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Chemical fingerprints of hydrological compartments and flow paths at La Cuenca, western Amazonia

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Abstract. A forested first-order catchment in western Amazonia was monitored for 2 years to determine the chemical fingerprints of precipitation, throughfall, overland flow, pipe flow, soil water, groundwater, and streamflow. We used five tracers (hydrogen, calcium, magnesium, potassium, and silica) to distinguish "fast" flow paths mainly influenced by the biological subsystem from "slow" flow paths in the geochemical subsystem. The former comprise throughfall, overland flow, and pipe flow and are characterized by a high potassium/silica ratio; the latter are represented by soil water and groundwater, which have a low potassium/silica ratio. Soil water and groundwater differ with respect to calcium and magnesium. The groundwater-controlled streamflow chemistry is strongly modified by contributions from fast flow paths during precipitation events. The high potassium/silica ratio of these flow paths suggests that the storm flow response at La Cuenca is dominated by event water.

Introduction

Recent attempts to infer hydrologic pathways from the interpretation of stream chemistry as a mixture of contributing sources [e.g., *Christophersen et al.*, 1990; *Hooper et al.*, 1990; *Genereux et al.*, 1993; *Hinton et al.*, 1994] have appreciably elucidated the fate of rainfall in the terrestrial phase of the hydrologic cycle. This approach relies on the identification of hydrologic compartments with distinctive chemical fingerprints and on the belief that the streamflow hydrochemical signal alone contains all the information about flow paths. Several studies have supported their hydrochemistry-based inference with independent hydrometric evidence [e.g., *Mulholland*, 1993; *Bazemore et al.*, 1994]. The applicability of the purely hydrochemical approach to infer hydrologic pathways is questionable in the case of fast flow path–dominated catchments [*Elsenbeer et al.*, 1995], unless such fast flow paths are explicitly considered as contributing sources [*Muscutt et al.*, 1990; *Chapman et al.*, 1993; *Elsenbeer et al.*, 1994] whose chemical fingerprint is reflected in the stream chemistry. In this case, an independent hydrologic study must precede the hydrochemical investigation to identify the relevant pathways and compartments.

We conducted a hydrologic study from late 1986 to early 1989 in a highly responsive catchment in western Amazonia. Overland flow was first observed during several events in 1986, after which a reconnaissance study was made to establish its temporal and spatial frequency [*Elsenbeer and Cassel*, 1990]. In several instances, overland flow could be traced to pipe outlets on hillslopes. A rationale for the generation of overland and pipe flow in this environment is presented by *Elsenbeer and Cassel* [1990, 1991]. The results of this hydrologic study provided the framework for our hydrochemical study of flow paths and compartments in this tropical rain forest catchment.

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Research Site

La Cuenca is situated at 75°5′W, 10°13′S and 300 m above mean sea level (Figure 1) in the Rio Pichis valley in the sub-Andean foreland basin. The Pichis is one of the two headwater rivers of the Pachitea, which joins the Ucayali south of Pucallpa. Within Peru the area is known as Selva Central. Like elsewhere in the Ucayali basin, at least three distinct geomorphic surfaces of different relative ages can be distinguished. The research catchment (0.75 ha in area) (Figure 2) is located on the highest and oldest surface, characterized by an advanced stage of dissection with spur-like interfluves and steep convexolinear side slopes. Prominent geomorphic features are a narrow valley floor, an intermediate, nearly flat terrace between an upper slope reaching the interfluve, and a much steeper lower slope joining the valley floor at a sharp angle. Gullies, rills, and numerous pipe outlets on the slopes (Figures 2 and 3) indicate fast flow paths and imply active surficial processes. The existence of a pipe network at a shallow depth was further confirmed in soil pits. Apart from one exception (Figure 2), gullies and rills are connected directly with the stream channel without passing over the narrow valley floor.

Sandstones, siltstones, and shales of Tertiary "red beds" are the dominant parent material from which Ultisols developed. On the steep side slopes adjacent to the valley floor, these grade into Inceptisols.

A multistoried, primary rain forest with a sparsely developed understory covers the catchment, the dominant families being Moraceae, Sapotaceae, and Euphorbiaceae. We could not find any accounts of former agricultural land use in the forest reserve that includes La Cuenca.

Mean annual temperature for the area is 25.5°C, and mean annual precipitation is about 3300 mm. The rainfall at La Cuenca was 3190 mm in 1987 and 2750 mm in 1988. The

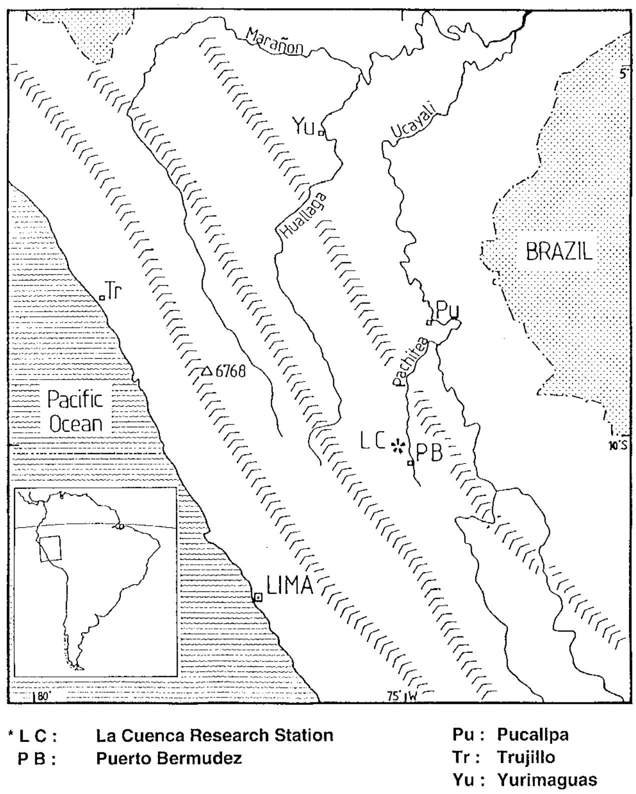

Figure 1. The location of the research catchment at La Cuenca, in Peru.

months June through September are considerably drier than the rest of the year, with monthly totals even below 100 mm. From December through March, monthly totals can reach 900 mm; details about rainfall characteristics are presented by *Elsenbeer et al.* [1993].

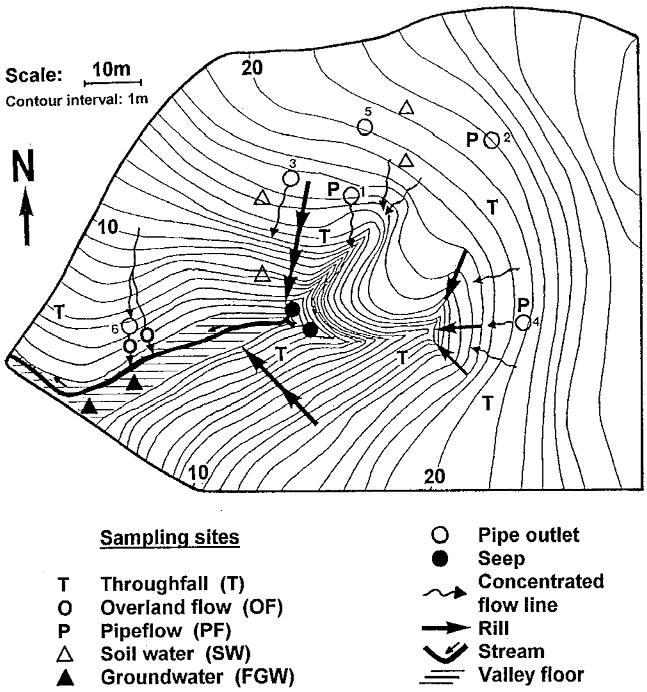

Figure 2. The research catchment at La Cuenca.

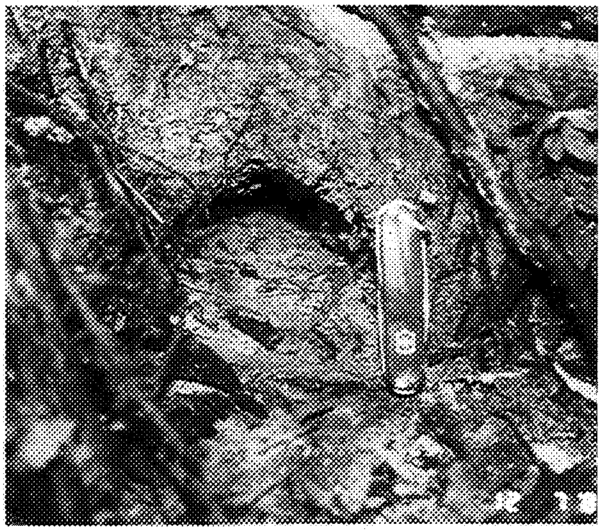

Figure 3. The outlet of pipe 2 (see Figure 2 for location).

Methodology

Field Sampling and Chemical Analysis

Table 1 shows the hydrologic pathways and compartments sampled, sampling strategy, and sample sizes; the sampling locations are indicated in Figure 2. Precipitation (P) was collected in a small clearing adjacent to the catchment; a lid was kept on a plastic funnel feeding into a 5-gal container until an event occurred or until 10:00 P.M. each night. The longest possible period of dry deposition before an event was 8 hours, as the funnel was rinsed at dawn. Usually, the period was shorter, because rainfall usually began between 10:00 P.M. and 2:00 A.M.

Throughfall (T) was collected at six sites in the catchment; 1-L plastic containers were equipped with mesh-covered funnels to minimize the inclusion of particulate matter, and organic debris was removed daily to eliminate an undesired source of leachate. The results from the six sites were averaged.

Overland flow (OF2) was sampled from a runoff plot equipped with three interconnected 55-gal drums; subsamples were taken from each, and the average was used for data analysis. This runoff plot intercepted a concentrated-flow line which was later found to be fed by pipe flow (Figure 2). There-

Table 1. Sampling Approach

Compartment	Code	Frequency	Sample Size
Precipitation	P	event-based	62[a]
Throughfall	T	event-based	55[a]
Overland flow	OF1	event-based	30[a]
Overland flow	OF2	event-based	119[a]
Pipe flow	PF	event-based	58[a]
Soil water at 0.3 m	SW3	fixed-interval	119[b]
Soil water at 0.6 m	SW6	fixed-interval	123[b]
Soil water at 0.9 m	SW9	fixed-interval	126[b]
Floodplain groundwater	FGW	fixed-interval	168[b]
Hillslope groundwater	Seep	fixed-interval	267[b]
Stream water, base flow	BF	fixed-interval	276[b]
Stream water, storm flow	SF	within event	30

[a]Number of events.
[b]Number of daily samples.

fore samples were also taken from a second concentrated-flow line (OF1) to which there were no visible pipe flow contributions. Both flow lines discharged directly into the stream without passing over the valley floor. Outflow from pipe 1 was collected in a 55-gal drum; outflow from pipes 2 (Figure 3) and 4 was collected in smaller containers.

Streamflow was sampled manually at 3-day intervals from an H flume that defines the catchment outlet (Figure 2). The timing of sampling, in nearly all cases at noon, ensured that the samples represented base flow (BF). During 30 events, stream water samples were taken at short intervals to assess storm flow chemistry (SF).

Hillslope groundwater was collected at 3-day intervals from a seep at the origin of the first-order stream (Figure 2). Floodplain groundwater samples were taken initially at 3-day, later at 6-day, intervals from three shallow boreholes (FGW), equipped with perforated polyvinyl chloride (PVC) pipes, in the valley floor (Figure 2). The boreholes were located within a distance of 10 m of one another and about 2 m from the stream channel. The minimal intersite variability suggested averaging the separate results. Streamflow (BF), spring water (seep), and floodplain groundwater (FGW) were collected at the same time.

Soil water was sampled with suction lysimeters (pressure = −700 mbar) at four sites from three depths (SW3, SW6, and SW9). The results from these sites were averaged for the purpose of this study because of their minimal differences. Samples were taken initially every 6 days, later every 12 days, owing to negligible temporal variation. Samples from the first 6 weeks following installation were discarded. The sampling dates coincided with those for streamflow (BF) and groundwater (FGW, seep).

The pH was determined potentiometrically with an Orion combination electrode immediately after sampling. One hundred–milliliter unfiltered subsamples with 1% (vol/vol) phenylmercury-acetate (to prevent microbial growth) were transported to the La Molina Agricultural Research Station in Lima within a week and filtered (0.45 μm) before further analysis. Potassium, calcium, and magnesium were determined by conventional atomic adsorption spectrometry (Perkin Elmer 2380), and molybdate-reactive silica was determined colorimetrically at 660 nm. The relative precision for these analyses was 5% for the cations and 10% for silica.

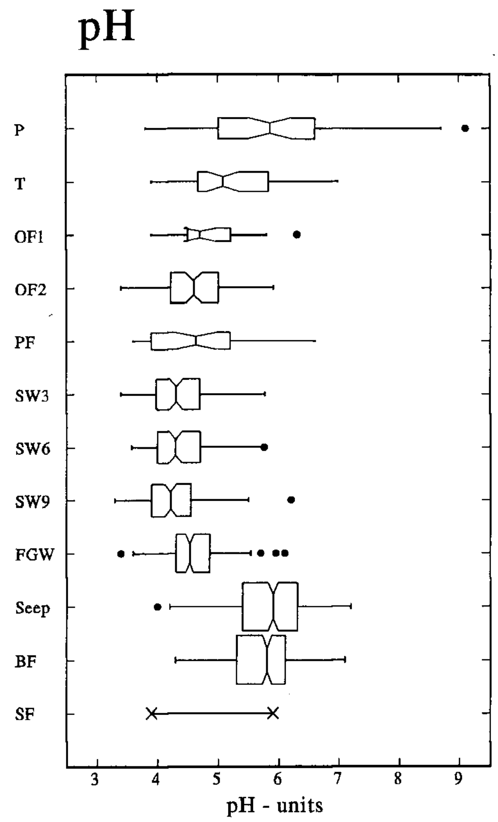

Figure 4. Box plot comparison of hydrologic compartments and flow paths: pH. Abbreviations are P, precipitation; T, throughfall; OF1, overland flow with no pipe flow contribution; OF2, overland flow with pipe flow contribution; PF, pipe flow; SW3, soil water from 0.3 m; SW6, soil water from 0.6 m; SW9, soil water from 0.9 m; FGW, floodplain groundwater; Seep, hillslope groundwater; BF, stream water under base flow conditions; and SF, storm flow.

Data Analysis

Our study was observational, as opposed to experimental: We did not formulate any hypotheses and then collect data to test them according to the appropriate experimental design. Data from observational studies are likely to be "non-normal, non-random, heavy prior, and small sample" [*Wang*, 1993, p. 33] (the latter characteristic, however, does not apply here; see Table 1). For example, the sampling of precipitation (P), throughfall (T), overland flow (OF), and pipe flow (PF) was not strictly random. We focused on events that resulted in sizable rainfall (P) and throughfall (T) samples and in overland flow (OF) and pipe flow (PF) samples; such samples should be referred to as "convenience" or "judgment" samples [*Hahn and Meeker*, 1993].

We distinguished two phases of data analysis: exploratory data analysis (EDA) and confirmatory data analysis (CDA) [*Tukey*, 1977]. EDA reveals the structure of the data, provides information necessary for the choice of appropriate estimators, and suggests comparisons of batches, in our case compartments and flow paths. CDA evaluates the evidence provided by EDA; it includes quasi-inferential statistics, a term we adopted from *Wang* [1993, p. 34] to emphasize that calculations of confidence intervals and hypothesis testing after "data snooping" and without proper randomization are incompatible with orthodox statistical inference.

The first step in EDA is the construction of box plots [*Emerson and Strenio*, 1983] (see Figures 4–8): They display the essential features of each batch, and grouping them by solute allows a comparison of compartments and flow paths. Additional plots reveal deviations from Gaussian shape and lack of symmetry: quantile-quantile (Q-Q) plots [*Hoaglin*, 1985, p. 432] and plots of midsummaries versus the square of the corresponding Gaussian quantiles (mid-versus-z^2) [*Hoaglin*, 1985, p. 448]. In case of obvious non-Gaussian behavior, we employed cube-root, fourth-root, and logarithmic transformations in an attempt to promote Gaussian shape.

The first step in CDA was testing for Gaussian shape with the Shapiro-Wilk W test [*Shapiro and Wilk*, 1965]. Next, confidence intervals were calculated for the location estimate inferred from EDA. Last, we made formal comparisons suggested by EDA and subject matter. The SAS language and procedures were used for all calculations [*SAS Institute Inc.*, 1990a, b].

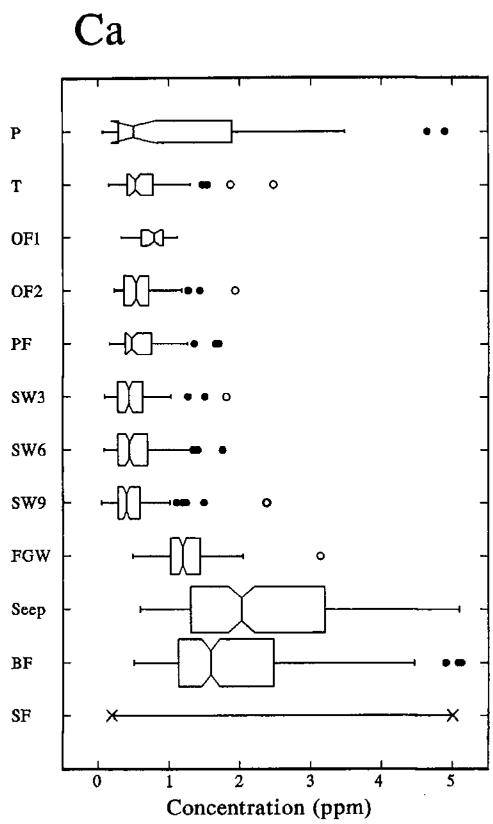

Figure 5. Box plot comparison of hydrologic compartments and flow paths: calcium. See Figure 4 for abbreviations.

Results and Discussion

The outcome of EDA is summarized in the box plot comparisons of Figures 4–8; they leave no doubt about the non-symmetric and heavy-tailed situation in most batches. Q-Q and mid-versus-z^2 plots of nearly all 66 batches displayed departure from Gaussian shape outside of the middle of the batch and skewness. While some of the above mentioned transformations successfully promoted Gaussian shape in some batches, no single transformation worked for more than a third of the batches. Hence after confirming these graphical results by formal testing, we opted for a distribution-free method to obtain location estimates and confidence intervals. Specifically, the general lack of symmetry in the batches favors the median as estimator of location and hence sign tests [*Dixon and Mood*, 1946] over Wilcoxon procedures [*Wilcoxon*, 1945; *Mann and Whitney*, 1947]. We prefer stating confidence intervals to stating test results when we compare batches, because confidence intervals implicitly contain tests in addition to providing location estimates. The outcome of CDA is summarized in Tables 2–6, which provide batch size, median and 95% confidence interval, MAD (median absolute deviation from the median) as a resistant measure of scale [*Hoaglin et al.*, 1983, p. 291], arithmetic mean, and standard deviation. The latter two statistics, which according to our data analysis are rather meaningless, save a few batches, are included only for the sake of comparison.

Hydrogen (*p*H). A decrease of *p*H occurs as rainwater passes through the forest ecosystem, with the lowest value in the subsoil (Figure 4). The highest *p*H was found in the compartment called "seep," which we assume has the chemical fingerprint of the weathering zone. The *p*H of groundwater collected in the valley floor (FGW) is considerably lower than that of hillslope groundwater (seep), which indicates that these two compartments are chemically distinct. The box plots hint at a small difference between OF1 and PF, and PF and shallow soil water (SW3), but these differences are not significant (Table 3). Hence *p*H is not a suitable tracer to distinguish between near-surface flow paths and compartments.

Calcium. Rainfall does not become enriched in calcium as it passes through canopy (T) and soil (SW), although overland flow (OF1) is distinctive (Figure 5). The weathering zone appears to be the only source of Ca. Valley bottom (FGW) and hillslope (seep) groundwater differ significantly (Table 3), and base flow (BF) appears to be a mixture of both. Considerable dilution of streamflow occurs during events (SF), which we tentatively attribute to the contribution of fast flow paths (OF, PF); alternatively, one might consider a mobilization of floodplain groundwater (FGW) during events. A difference between overland flow (OF1) and pipe flow (PF) is evident and confirmed by Table 3.

Magnesium. The highest Mg concentrations are found in groundwater (FGW, seep) (Figure 6). Unlike Ca, however, the hillslope groundwater (seep) has a significantly lower Mg concentration than groundwater from the valley floor (Table 4). The ranges of storm flow and base flow concentrations nearly coincide. The concentration in OF not associated with return flow from a pipe (OF1) is higher than in either a mixture of pipe flow and overland flow (OF2) or pipe flow alone (PF); these differences are significant (Table 4). The concentrations in pipe flow (PF) and soil water (SW) do not differ significantly (Table 4).

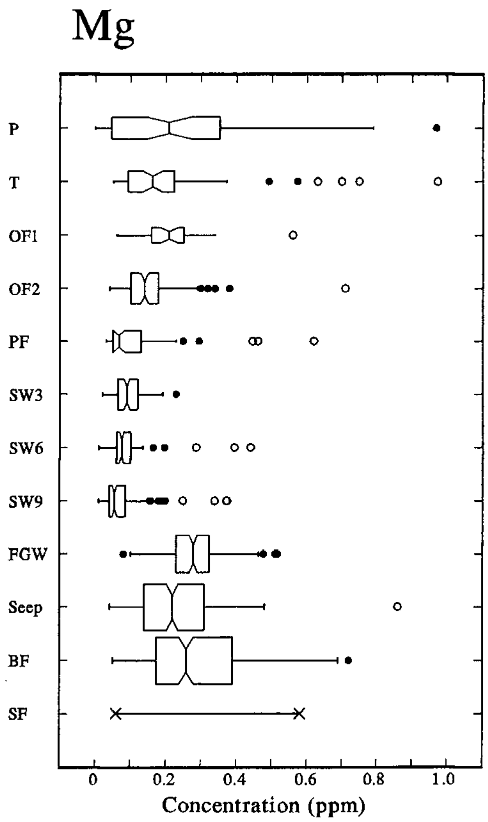

Figure 6. Box plot comparison of hydrologic compartments and flow paths: magnesium. See Figure 4 for abbreviations.

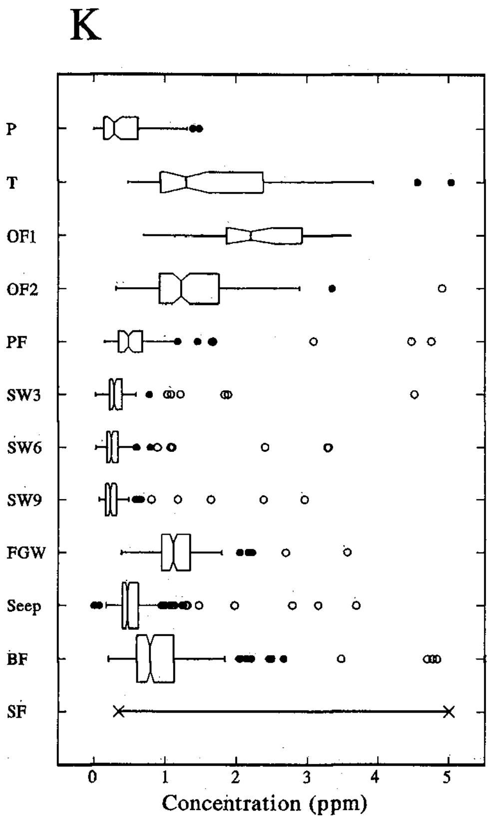

Figure 7. Box plot comparison of hydrologic compartments and flow paths: potassium. See Figure 4 for abbreviations.

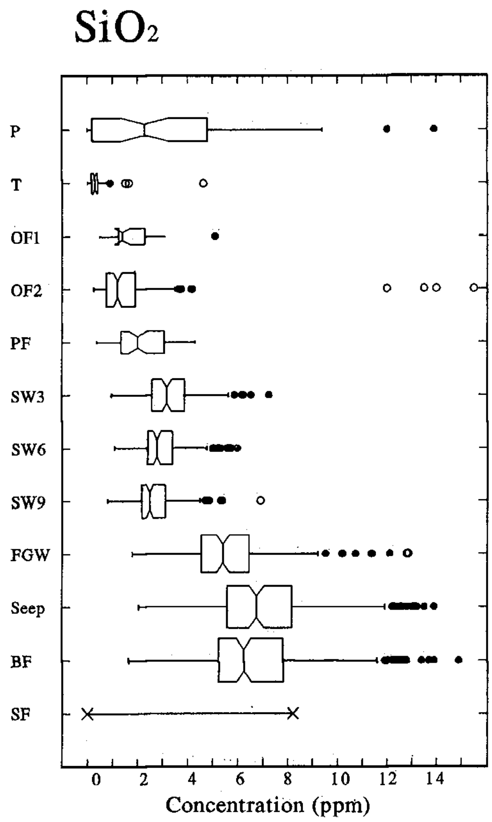

Figure 8. Box plot comparison of hydrologic compartments and flow paths: silica. See Figure 4 for abbreviations.

Potassium. The pattern of K contrasts with the other cations (Figure 7). Rainfall acquires K passing through live and dead biomass (T, OF1); the highest concentration is found in overland flow not generated by return flow (OF1), and it is significantly higher than in pipe flow (PF, Table 5). Pipe flow (PF) is significantly enriched in potassium with respect to soil water (SW). Rapidly infiltrating throughfall is the most likely supplier of K to pipe flow, although some mixing with potassium-poor preevent soil water must occur. The comparison between OF1, OF2, and PF confirms the field observation that in some places, overland flow is a mixture of return flow, i.e. pipe flow, and overland flow actually generated at the surface. The lowest concentrations are found in soil water (SW) and hillslope groundwater (seep, Table 5), which implies that the weathering zone is only a minor source of this ion. K decreases significantly from 0.3 to 0.9 m within the soil (Table 5), although the absolute change is minimal. Floodplain groundwater (FGW) has a significantly higher K concentration than hillslope groundwater (seep, Table 5); base flow appears to represent a mixture of both. The range in storm flow (SF) K values suggests that precipitation events entail a concentration effect. This interpretation is compatible with K concentrations observed in fast flow paths (OF). As was argued above, rapid mobilization of groundwater from the valley floor (FGW) could also account for a strong K signal in storm flow; however, we have no observational evidence for a mechanism causing such a mobilization, such as the capillary fringe effect suggested by *Gillham* [1984]. In contrast, the spatial and temporal extent of overland flow, functioning as a vector for K, is sufficiently documented [*Elsenbeer and Cassel*, 1990].

Silica. The SiO_2 pattern (Figure 8) is nearly a mirror image of the K pattern: depletion versus enrichment in fast flow paths (OF) and enrichment versus depletion in hydrologic compartments (SW, seep) with a longer residence time. As fast flow paths explain best the K concentration (Figure 7) in storm flow (SF) when compared to base flow (BF), they also explain best the dilution of SiO_2 in storm flow (Figure 8). As with all other solutes, the two groundwater bodies, valley floor (FGW) and hillslope (seep), also differ significantly in their SiO_2 concentrations (Table 6). Pipe flow differs significantly from shallow soil water (SW3), but not from deeper soil water (SW9) and overland flow (OF1) (Table 6). SiO_2 must be supplied by the soil; either pipe flow represents a mixture of soil water and

Table 2. Descriptive Statistics: pH

Compartment	N	LCL	Median	UCL	MAD	Mean	SD
P	50	5.10	5.85	6.20	0.85	5.86	1.29
T	45	4.80	5.08	5.37	0.43	5.28	0.78
OF1	18	4.50	4.70	5.20	0.35	4.86	0.60
OF2	103	4.40	4.60	4.70	0.40	4.61	0.60
PF	33	3.95	4.63	5.00	0.67	4.62	0.80
SW3	108	4.15	4.31	4.50	0.36	4.38	0.51
SW6	111	4.20	4.30	4.50	0.35	4.40	0.50
SW9	114	4.10	4.22	4.33	0.32	4.27	0.50
FGW	168	4.47	4.53	4.60	0.27	4.60	0.47
Seep	262	5.80	5.90	6.00	0.50	5.85	0.62
BF	262	5.70	5.80	5.90	0.40	5.73	0.54

Statistics abbreviations are N, sample size; LCL, lower 95% confidence limit; UCL, upper 95% confidence limit; MAD, median absolute deviation from the median; and SD, standard deviation. See Table 1 for abbreviations of compartments.

Table 3. Descriptive Statistics: Calcium

Compartment	N	LCL	Median	UCL	MAD	Mean	SD
P	62	0.63	0.50	0.92	0.37	1.11	1.16
T	54	0.44	0.52	0.67	0.18	0.66	0.44
OF1	30	0.62	0.79	0.85	0.17	0.94	1.14
OF2	115	0.47	0.53	0.59	0.18	0.58	0.29
PF	58	0.42	0.47	0.58	0.17	0.59	0.37
SW3	118	0.39	0.43	0.50	0.17	0.49	0.29
SW6	122	0.37	0.44	0.49	0.18	0.51	0.32
SW9	125	0.36	0.40	0.45	0.15	0.47	0.36
FGW	168	1.15	1.19	1.27	0.21	1.25	0.35
Seep	267	1.88	2.02	2.20	0.83	2.67	1.14
BF	276	1.52	1.585	1.68	0.60	1.84	0.92

See Tables 1 and 2 for abbreviations of compartments and statistics, respectively.

Table 5. Descriptive Statistics: Potassium

Compartment	N	LCL	Median	UCL	MAD	Mean	SD
P	62	0.22	0.29	0.38	0.165	0.43	0.38
T	54	0.19	1.30	1.78	0.45	1.83	1.49
OF1	29	1.96	2.20	2.85	0.50	2.96	3.15
OF2	116	1.06	1.23	1.38	0.36	1.43	0.71
PF	58	0.385	0.485	0.59	0.16	1.12	2.39
SW3	119	0.26	0.29	0.31	0.075	0.39	0.46
SW6	122	0.22	0.24	0.27	0.08	0.35	0.46
SW9	125	0.20	0.225	0.25	0.075	0.31	0.36
FGW	168	1.05	1.15	1.21	0.20	1.18	0.37
Seep	267	1.45	0.47	0.50	0.09	0.56	0.37
BF	275	0.73	0.79	0.86	0.23	1.03	0.87

See Tables 1 and 2 for abbreviations of compartments and statistics, respectively.

throughfall, or SiO_2 is present in an easily soluble form taken up by throughfall as it infiltrates. The significantly higher SiO_2 concentration in shallow soil water (SW3) compared to deeper soil water (SW9) (Table 6) implies a biological cycling mechanism for Si.

The potassium/silica ratio offers a possibility to distinguish among hydrologic compartments and pathways: Fast pathways interacting with the biological subsystem are characterized by a high K/Si ratio, while the ratio is reversed in slow pathways interacting with the geological subsystem. This suggestion is based on the plausible assumption that K is mainly derived from the vegetation and SiO_2 from the weathering zone. The apparent exception, floodplain groundwater (FGW), is easily explained by the nature of the sedimentary deposits, i.e., a mixture of loamy sand and organic debris. The organic portion of these sediments might account for the high K and Mg concentration in floodplain groundwater (FGW) compared to hillslope groundwater (seep). Tables 5 and 6 yield the following rough (molar) ratios: Throughfall, representing a fast flow path and the biological subsystem alone, has a K/SiO_2 ratio of 6.0. The other extreme, hillslope groundwater, has a ratio of 0.11. In between these two extremes we find "pure" overland flow with a ratio of 2.4, return flow with a ratio of 1.6, pipe flow with a ratio of 0.36, and soil water with a ratio of 0.13, which is hardly different from hillslope groundwater. Floodplain groundwater has a high ratio of 0.32, owing to the high content of organic debris in the valley floor sediments. Accordingly, the base flow K/SiO_2 ratio of 0.19 reflects the contribution of both types of groundwater.

The origin of overland flow as pipe flow in several places (see Figures 2 and 3) raises the question of whether the two flow paths have distinctive chemical fingerprints. They do not differ significantly concerning pH and SiO_2 (Tables 2 and 6), but their Ca, Mg, and K concentration are significantly different (Tables 3, 4, and 5). The K signal is most suitable for distinguishing between overland flow and pipe flow. The strong K signal associated with overland flow was confirmed in another tropical rain forest catchment [*Elsenbeer et al.*, 1994]. This signal is also useful for distinguishing between pipe flow and near-surface soil water (Table 5), as is SiO_2 (Table 6). This was also shown in a similar context elsewhere [*Muscutt et al.*, 1990, Table 1; *Wilson et al.*, 1991, Figure 11]. Their K/SiO_2 ratios differ by an order of magnitude (see above).

Floodplain groundwater (FGW) and hillslope groundwater (seep), which mix to produce base flow, differ significantly with respect to all species considered (Tables 2–6). The implication is that the proportion of catchment area occupied by the valley floor codetermines the streamflow chemistry in this ecoregion. This proportion, in turn, depends on the stage of landscape development [*Elsenbeer and Cassel*, 1988]. The valley floors of first-order catchments expand into headwater swamps at the expense of hillslopes. The documented difference between hillslope and floodplain groundwater at least partly accounts for the previously unexplained spatial variability of streamflow chemistry [H. Elsenbeer, unpublished results, 1989] in this area.

Comparisons With Other Studies in Amazonia

Forti and Neal [1992] summarized the chemical composition of rainfall, throughfall, soil water, groundwater, and stream-

Table 4. Descriptive Statistics: Magnesium

Compartment	N	LCL	Median	UCL	MAD	Mean	SD
P	61	0.09	0.21	0.29	0.16	0.24	0.21
T	55	0.12	0.16	0.19	0.065	0.21	0.19
OF1	30	0.18	0.21	0.24	0.045	0.22	0.09
OF2	115	0.12	0.14	0.15	0.04	0.15	0.08
PF	58	0.06	0.07	0.09	0.03	0.11	0.11
SW3	119	0.08	0.09	0.10	0.03	0.10	0.04
SW6	123	0.07	0.075	0.08	0.02	0.09	0.06
SW9	126	0.05	0.055	0.06	0.02	0.07	0.06
FGW	168	0.27	0.28	0.29	0.05	0.28	0.08
Seep	267	0.20	0.22	0.24	0.08	0.23	0.12
BF	276	0.24	0.26	0.28	0.10	0.28	0.15

See Tables 1 and 2 for abbreviations of compartments and statistics, respectively.

Table 6. Descriptive Statistics: Silica

Compartment	N	LCL	Median	UCL	MAD	Mean	SD
P	56	0.50	2.30	3.45	2.10	3.83	5.39
T	44	0.23	0.30	0.36	0.12	0.47	0.73
OF1	26	1.25	1.40	2.30	0.575	1.26	1.01
OF2	119	1.05	1.20	1.40	0.48	1.82	2.40
PF	54	1.70	2.00	2.70	0.775	2.23	1.15
SW3	111	2.85	3.175	3.30	0.625	3.30	1.23
SW6	115	2.58	2.775	2.95	0.45	3.04	1.07
SW9	116	2.31	2.49	2.67	0.39	2.72	1.00
FGW	148	5.22	5.42	5.65	0.94	5.76	2.09
Seep	186	6.40	6.75	6.90	1.28	7.17	2.61
BF	196	5.80	6.25	6.60	1.25	6.80	2.63

See Tables 1 and 2 for abbreviations of compartments and statistics, respectively.

flow from several studies at the Reserva Ducke in central Amazonia. None of the referenced studies included sampling of fast flow paths, which limits the comparability of our investigation. The comparability is further limited in that arithmetic means are presented without confidence limits. Given the generally asymmetric nature of small, environmental data sets, the arithmetic mean is likely to yield a too large estimate of location.

Our Ca estimate in throughfall (Table 3) of 0.52 ppm is marginally higher than the values reported for central Amazonia [*Forti and Neal*, 1992, Table 3]. The shallow soil water (Table 3, SW3) at La Cuenca has a slightly lower calcium content than the corresponding soil water from the Reserva Ducke [*Forti and Neal*, 1992, Table 4], whereas the groundwater (both FGW and seep) has a considerably higher Ca concentration at La Cuenca. Accordingly, the Ca concentration in streamflow is higher at La Cuenca than at the Reserva Ducke [*Forti and Neal*, 1992, Table 5].

A comparison of Table 4 with Tables 3–5 of *Forti and Neal* [1992] points to smaller Mg concentrations in throughfall (T) and shallow soil water (SW3) but higher concentrations in groundwater (FGW, seep) and streamflow (BF) at La Cuenca. Both the Ca and Mg values in groundwater and streamflow suggest the presence of primary minerals in the weathering zone of La Cuenca, minerals that the Barreiras formation at the Reserva Ducke is apparently devoid of.

Except for one value, the throughfall potassium concentrations *Forti and Neal* [1992, Table 3] reported for Reserva Ducke fall within the confidence limits given for La Cuenca (Table 5). The shallow soil water at Reserva Ducke [*Forti and Neal*, 1992, Table 4] has a considerably higher K content compared to La Cuenca (Table 5, SW3). The potassium concentration of 1.2 ppm in groundwater reported by *Forti and Neal* [1992, Table 4] is not significantly different from La Cuenca, if floodplain groundwater is considered (FGW, Table 5). Given the location of the wells in the Reserva Ducke [*Nortcliff and Thornes*, 1978, Figure 2 and p. 250], the comparison with FGW from La Cuenca appears appropriate. A comparison of streamflow potassium values (see Table 5 and *Forti and Neal* [1992, Table 5]) is inconclusive.

In the absence of information about data-analytical methods, it is uncertain whether the differences between the two Amazonian sites are due to geoecological factors such as soils (Oxisols at Reserva Ducke versus Ultisols at La Cuenca) or to estimation procedures. Any explanation of the differences is therefore speculative. Although we concur with *Forti and Neal* [1992, p. 113] "that ionic species are not being transported to the subsoil and groundwater," we do not agree with their conclusion of a closed nutrient cycle in the root mat: As we showed for La Cuenca, ecosystems "leak" during precipitation events due to fast pathways. Knowledge of such pathways or stream water sampling during storms is a prerequisite for judging cycling of elements.

Conclusions

The chemical characterization of hydrologic pathways at La Cuenca demonstrates that knowledge of fast pathways is mandatory for a complete description of watershed chemistry. By implication, it is also mandatory for hydrochemical modeling based on mixing of end-members or components. The chemical signature of fast flow paths is distinct from that of slow flow paths in the soil and weathering zone, and an attempt to explain stream water chemistry as a mixture of groundwater and soil water would ignore a dominant hydrologic process in this environment. Indeed, soil water itself does not appear to affect streamflow chemistry: During base flow conditions the groundwater chemical signal is overwhelming, and during storm flow conditions, fast flow paths leave their imprint.

Given that overland flow is in many places generated by pipe flow, the chemical distinction between the two becomes questionable: Whatever runoff reaches the stream channel via the soil surface is likely to be a mixture of pipe flow, and overland flow actually generated at the soil surface, unless there is evidence that a substantial amount of water reaches the stream directly via pipes or as overland flow not generated as return flow. From a catchment perspective the distinction between pipe flow and overland flow is meaningless: There is one fast flow path, exemplified by OF2, which is neither entirely at the soil surface nor entirely below it. The hydrochemical fingerprint of this fast flow path differs significantly from the respective soil water and groundwater signals. As was shown, a detailed investigation of individual flow paths is required to separate pipe flow and "true" overland flow contributions. To avoid the exclusive subsurface connotation of pipe flow (often classified as subsurface storm flow) and the exclusive surface connotation of overland flow, the term return flow [*Kirkby*, 1988], much ignored in hydrology or used only in a very restrictive sense, is certainly more appropriate: It captures the origin of overland flow in this environment while acknowledging the existence of pipe flow.

Inasmuch as K and SiO_2 are the characteristic tracers of fast and slow flow paths, respectively, they may be used implicitly as new-water and old-water signals under the plausible assumption that they are almost exclusively supplied by vegetation and weathering zone, respectively. Vegetation interacts mainly with near-surface fast flow paths in response to precipitation events, so the high K/SiO_2 ratio of these flow paths is clearly a result of the event itself. In other words, it is new water. To add to the "old and new water versus slow and fast pathways" controversy, our results emphasize the importance of fast pathways transporting new water at La Cuenca. Considering only responsive forested catchments, the Maimai catchments [*McDonnell*, 1990], with fast pathways transmitting old water, represent the other end of the spectrum. South Creek in northeast Queensland appears to hold the middle ground, with both old and new water in fast pathways [*Elsenbeer et al.*, 1994].

Although our study has a hydrologic origin and purpose, it provides a message for ecological studies of the nutrient budget type. *Bruijnzeel* [1991, p. 7] comments on the "rather flimsy hydrological foundations on which some often quoted budgets are based." Our results suggest that budget studies whose sampling scheme is not based on knowledge of hydrologic pathways are apt to provide false output estimates at least of some nutrients. In the case of K, neglecting the action of fast pathways will result in an underestimation of its output. As a consequence, one may prematurely infer a nutrient-tight catchment. By the same token, comparing only throughfall and soil water composition invariably results in the common conclusion of a tight nutrient recycling in the root mat (see, for example, *Forti and Neal* [1992, p. 113, and references therein]). Such a recycling may partly or even wholly explain the difference between throughfall and soil water composition, but ignorance of flow paths renders such an explanation purely hypothetical.

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