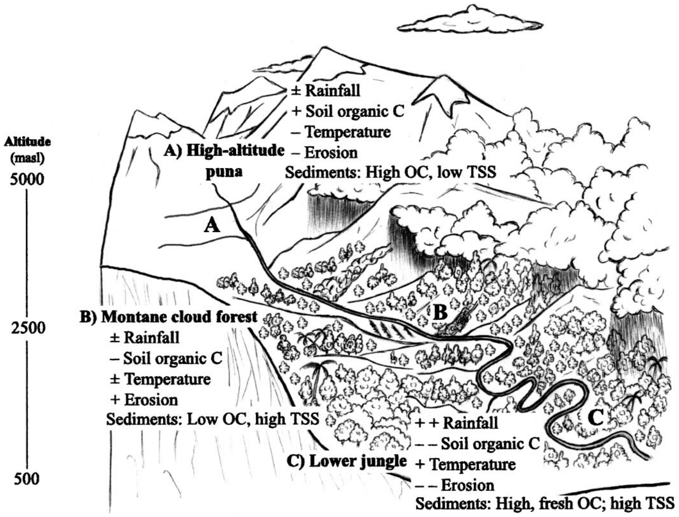

Fig. 6. Conceptual diagram of organic matter dynamics in the Peruvian Andean Amazon. Three major zones are depicted: (A) the high-altitude *puna,* located above the tree line, or from about 3,500 to 4,500 masl; (B) the montane cloud forest, situated between 2,000 and 3,500 masl; and (C) the low jungle, or *selva baja,* which extends from 750 to 2,000 masl, approximately.

positional patterns are due to changes in terrestrial sources. However, important differences from the regional chromatography model are apparent in Andean riverine OM dynamics, namely, the much greater roles for altitude and climate-correlated soil diagenesis and erosion in the Andes.

Based on the results of this study, we propose a preliminary conceptual model of OM dynamics in the Andean Amazon (Fig. 6). At the highest reaches of the Amazon (region A, Fig. 6), above about 3,000 masl, catchments and streams are small and rainfall is reduced. Low temperatures slow decomposition and soils accumulate particulate and dissolved OC. Erosion of mineral soils is low and erosion of surface (high OC) riparian soils dominates particulate loading to streams. Because streams and catchments are smaller, $\delta^{15}NO_3^-$ and DOC concentrations are highly variable. Between about 3,500 and 2,000 masl (region B, Fig. 6), greater rainfall leads to rapid, constant OC leaching and erosion of mineral-rich, OC-poor soils. Soil OM is more degraded due to warmer temperatures and rapid flushing, and river FPOM reflects the input of soil OM from erosion. DOC is lower than in high-altitude streams draining peat soils and $\delta^{15}NO_3^-$ values are constant, reflecting the integrating nature of the larger rivers in this region. Finally, in the foothills of the Andes (2,000–750 masl), where rainfall is at a maximum and topography is gentler, FPOM and CPOM begin to reflect the input of less degraded surface soil and leaf-litter inputs (region C, Fig. 6). DOC concentrations remain low and $\delta^{15}NO_3^-$ values are consistent throughout the landscape. The assumptions of this model can be tested in future studies of the Andes, optimally including broader spatial coverage, identification of salient geomorphological features, river discharge, and more measurements of OM sources, transport, and residence times.

This study allows for several conclusions about carbon and nitrogen cycling in the Andean Amazon. Plants show a positive correlation of $\delta^{13}C$ with altitude consistent with other studies, but the negative correlation of foliar N content with altitude indicates that nutrient limitation, water stress, or species composition are more important in determining foliar chemistry than internal CO_2 levels. Soil OM is consistently degraded beyond the leaf-litter stage, with a strong gradient in weight %OM with altitude. At all sites, riverine suspended FPOM is predominantly soil derived and becomes progressively enriched in $\delta^{13}C$ at low altitudes, whereas CPOM compositionally resembles minimally or partially degraded leaf litter. Overall, riverine FSS and CSS are enriched in OC and N over soils, indicating additional contributions from either sorption of DOM or C-rich POM sources such as leaf litter. Such leaf litter inputs may become an important source of FPOC to rivers at the lowest altitudes in our system. In general, riverine OM compositions are driven by erosion-dominated soil inputs, which are in turn controlled by physical factors such as rainfall, temperature, and topography. High-altitude OM-rich soil inputs give way to OM-poor soil inputs at mid to low altitudes, resulting in a sharp gradient in riverine %OM with altitude. The high levels of degradation experienced by most Andean soils prior to transport to rivers and out to the main basin, as well as sorptive protection on mineral surfaces, may be primary reasons why this material survives in-river processing to provide a significant source of organic matter to the Amazon River. $\delta^{15}N$ values indicate that riverine NO_3^- is derived from soils or POM. Dissolved-OC concentrations observed at high altitudes ($>$2,000 masl) were variable, but correlated with storm events, and decreased to relatively low values (1–2 mg L^{-1}) in the lower basin. Indeed, all three solute parameters, $\delta^{18}O$ of H_2O, $\delta^{15}N$ of NO_3, and DOC concentration, in headwater streams were highly variable. This illustrates the need to consider rivers, especially their mountain headwaters, within a longitudinal (e.g., Vannote et al. 1980) as well as a lateral framework embracing variability and abrupt geochemical transitions (e.g., Poole 2002). Perhaps the most important finding of this work is that soils are a more important source of riverine FPOM in Andean rivers as compared with rivers of the lower Amazon (Hedges et al. 1986*a,b,* 1994, 2000). Moreover, in sharp contrast with the stable longitudinal biogeochemical patterns that characterize lowland rivers, the concentration and composition of various OM size classes, in plant and soil sources as well as riverine particulate exports, vary with altitude and downstream distance in the Andean Amazon.

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