

## Major element chemistry, weathering and element yields for the Caura River drainage, Venezuela

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**Abstract.** The Caura River, a major tributary of the Orinoco River, was sampled at bi-weekly intervals for two years. Because the watershed is covered with undisturbed forest overlying a Precambrian shield, the water of the Caura River has low conductivity (mean, 15 uS/cm), contains small amounts of particulate material (mean, 11 mg/l), and is slightly acidic (median pH, 6.8). Concentrations of total dissolved solids vary less than two-fold in response to the seasonal ten-fold variation in discharge; concentrations of particulate material vary more (ten-fold) and are lowest at the time of peak discharge. Seasonal changes in concentrations of Si, major metal cations, and hydrogen ion are complementary to each other and indicate regular seasonal changes in weathering rates. Measurements of bulk atmospheric deposition and the observed runoff yield of Cl and S were used in estimating the basin-wide atmospheric deposition of major elements, which were as follows (kg/ha/yr): Ca, 1.3; Mg, 0.29; Na, 8.2; K, 1.0; Cl, 12; S, 2.8; P, 0.14. Element ratios show that terrestrial sources contribute strongly to the atmospheric deposition of Ca, K, S, and P. From the atmospheric contributions and runoff yields, watershed retention was computed for major elements with reference to Si. The watershed accumulates Al, Fe, and P, whereas losses of Ca, Mg, Na, K, and S originating from non-atmospheric sources exceed the relative loss rates of Si. The rock weathering rate based on Si is 1.8 cm/1,000 years. Although significant amounts of Ca, Mg, Na, and K are found in atmospheric deposition, the dominant influence on the mass balances of these elements is weathering rather than deposition. Weathering has a trivial influence on the cycles of Cl and S. Both atmospheric deposition and weathering are important in the mass balance of P. The ecosystem does not effectively conserve most biologically active elements (Ca, Mg, Na, K). The ecosystem conserves significant amounts of phosphorus (31% of total input), but probably by abiotic mechanisms.

### Introduction

The yield of elements in runoff from large, undisturbed watersheds draining tropical moist forests is not well known (Meybeck 1982). Such information is of interest in that it serves as a basis for the computation of weathering and erosion rates and of the retention capacities of mature tropical forests for specific elements. Most of the comprehensive chemical analyses of tropical rivers have been based on relatively few samples. Information of this type, although useful in a number of ways, does not provide an ideal basis for quantifying element yields. Because runoff from tropical moist forests often varies seasonally, fre-

quent sampling over one or more annual cycles provides the best basis for estimating element yields. We report here the results of a two-year study of element yields for the drainage of the Caura River, Venezuela.

The Caura River, a tributary of the Orinoco River, drains an area of 47,500 km<sup>2</sup> in southern Venezuela (Fig. 1). The watershed occupies a portion of the Guayana Shield and is covered by a mixture of premontane rain forest, very humid premontane and tropical forest, and humid tropical forest (Ewel *et al.* 1976). The rainfall associated with these forest types ranges from 2200 mm/yr to 6000 mm/yr. The average runoff during the two years of study was 2420 mm/yr, which would correspond to an average rainfall for the drainage of approximately 4500 mm/yr, according to the runoff estimates given by Ewel *et al.* (1976). The vegetation and running waters of the Caura River drainage are essentially undisturbed.

Near the Orinoco, the Caura River passes through gently undulating savannas at an elevation of about 17 m asl. South of the Orinoco, the terrain becomes more hilly. Far to the south, the river valleys steepen and the surrounding plateaus rise to peaks as high as 2500 m asl near the Venezuelan-Brazilian border.

The Caura basin is lithologically complex. Very generally, rocks in the western part of the basin are Precambrian granites. To the east are highly deformed, Precambrian, silica-rich iron formations, as well as other metasedimentary and

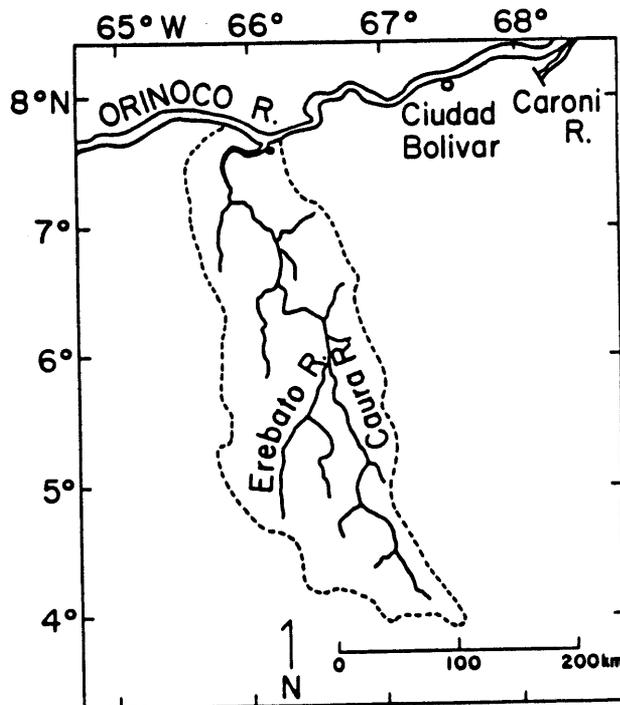


Fig. 1. Map of the Caura River drainage showing its relationship to the Orinoco River.

metavolcanic rocks. To the south and south-east there are Precambrian silicic lava flows, tuffs, and ignimbrites, and remnants of Precambrian sandstones, conglomerates, and shales that are metamorphosed and intruded by basic sills and dikes (Bellizzia 1966, Case and Holcombe 1980, Case *et al.* 1984).

The rocks of the Caura River drainage contain some easily weathered minerals, including feldspars and hornblends in the granitic rocks that are expected to contribute major amounts of  $\text{SiO}_2$ , and Na, plus some Ca, Mg, and K. Additional Fe and  $\text{SiO}_2$  would be released from the iron formations and volcanic rocks. Biotite and pyroxene in more basic igneous rocks, intruded as sills and dikes, would contribute  $\text{SiO}_2$ , Ca, Mg, and K (Drever 1982).

## Methods

Samples were taken near the mouth of the Caura River at bi-weekly intervals between 1 May 1982 and 30 April 1984. Because dissolved and suspended materials may be distributed unevenly in large tropical rivers (Curtis *et al.* 1979, Lewis *et al.* 1984), the river was sampled with a flow-integrating sampler (United States Geological Survey, C. Nordin, pers. comm.; Stevens *et al.* 1980) from top to bottom at several (3–5) points across its width.

Samples were stored in a dark cooler during transport to a field laboratory at Ciudad Bolivar. The samples were filtered immediately upon return to the laboratory through dry, ashed, preweighed glass-fiber paper (Whatman GF/C, effective pore size  $< 0.7 \mu\text{m}$ ; Sheldon 1972). The filters were dried to constant weight at  $60^\circ\text{C}$  and were reweighed to provide an estimate of the total amount of particulate material in the sample. A correction was made subsequently for structural water in clays. On the basis of X-ray diffraction data for clays, this correction was set at 10% of the inorganic fraction of particulate material.

Portions of filters with particulate material were combusted in a CHN analyzer, which produced, after corrections for blanks, estimates of percent carbon and nitrogen in the sample. The combustions were done in triplicate, and the analyzer was calibrated for each set of samples against US National Bureau of Standards orchard leaves or reagent-grade EDTA. Separate filters from each sample were also analyzed for particulate phosphorus by pyrolysis and subsequent orthophosphate determination according to the method of Solorzano and Sharp (1980).

A liter of unfiltered sample was allowed to stand for a week, after which most of the water was removed without disturbing the sedimented material. The sedimented material was transferred quantitatively to a 125-ml polyethylene bottle, dried at  $60\text{--}70^\circ\text{C}$ , and capped pending analysis. At the time of analysis, 30 ml of laboratory deionized water was added to the bottle and the mixture was allowed to stand for 30 minutes. Particulate material on the sides of the bottle was then dislodged with a rubber policeman and the bottle interior was sonicated for five minutes to disperse and dislodge particulate material. The sample was placed in an uncovered teflon-lined bomb and dried at  $80^\circ\text{C}$  in an oven

(Bernas 1968). The sample material was treated with 0.5 ml of aqua regia, after which 2.1 ml of 70% hydrochloric acid was added. The bomb was then sealed immediately and placed in an oven at 145 °C for eight hours.

After combustion, contents of the bomb were emptied into a 25-ml volumetric flask and deionized water (5 ml) was used to rinse the bomb. Then 1.66 g of  $H_3BO_3$  in the form of a saturated solution was added to the sample to dissolve metal fluorides (Bernas 1968). The sample was stirred until it cleared, was made up to 25 ml with deionized water, and was transferred to a polyethylene bottle. Lanthanum and cesium solutions were added to enhance atomic absorption analysis. Seven elements were determined by atomic absorption analysis: calcium, magnesium, sodium, potassium, iron, manganese, and aluminium. Standard additions were used in the preparation of standard curves. The seven elements, when expressed as their oxides, were summed and were added to the amount of particulate phosphorus and organic carbon expressed as oxides. The difference between this sum and the total weight of particulate material in the sample was assumed to be  $SiO_2$ . Standard rock samples from the United States Geological Survey were analyzed simultaneously; recovery of the elements from these standards was good (mean 90%, std error 11%).

The pH of the unfiltered samples just after their arrival at the laboratory was determined with a pH meter and combination electrode standardized prior to each reading against dual buffers. In addition, a conductivity reading was taken. Neither the pH readings nor the conductivities were very stable; both could be altered by simple filtration of the sample. These instabilities are probably explained by the combination of relatively high amounts of particulate and organic matter in a very dilute solution of ions.

The Caura River is weakly buffered, and therefore carries very low concentrations of inorganic carbon. For this reason, inorganic carbon was analyzed by two separate methods: gas chromatography and titration. For the gas chromatographic determinations, dissolved inorganic carbon was stripped from the sample in the field. An Erlenmeyer flask (500-ml) was prepared in the laboratory for each sample. The flask was filled with deionized water through a rubber stopper containing two ports. The water was then displaced with an inert gas (either nitrogen or argon) and both of the ports were closed. In addition, a number of 10-ml evacuated containers were prepared in the laboratory prior to sampling. Because these vacutainers frequently contained  $CO_2$  at concentrations higher than the ambient atmospheric concentration, they were disassembled and flushed with an inert gas, after which they were reassembled. The vacuum within the tubes was then restored with a gas syringe.

In the field, a 200-ml portion of the inert gas inside the flask was displaced with river water. After introduction of the river water, the ports of the flask were closed. Concentrated sulfuric acid (18 N, 1 ml) was then added by syringe through one of the ports. The flask was inverted numerous times to cause mixing. A gas syringe was used to withdraw 5 ml of gas from the headspace of the flask, and this gas was introduced directly into an evacuated container. A second container, which served as a replicate, was also filled in this manner from

each flask. Blanks were also made for each sample set. These consisted of evacuated containers to which no water was added. The gas in all of the evacuated containers was analyzed by gas chromatography. From the concentration of CO<sub>2</sub> in a given container, the amount of dissolved inorganic carbon in the original sample was computed by use of the gas laws, partition coefficient, and the amounts of water and headspace within the flask. The blanks were consistently very low. All analyses were done in duplicate; variation in duplicates showed that the standard error for the mean of two analyses used in representing a given date at a given site is 6.2% of the mean.

A parallel set of inorganic carbon analyses was conducted by Gran titrations (Gran 1952, Stumm and Morgan 1981) for a full year and fixed-endpoint titrations at other times based on the empirically-established relationship between the outcome of a Gran titration and a fixed-endpoint titration for the Caura River. Titrations showed a median deviation from gas chromatography of 13%. Inorganic carbon estimated from chromatography is generally lower than estimates based on titrations. However, these differences are not significant for present purposes; results reported here are based on titrations rather than gas chromatography.

For the analysis of total dissolved solids, filtered water was evaporated to constant weight in a tared crucible at 60–70 °C. Higher temperatures were avoided in order to reduce losses of organic matter.

A filtered subsample was treated with cesium chloride to make a concentration of 100 mg/l and with lanthanum oxide to make 10,000 mg/l. The lanthanum oxide was dissolved in an HCl solution of sufficient strength to depress the subsample pH below 2.0. Atomic absorption analysis was done on this subsample for soluble calcium, magnesium, sodium, and potassium.

Another filtered subsample was analyzed by ion chromatography for sulfate and chloride. A number of other substances, including nitrate, ammonium, and dissolved organic carbon (DOC), were analyzed, but are outside the scope of this paper. Nitrate, ammonium, and DOC are reported here only in connection with analytical ion balance; complete data for these substances are given by Lewis (1986) and Lewis *et al.* (1986).

Deposition of elements from the atmosphere was measured at a single location near the mouth of the Caura River. The collector, which was of the type described by Lewis and Grant (1978), had a surface area of 0.125 m<sup>2</sup> and was mounted 10 m above the ground on a tower. There were no significant nearby sources of contamination, and no tall vegetation was growing within 50 m of the collector. The collector was emptied bi-weekly and the collecting surface was rinsed. The wet precipitation was then subjected to analysis according to a protocol similar to that described above for river water. On three occasions there was no measurable precipitation, and in these instances the dry deposition was collected along with the rinse water for analysis. Because the collector was open continuously, the accumulation rates correspond to bulk atmospheric deposition.

The single precipitation collection station used in this study is not an adequate

substitute for a network covering the entire Caura River drainage. The purposes of the atmospheric deposition measurements were (1) to provide a comparison with the atmospheric deposition computed from mass balance, and (2) to indicate the proportions of ions in atmospheric deposition within the watershed in support of the mass-balance calculations.

## Results

### *Dissolved and suspended materials*

Figure 2 shows the concentrations of total dissolved solids and total particulate material in relation to discharge. The discharge of the Caura River is highly

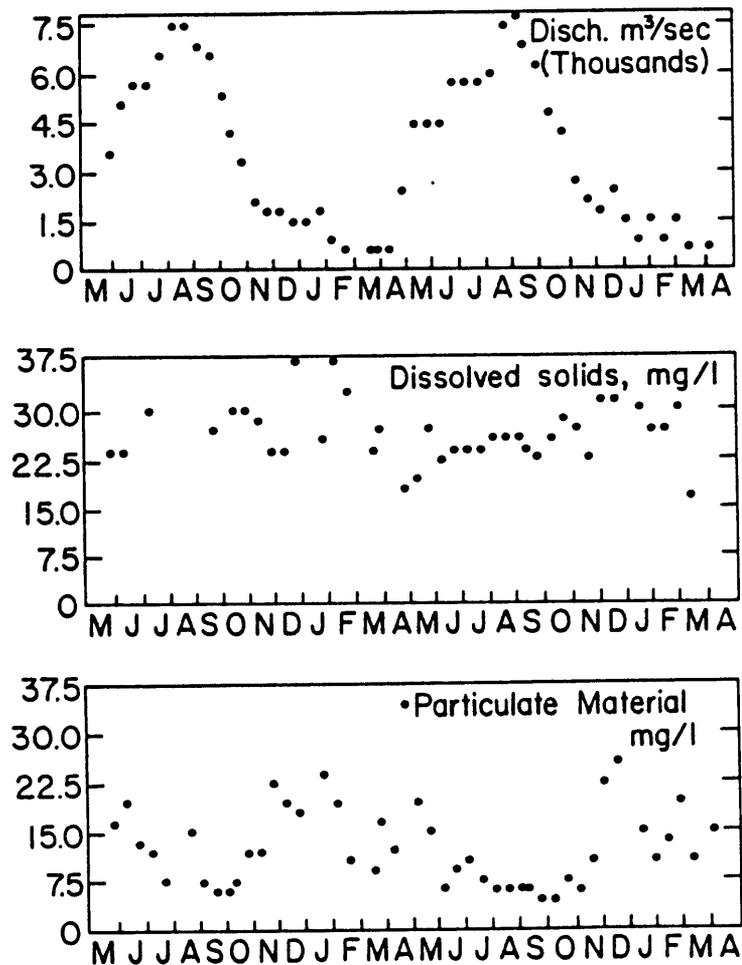


Fig. 2. Discharge and the concentrations of total dissolved solids and total particulate material over the two-year study interval.

seasonal. The amount of runoff varies more than ten-fold over the course of the year and the seasonal pattern, as shown not only by Fig. 2 but also by stage height records for other years, is repeated with great fidelity from one year to the next. As shown by Fig. 2, the concentration of total dissolved solids is insensitive to variations in discharge. There is a slight increase in total dissolved solids at the time of lowest discharge and a slight dilution effect just as discharge begins to rise. These trends are far less pronounced, however, than the trend in discharge.

The amount of particulate material in suspension is somewhat more sensitive than total dissolved solids to changes in discharge. Contrary to expectation, the lowest concentrations of particulate material occur at peak discharge. There is a sudden increase in the concentration of particulate material associated with the first week of rising water, but otherwise, the highest concentrations are associated with periods of low discharge.

Figure 3 shows the patterns of pH and soluble silicon in relation to discharge. The pH drops sharply as the water begins to rise and remains low until discharge nears its peak, at which time pH begins to rise. The amount of soluble silicon runs parallel to the pH, although the concentration of silicon is more stable than the pH.

Figure 4 shows the concentrations of soluble cations. All soluble cations show a notable depression of concentration just as the water begins to rise. The effect is least pronounced for potassium. Subsequent to the depression, concentrations of all cations increase slowly but steadily through the entire cycle of rising and falling water, culminating in peak concentrations at low water just prior to the onset of rising water.

Figure 5 shows the major anions. Concentrations of inorganic carbon, reflecting the amount of bicarbonate, are somewhat erratic, as might be expected in such poorly buffered waters subject to biological perturbation of the amount of inorganic carbon in solution. However, peak concentrations of inorganic carbon clearly occur toward the end of the dry season, and the onset of rising water sharply depresses the amount of inorganic carbon in solution.

Sulfate shows only a weak pattern, and chloride shows almost no pattern. High water appears to produce higher sulfate concentrations, but the initial period of rising water is not accompanied by sudden changes in concentration, as is the case for some substances.

Table 1 gives the discharge-weighted mean concentrations for major ions and other variables of interest. The Table also gives the yield of each species in its soluble form. On an equivalent basis, sodium is the dominant cation. Calcium is a strong secondary cation, and magnesium and potassium rank below this. Among the anions, bicarbonate is dominant. Organic anions must also be considered potentially significant in waters of low ionic content (Lazerte and Dillon 1984). For the Caura River, the anion equivalent for organic carbon was estimated from information given by Oliver *et al.* (1983). Although separation of fractions has not been done for the Caura River, it seems likely on the basis of studies on the Amazon (Ertel *et al.* 1986) that more than half of the DOC

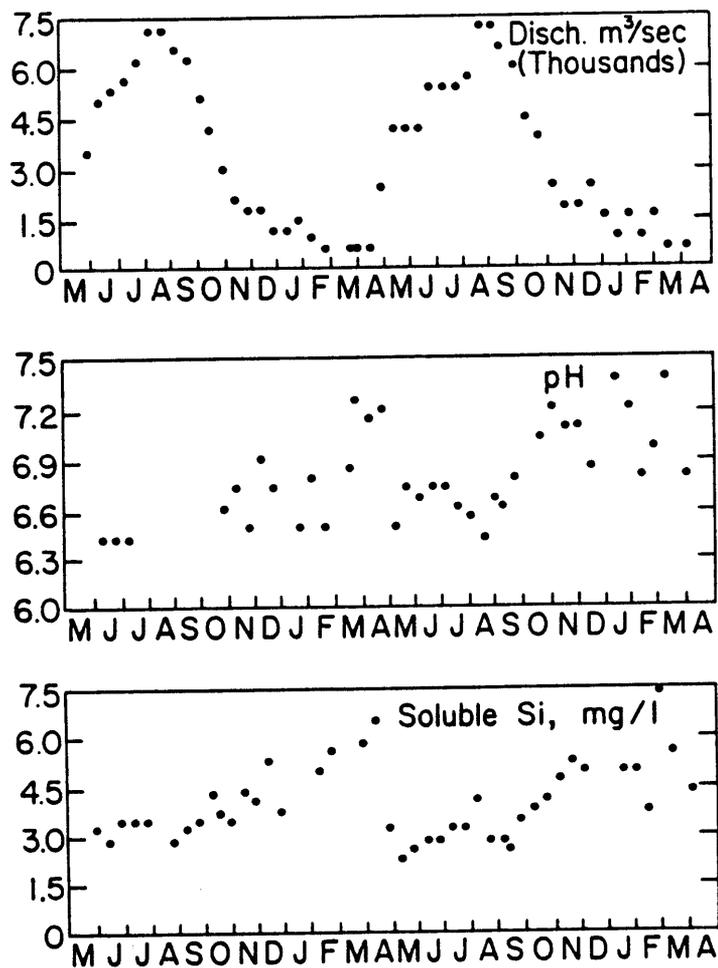


Fig. 3. Patterns of pH, soluble silica, and discharge over the two-year study interval

would be humic acids (ca. 7.7 ueq/mg C) or fulvic acids (10.7 ueq/mg C). As an approximation taking into account all classes of organic matter, we have used 5 ueq/mg C. On the basis of this estimate, the milliequivalent concentration of organic carbon is second only to the milliequivalent concentration of bicarbonate. Sulfate and chloride, although secondary to organic carbon and bicarbonate, are also important.

The sum of dissolved ionic solids, soluble organic matter (computed from DOC analysis) and soluble silica ( $\text{SiO}_2$ ) is the expected total dissolved solids, and can be compared with total dissolved solids as measured directly by evaporation. The directly measured total dissolved solids correspond to a yield of 593 kg/ha/yr, and the expected total dissolved solids correspond to a yield of 605 kg/ha/yr.

For particulate material, analysis of biweekly samples over an entire year

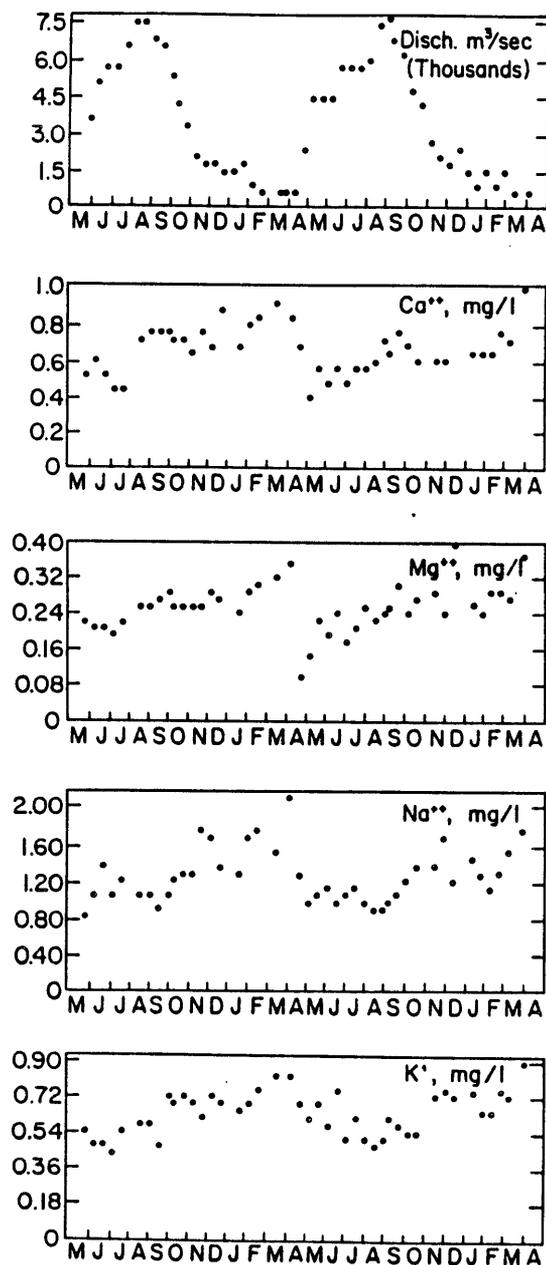


Fig. 4. Concentrations of soluble cations over the study interval.

shows that there are no major seasonal trends in percent composition, despite the large changes in concentration. For this reason, we need only use the discharge-weighted average concentrations of elements in particulate form (Table 2) for the computation of yields. For each element, the yield in particulate form has

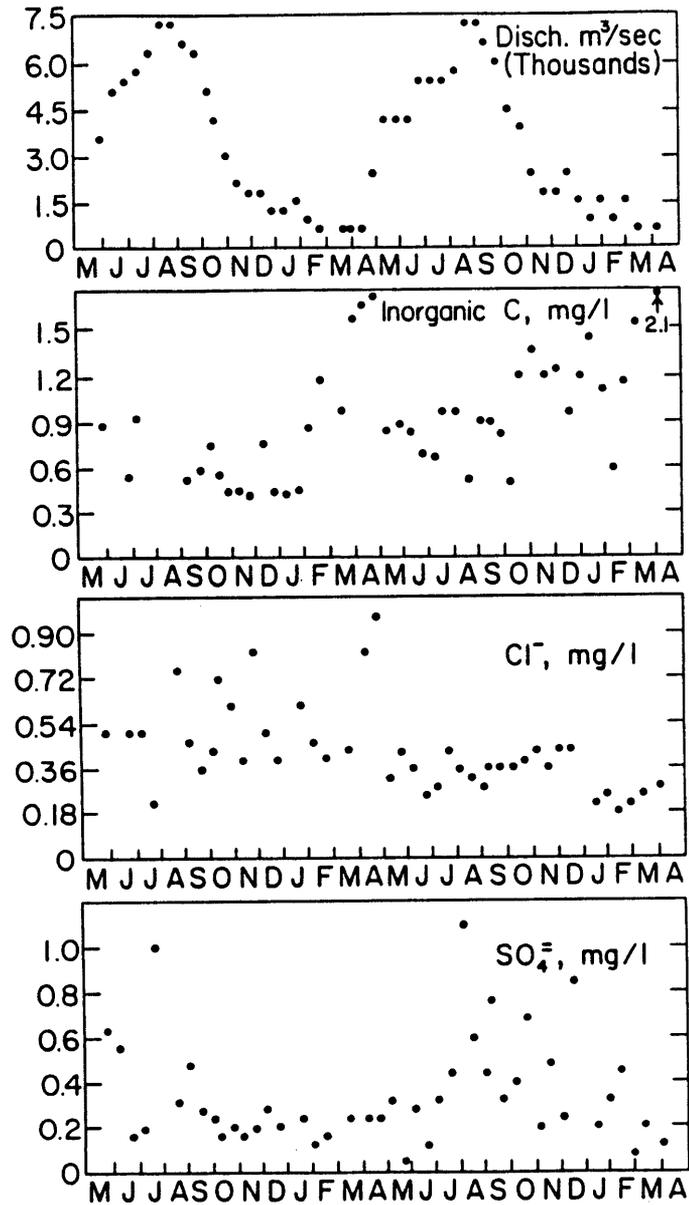


Fig. 5. Concentrations of major anions over the study interval.

been added to the yield in soluble form (Table 1) to give the total yield (Table 2). The yields shown in Table 2 do not include an allowance for bedload. For aluminum, iron, manganese, and silicon, which are transported to a large degree in particulate form, failure to include bedload is unlikely to result in underestimates above 10% (Richards 1982). For other elements, which are principally transported in the soluble phase, bedload is negligible.

Table 1. Discharge-weighted mean concentrations and yields for the two-year study of the Caura River.

	mg/l	meq/l	kg/ha/yr	eq/ha/yr
<b>Cations</b>				
Ca <sup>++</sup>	0.64	0.032	15.5	733
Mg <sup>++</sup>	0.25	0.020	6.01	495
Na <sup>+</sup>	1.14	0.050	27.6	1201
K <sup>+</sup>	0.60	0.015	14.6	373
NH <sub>4</sub> <sup>+</sup>	0.05	0.003	1.15	64
Total	2.68	0.120	64.9	2906
<b>Anions</b>				
HCO <sub>3</sub> <sup>-</sup>	5.10	0.084	124	2032
SO <sub>4</sub> <sup>-</sup>	0.41	0.008	10.0	208
Cl <sup>-</sup>	0.42	0.012	10.3	290
Organic soluble C	3.99*	0.020	96.8	484
NO <sub>3</sub> <sup>-</sup>	0.27	0.004	6.60	106
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	0.008	0.000	0.20	2
Total	10.2	0.128	247.9	3122
<b>Other variables</b>				
Total particulates	11.33	—	274	—
Organic	2.19	—	53	—
Inorganic	9.14	—	221	—
pH, units (median)	6.8	—	—	—
Conductivity, uS/cm	15.4	—	—	—
Soluble Si	3.78*	—	91.5	—
Total dissolved solids	24.5	—	593	—

\*C is 8.00 as organic matter; Si is 8.09 as SiO<sub>2</sub>

### *Mass transport in relation to geologic sources*

Two possible sources of data on composition of the shield rock were considered. The first of these is a regional data set based on analyses of the La Paragua granite from a point east of the Caura River drainage (Pasquali *et al.* 1972) and of the Rapakivi granite from a point west of the Caura River drainage (Mendoza 1978). The second source is the general compilation of data on shield rock composition by Holland (1978, Tables 4–13). Although the regional data sources would seem to be most appropriate, they are based on fewer analyses and were not actually drawn from the Caura watershed. Furthermore, for some elements (Ca and Mg especially) the composition shown by the regional data is substantially divergent from the more broadly based averages reported by Holland, and some of the observed yields are logically inconsistent with the regional data but not with the more broadly-based data of Holland. For this reason, Holland's data were used in computing the percent elemental composition of the shield as shown in Table 2. It will be noted in the presentation of results where this assumption makes a significant difference. Holland's data were used from column 1 of his Tables 4–13 except in the case of chlorine and

Table 2. Element yields from the Caura River watershed, composition of shield rock, and the observed atmospheric deposition at the sampling station.

Element	Soluble yield (kg ha yr)	Composition of inorganic particulates (%)	Particulate yield (kg/ha/yr)	Total yield (kg/ha/yr)	Soluble as % of total	Rock composition (%*)	Observed atmospheric (kg/ha/yr)
Ca	15.5	1.20	2.66	18.2	85	2.7	1.70
Mg	6.01	0.68	1.51	7.52	80	1.2	0.37
Na	27.6	6.22	13.8	41.4	67	2.6	10.6
K	14.6	2.21	4.90	19.5	75	2.7	1.33
Al	0.10	10.36	23.0	23.1	<1	8.2	0.0
Fe	0.42	5.52	12.2	12.7	4	3.2	0.0
Mn	0.00	0.21	0.46	0.46	<1	0.08	0.0
P	0.24	0.10	0.23	0.47	51	0.11	0.18
Si	91.5	27.15	60.2	152	60	31	0.0
Cl	10.3	0.05**	0.11	10.4	99	0.05	15.1
S	3.34	0.05**	0.11	3.46	97	0.05	3.65

\*From Holland (1978, 4-13, see text)

\*\*Estimated, not measured.

sulfur, for which we used column 4, which is the only one that provides estimates of these elements.

Given the percentage composition from Holland's table and the observed yields of silicon from the watershed, the implied rock weathering rates are 546 kg/ha/yr. At a rock density of 2.7 g/cm<sup>3</sup>, this corresponds to a weathering rate of 1.8 cm/1000 yr. If the regional estimates of rock composition had been used, the estimated weathering rate would have been 1.7 cm/1000 yr. From the data in Table 1, chemical erosion is 281 kg/ha/yr plus an uncertain but small contribution of geologic carbonates, and the mechanical erosion rate is 221 kg/ha/yr for a total loss rate of 502 kg/ha/yr, or very close to the implicit weathering rate based on silicon.

#### *Atmospheric deposition*

Although atmospheric deposition was collected continuously over the entire study interval, the estimates in Table 2 are based on deposition between the first of July and the last of February over the two years of the study. The dry season and the earliest part of the rainy season fall between the first of March and the last of June; over this interval, the deposition rates for the metal cations and for chloride are much higher than they are the rest of the year. The prevailing winds, which are from the east and northeast and thus blow directly from the Atlantic, are especially strong at this time (Venezuelan Air Force, unpubl. data), and the amount of atmospheric moisture over the path of the air mass moving up the Orinoco River from the Atlantic is minimal. The high chemical deposition rates for the dry season suggest that there is an unusually efficient transport of aerosols, mostly of marine origin, that remain in the air mass because of the lack of moisture at this time. Precipitation collection at other stations (Lewis, unpubl. data) and chloride yields from the Caura River drainage (Table 1) both strongly suggest that the pulse of ionic materials during the dry season and along with the first rains of the wet season at the precipitation collection station correspond to a local phenomenon associated with exceptionally efficient seasonal atmospheric transport of materials up to the river channel, and that this is not characteristic of the entire drainage. Consequently the atmospheric deposition for these months has been omitted in calculating the observed atmospheric deposition as shown in Table 2.

The total annual atmospheric deposition of insoluble particulate material is 15 kg/ha/yr, of which approximately 50% is organic and 50% is inorganic. Except for phosphorus, deposition of insoluble particulate material is not included in Table 2 because it accounts for insignificant element transport.

#### **Discussion**

The yield of elements from the watershed, the composition of the parent material, and the molar ratios of elements in atmospheric deposition as observed at the collection station can be used in reconstructing mass balances of the major elements. The principal difficulty is separation of atmospheric deposi-

tion from differential retention of elements in the watershed. However, this separation can be achieved with reasonable confidence by a three-step sequence: (1) estimation of mass balance for chlorine and sulfur, for which weathering contributions are trivial by comparison with atmospheric transport, (2) estimation of mass balance for silicon, iron, and aluminum, for which atmospheric transport is trivial by comparison with weathering, and (3) estimation of mass balance for calcium, magnesium, sodium, and potassium, for which both atmospheric transport and weathering can be major considerations. Estimates can then also be made of the mass balances for manganese and phosphorus, although these estimates are more subject to error than the other estimates because of greater uncertainties in the amounts of these elements in the shield rock.

*Mass balance of elements originating mainly from the atmosphere*

The observed total yield of chlorine from the watershed is 10.4 kg/ha/yr, and the observed total yield of sulfur from the watershed is 3.46 kg/ha/yr. Corrections for the contribution of the parent material of this total are very small and are therefore not critical. Approximate corrections based on the weathering rate of silicon would be 0.2 kg/ha/yr for chlorine and 0.36 kg/ha/yr for sulfur. The estimate of yields not accounted for by weathering would thus be 10.2 kg/ha/yr for chlorine and 3.10 kg/ha/yr for sulfur. It will be assumed that the watershed, because of its maturity, is very close to equilibrium with respect to these two elements and, for this reason, that the yields, after correction for the small contributions of parent material, are estimates of the atmospheric deposition for the watershed as a whole.

One additional correction is made in order to bring the estimates of atmospheric deposition for chlorine and sulfur into line with each other so they can be used together in subsequent calculations of atmospheric contributions for other elements. In making this additional correction, we assume that the molar proportions of sulfur and chlorine in the deposition for the entire watershed should be the same as the observed molar proportions of these elements in atmospheric deposition at the sampling station. On this basis, the ratio of chlorine to sulfur in the measured yields is slightly too low. This imbalance is corrected by upward adjustment of the chlorine and downward adjustment of the sulfur by equal amounts to achieve the molar balance that was observed in the atmospheric deposition. The resulting corrected numbers for computed atmospheric deposition over the entire watershed are shown for chlorine (11.7 kg/ha/yr) and for sulfur (2.83 kg/ha/yr) in Table 3. These estimates will be used in all subsequent computations involving atmospheric contributions of these two elements.

The computed atmospheric deposition for both chlorine and sulfur as shown in Table 3 is slightly lower than the observed atmospheric deposition (Table 2) of these elements at the collection site near the mouth of the Caura River. This

Table 3. Computed atmospheric contributions to the watershed and estimates of watershed retention.

Element	Computed atmospheric (kg/ha/yr)	Computed atmospheric as % observed yield	% Marine contribution to atmospheric*	Watershed retention** (kg/ha/yr)
Ca	1.32	7	19	- 3.73
Mg	0.29	4	100	- 1.39
Na	8.21	20	79	- 20.6
K	1.03	5	23	- 5.12
Al	0.0	0	0	+ 16.9
Fe	0.0	0	0	+ 2.99
Mn	0.0	0	0	- 0.07
P	0.14	30	0	+ 0.21
Si	0.0	0	0	—
Cl	11.7	112	100	—
S	2.83	82	19	—

\*Computed on the basis of chlorine deposition and the element ratios in seawater from Parsons *et al.* (1977).

\*\*Indicated with reference to Si: + = retained with respect to Si, - = released with respect to Si.

is expected for chlorine in view of the closer proximity of the collection site to the Atlantic, which is the major source of atmospheric chlorine (*cf.* Stallard and Edmond 1981). Specific sources of sulfur are unknown, but could include both coastal and inland environments, in which case the watershed as a whole would be more distant from the main sources than the collection station, as in the case of chlorine. Furthermore, we do not expect the observed deposition at a single station to equal exactly the atmospheric deposition computed from mass balance because of spatial variations in amount of rainfall and in atmospheric chemistry over the watershed and the uncertain relationship between deposition to a natural vegetated surface and deposition to a standard collector. Although the two estimates are relatively close, we take the computed atmospheric deposition as the more valid estimate of atmospheric contributions to the watershed.

#### *Mass balance of elements originating mainly from weathering*

For aluminum and iron, atmospheric contributions are trivial and the observed yield can therefore be accounted for by weathering of parent material. However, incongruent weathering can be expected to lead to differential loss rates from the parent material and its weathering products. Using silicon as an index, we calculate the yield of aluminum and iron that would occur if these two elements were released from the watershed in proportion of their abundance in relation to silicon within the shield rock. The deviation between this hypothetical yield and the observed yield is a measure of the watershed retention rates for aluminum and iron. As shown in Table 3, aluminum is retained at a rate of 17 kg/ha/yr, and iron is retained at a rate of 3 kg/ha/yr. These retention rates are

substantial in relation to the weathering rates and element yields, especially for aluminum (Table 2).

*Mass balance for elements affected by atmospheric deposition and weathering*

For calcium, magnesium, sodium, and potassium, the mass balance calculations are complicated by the need to take into account both atmospheric transport and weathering as potentially significant sources. In estimating the atmospheric sources of these four elements, we use the mean of the molar ratios of each element in relation to chlorine and sulfur as established by measurement of deposition chemistry at the monitoring station. These molar proportions are then applied to the computed basin-wide atmospheric of sulfur and chlorine, resulting in estimates of basin-wide atmospheric deposition for each element. The results are shown in the second column of Table 3. The estimates are reasonably close to the observed atmospheric deposition of the elements at the monitoring station (last column, Table 2). For each of the elements, the computed basin-wide deposition is slightly lower than the observed deposition, which is reasonable in view of the closer proximity of the monitoring station to the major marine and terrestrial sources of ionic materials.

Hypothetical yields of calcium, magnesium, sodium, and potassium in runoff can be estimated as the sum of atmospheric deposition plus the geologic source corresponding to the elemental composition of the parent material and the weathering for the silicon. As shown in the last column of Table 3, deviations between these hypothetical yields and the observed yields in each case are negative, *i.e.*, the observed yields are higher than can be accounted for by atmospheric deposition plus weathering of the parent material at a rate equal to that of silicon. The negative residuals are estimates of the watershed retention rates, which are negative, indicating that each of these elements leaves the weathering parent material at a rate faster than the silicon making up the bulk of the rock matrix.

The rapid loss of calcium, magnesium, sodium, and potassium makes sense geochemically because of the high mobility of these elements in the ionic form, especially in areas of high rainfall. It is nevertheless surprising that the mature tropical ecosystem does not offset high mobility by selective retention of some or all of these elements, all of which are important components of biomass. We conclude that recycling of these elements in the biologically active portions of the ecosystem must fulfill the needs of organism growth, leaving the overall mass balance of the elements without any clear sign of biological intervention.

Calculations were also done for manganese and phosphorus (Table 3), even though potential errors are greater because uncertainties in the amounts of these elements in the shield rock. Manganese shows a slight negative balance, whereas phosphorus shows a positive one. For phosphorus, significant components of the mass balance can be traced both through the atmosphere and through weathering.

The retention rate of phosphorus by the watershed is surprisingly high in relation to the total flux of phosphorus. If we consider the total annual addition of phosphorus to the ecosystem to equal the atmospheric deposition of phosphorus plus the release of phosphorus from the rock at a rate determined by the weathering of silicon, the annual addition of phosphorus to the system would be 0.68 kg/ha/yr. The mass balance calculation shows that 0.21 kg/ha/yr, or 31% of this amount, is retained by the ecosystem. This amount of phosphorus cannot be stored in living biomass, since the molar ratio of carbon to phosphorus in woody plants (2040:1; Likens *et al.* 1981) dictates that only a few centuries would pass before the standing stock of woody biomass would substantially exceed that of any conceivable plant community. However, it is feasible for significant phosphorus storage to occur in soil. Soils moderately enriched in phosphorus (ca. 0.2%) would need to accumulate at only approximately 1 mm/100 yr in order to account for an ecosystem phosphorus retention of 0.2 kg/ha/yr. Some minerals likely to be present in the watershed may account for significant P storage; phosphates can be adsorbed strongly by goethite (about 50  $\mu\text{mole/g}$  at pH 6.8; Dixon and Weed 1977). Efficient removal of phosphate by halloysite, a hydrated kaolinitic clay, in lateritic soil has also been reported (Raymahashay *et al.* 1984).

Tropical moist forests are thought to be commonly phosphorus-deficient (Vitousek 1984), and it is well known that soils in the shield area of Venezuela and Brazil are very poor in phosphorus (Sanchez *et al.* 1982). The mass balances for nitrogen and phosphorus also suggest that phosphorus is more likely to be limiting than nitrogen in the Caura River watershed (Lewis 1986). The Caura watershed may be storing phosphorus in locations or in chemical forms that are not readily available to the biota. In this case, deficiencies of phosphorus in the biota would not be caused by a low phosphorus inventory, but rather by poor availability of the phosphorus that is retained by the watershed. Retention of phosphorus by the watershed could also be considered grounds for examining more carefully the conclusion that the ecosystem is indeed phosphorus-deficient.

#### *Overview of mass balances*

Atmospheric contributions to the mass balance of watersheds are typically estimated from the collection of atmospheric deposition, even though it is widely acknowledged that actual deposition to a vegetated watershed surface may differ considerably from measured deposition to a standard collector. The data for the Caura River drainage are encouraging in that observed deposition to a collector surface does not differ greatly from the deposition estimated more properly on the basis of mass balance.

The observed atmospheric deposition rates for a number of elements are among the lowest reported for bulk deposition sampled over annual intervals at tropical sites (Lewis 1981). However, the data base for the tropics is still very

small. Among the cations, only the atmospheric contributions of sodium might be considered somewhat higher than expected, as is the deposition of chlorine. The amounts of these two elements deposited at a given site are closely related to distance from coast (Stallard and Edmond 1981), and may also be affected in the case of the Caura River drainage by strong prevailing northeasterly winds blowing directly from the Atlantic.

The atmospheric deposition of sulfur is considerably lower than that of much of the United States (Munger and Eisenreich 1983), as might be expected, but is approximately equal to sulfur deposition in central Colorado or some parts of the Canadian Shield (Lewis 1981, Lewis *et al.* 1984). Whereas the mass ratio of sulfur to chlorine in seawater is approximately 1:20, the mass ratio in the computed atmospheric deposition within the Caura River watershed is 1:3. Strong enrichment of the atmospheric component with sulfur of terrestrial or estuarine origin is thus indicated. Stallard and Edmond (1981) have documented a qualitatively similar phenomenon for the Amazon drainage.

The amounts and proportions of dissolved substances in the Caura River fall within the midrange of values reported by Stallard and Edmond (1983) for various locations in the lowlands of the Amazon drainage, including the Rio Negro system. As shown by the mass-balance analysis, the metal cation chemistry of the Caura River can be explained principally by weathering. This is contrary to the hypothesis of Gibbs (1970) that chemistry of waters in the lowland Amazon could be largely explained by atmospheric deposition. Our data, like those of Stallard and Edmond (1983), suggest that the atmosphere accounts for much less than half of the flux of major metal cations, although the percentages attributable to atmospheric deposition in the Caura River drainage are considerably greater than those estimated by Stallard and Edmond. This is at least partly explained by the greater distance from the sea for most of sampling by Stallard and Edmond, but also possibly by our reliance on computation of actual deposition by mass-balance methods rather than selective sampling of rainshowers, as in the case of Stallard and Edmond.

The close relationship between the concentrations of soluble silica and major metal cations in the river provides some insight into weathering mechanisms (Figs. 3-5). Spearman rank correlations with soluble Si are as follows: sodium, 0.76; potassium, 0.55; calcium, 0.51; magnesium, 0.66; all are significant at  $p < 0.001$ . It is very likely that seasonal cycles in the concentration of silica, which are reflected in the concentrations of metal cations, are driven by cyclical changes in the amount of CO<sub>2</sub> in groundwater (Stumm and Morgan 1981). The amount of CO<sub>2</sub> in groundwater is in turn affected by the degree of soil saturation interacting with rates of decomposition. One possibility consistent with the data is that soils become water-logged and accumulate CO<sub>2</sub> during the rainy season, and that the subsequent drainage of water from the soils leads to more rapid weathering, as manifested by higher concentrations of silica, higher pH, and larger amounts of metal cations.

*Rate of weathering and erosion*

High rainfall and regional geology contribute to relatively rapid weathering in the Caura basin. In the elevated shield regions of the Orinoco and Amazon drainages, the slopes are either flat or very steep (Stallard 1985). The shield rocks can sustain steep slopes because they are massive, and many of the cliffs are topped by quartzites or laterites, rendering them more resistant to weathering (Stallard 1985). The rate estimated in the present study (1.8 cm/1000 yr) for the Caura River watershed falls within the range of values reported in the literature for watersheds overlying roughly comparable parent material. The rate lies within the upper range of values for shield rock, but is in good agreement with a different type of estimate made by Stallard (1985), who calculates that an overall chemical and mechanical erosional rate of 20 m/million yr (2 cm/1000 yr) would be required to generate the highest landscape elements of the elevated shields.

A rough estimate of the rate of erosion from the work of Gibbs on the Amazon (1972) is between 1 and 2 cm/1000 yr, which is also consistent with our estimate of 1.8 cm/1000 yr for the Caura drainage. Khadem *et al.* (1984) estimated an overall rate of erosion of less than 0.5 cm/1000 yr, for the shield drained by the Orinoco River; this estimate seems anomalously low in comparison to other published information and to our own results.

Also working in a humid climate, but with more easily eroded rocks, Norton (1974) reported a chemical weathering rate of nearly 3 cm/1000 yr in the Rio Tanama drainage, Puerto Rico. This small basin receives about 200 cm of rain annually and contains highly erodible limestones and hydrothermally altered igneous rocks. In North America, weathering rates of 4 cm/1000 yr have been reported (Velbel 1985). Garrels and MacKenzie (1971) estimated an average annual chemical denudation rate of 33 metric tons/km<sup>2</sup>, which, when combined with their estimated annual mechanical denudation rate (86 metric tons/km<sup>2</sup>), gives an overall rate of about 4 cm/1000 yr. For South America, Garrels and MacKenzie (1971) estimate 28 metric tons/km<sup>2</sup> of chemical weathering and 56 metric tons/km<sup>2</sup> of mechanical erosion per year, which would give an overall rate for the continent of about 3 cm/1000 yr.

Table 4 compares the present study to other published studies of mass balance, weathering, and major ion transport. The mass balance study of the watershed of Pond Branch, Maryland, by Cleaves *et al.* (1970) was also considered as a possible comparison, but was not used in Table 4 because the values for watershed export minus atmospheric deposition were skewed by major losses of ions to ground water storage and biomass within the watershed.

It is evident from Table 4 that leaching of silica and major cations is highly effective in the Caura River watershed. Only in the Catocin Mountain watershed (Katz *et al.* 1985), which is subject to acidic deposition, does the weathering of major cations approach that of the Caura River watershed. Silica transport from the Caura watershed is among the highest values that we could find in the literature.

Table 4. Net transport (export minus atmospheric deposition) of major ions, soluble silica, and suspended solids from the Caura River watershed in comparison to transport from other watersheds.

Watershed characteristics	Caura River Venezuela	Gambia River W. Africa <sup>1</sup>	Catoctin Mtns. Maryland <sup>2</sup>	Hubbard Brook New Hampshire <sup>3</sup>
Size, km <sup>2</sup>	47,500	42,000	5.5	2
Precipitation (cm)	450	94	112	130
Vegetation	Tropical forest	Savanna, forest	Temperate forest	Temperate forest
Soluble transport (kg/ha/yr)	•			
Na	19.4	3.9	7.3	5.6
K	13.6	1.4	14.1	1.0
Ca	14.2	4.0	11.9	11.5
Mg	5.7	2.0	15.6	2.5
HCO <sub>3</sub> <sup>-</sup>	124.0	20.3	78.1	7.7
Cl <sup>-</sup>	- 1.4	0.6	16.6	- 1.6
SO <sub>4</sub> <sup>+</sup>	1.5	0.4	21.2	14.8
SiO <sub>2</sub>	195.7	15.0	56.1	37.7
Solids transport (kg/ha/yr)	274	49	—	33

<sup>1</sup> Lesack *et al.* (1986), continental subbasin only, no correction for precipitation; Precambrian and Paleozoic metamorphics, sediments, volcanics.

<sup>2</sup> Katz *et al.* (1985), Hauver Branch watershed, corrected for road salt; metabasalts, sediments, some quartz and calcite.

<sup>3</sup> Likens *et al.* (1977), undisturbed portions only; metasediments, tills.

As shown in Table 4, silica makes up more than 52% of major solutes in the Caura River. Analyses of waters from three other tropical and subtropical areas (precipitation, 140–220 cm/yr) presented by Tardy (1971) showed the follow-

ing percentages  $\frac{\text{SiO}_2 \text{ (mg/l)}}{\text{SiO}_2 + \text{major solutes}}$ : 47% (Korhogo, Ivory Coast, dry sea-

son); 41% (Korhogo, wet season); and 52% (Malagasy, high plateaus, dry season). These percentages would be slightly higher with correction for salts in precipitation. All samples were taken from crystalline granitic massifs, but in areas that were less moist than the Caura River watershed. It appears that a difference between the Caura watershed and others with less rainfall is the efficiency with which the added rainfall leaches silica, in particular, but also major cations. A disproportionate amount of silica in the Caura drainage may be coming from rocks of high silica content, such as the Precambrian silica-rich iron formations, the Precambrian silicic volcanics, and the remnants of Precambrian sandstones, conglomerates, and shales.

## Conclusions

The results of the water chemistry and mass-balance analyses for the Caura River drainage are noteworthy for the degree to which they demonstrate the strong role of weathering in overall mass balance and for the high degree to which the atmospheric component of mass balance is influenced by terrestrial sources for some elements, especially calcium, potassium, sulfur, and phosphorus. The seasonal data demonstrate the important influence of the hydrologic cycle in regulating weathering and element export from the watershed. The mass-balance data also illustrate the importance of differential retention of elements in modifying the element inventory within the drainage.

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