

Concentration and transport of dissolved and suspended substances in the Orinoco River

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Abstract. The Orinoco River, which is hydrologically unregulated and has a minimally disturbed watershed, was sampled quantitatively over a four-year interval. In conjunction with the sampling, a method was developed for quantifying statistical uncertainty in the estimates of annual transport. The discharge-weighted mean concentration of total suspended solids in the Orinoco River is 80 mg/l, which corresponds to total annual transport of 90×10^6 t/y, or, expressed per unit of watershed area, 960 kg/ha/y, of which 96% is inorganic. The mean for dissolved solids is 34 mg/l, of which 25 mg/l is inorganic. The total transport of inorganic material, with a small allowance for bedload, is 128×10^6 t/y, which corresponds to an erosion rate of 4 cm/1000 y. Concentrations of dissolved and suspended constituents derived from rock weathering are very low because of dilution from high runoff (1190 mm/y), coverage of the southern part of the drainage by shield rock, and minimal watershed disturbance. Seasonal patterns in dissolved and suspended constituents are repeated with a high degree of consistency from one year to the next.

For most variables, relationships between transport and discharge are described adequately by a power function. There are three categories of response to changing discharge: purging (exponent > 1 : soluble organic fractions and all particulate fractions), dilution (exponent 0–1: major ionic solids and silicon), and conservation (exponent < 0 : nitrate, interannual). Variability across seasons and across years is highest for the particulate constituents, but within this group variability is lower for the organic than for the inorganic components. Major ions that originate primarily from the atmosphere have a higher seasonal variability than major ions that originate primarily from weathering. Potassium and soluble silicon have the lowest variabilities. Variability is much lower across years than across seasons for most constituents.

Because of high runoff per unit area, the Orinoco drainage has a high specific transport of organic carbon (72 kg/ha/y, 6.8×10^6 t/y, 1.6% of global river transport), even though the concentrations of organic carbon in the river are not exceptionally high (mean, 4.4 mg/l dissolved, 1.4 mg/l particulate). Concentrations of ammonium (35 μ g/l as N) and of nitrate (80 μ g/l as N) are high given the undisturbed nature of the watershed and the high amount of runoff. The high transport rate for total nitrogen (5.7 kg/ha/y, 0.54×10^6 t/y, 1.5% of global river transport) can be sustained only by high rates of nitrogen fixation within the watershed. Concentrations of soluble phosphorus are within the range expected for undisturbed river systems (20 μ g/l), but concentrations of particulate phosphorus are low because the amounts of particulate matter are small and the phosphorus per unit weight of suspended matter is low. Phosphorus transport (0.75 kg/ha/y) can be accounted for easily by weathering of the parent material, even within the Guayana Shield, where weathering rates are lowest. Biological modification of nutrient and carbon fractions during transit along the main stem are minimal.

Introduction

Opportunities to study large unregulated rivers draining minimally disturbed watersheds are rapidly disappearing with hydroelectric development of major rivers and worldwide deforestation. Despite major improvements in the data base on such rivers through the efforts of SCOPE (United Nations Scientific Committee on Problems of the Environment: Degens & Kempe 1982; Kempe 1985), much basic information is still unavailable. Because changes in water chemistry, transport, and biological characteristics will accompany development of these rivers, their natural regulatory mechanisms can be studied directly only in the near future.

To some extent, the characteristics of large rivers and their watersheds can be extrapolated from studies of smaller rivers. In other ways, however, the features of large rivers may not be projected easily or anticipated from studies of small rivers or streams. Special features of many large rivers include extensive floodplain-river interaction, high buffering of variance through differential phasing in system components, and significant modification of water chemistry during transport. In addition, large rivers provide synoptic information on the geochemical and nutrient mass balance of landscapes that are too large or too diverse to be studied as fragments.

The Orinoco is the world's third largest non-tributary river as measured by discharge ($36,000 \text{ m}^3/\text{second}$: Meade et al. 1983). The watershed is minimally disturbed and all of the major tributaries except one are unregulated. The major tributary watersheds of the Orinoco are ecologically and geochemically diverse, and the Orinoco annually inundates large expanses of floodplain. Thus studies of the Orinoco may help provide an understanding of the factors that regulate the biogeochemistry of large rivers in their natural state.

We present here information on chemistry and transport of the lower Orinoco River as estimated from sampling between 1982 and 1985. Chemistry and transport have been documented previously for the upper portion of the watershed and the major tributaries (Weibezahn 1985; Lewis et al. 1986, 1987; Lewis 1986, 1988; Saunders & Lewis 1988). We focus here on total transport of dissolved and suspended substances from the watershed, and on temporal variation in chemistry and transport in the lower main stem, particularly as it relates to the annual cycle of floodplain inundation and drainage.

Description of the Orinoco River

The Orinoco River has a length of 1970 km (MARNR 1983) and drains an area of approximately $1 \times 10^6 \text{ km}^2$ (Fig. 1). The watershed is located 70%

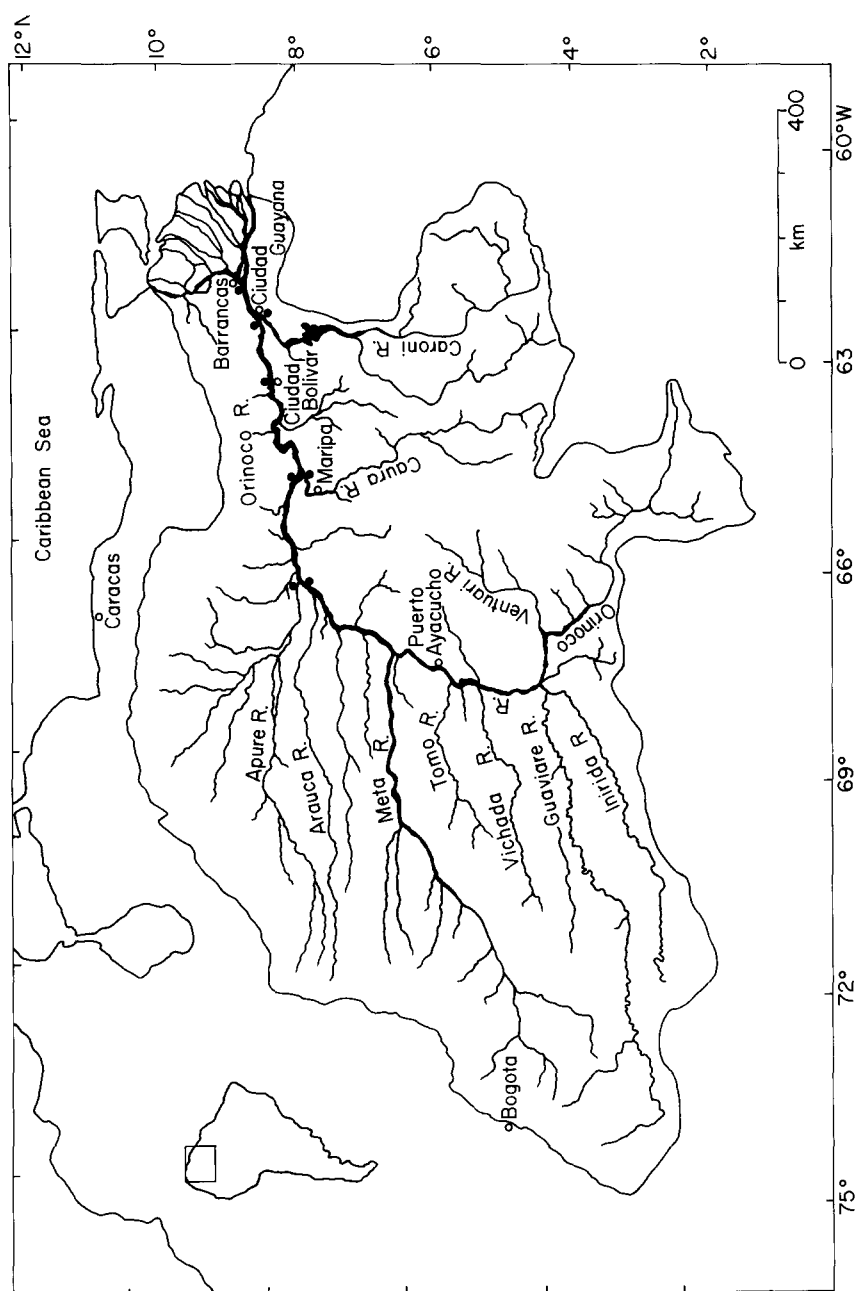


Fig. 1. Hydrologic map of the Orinoco drainage.

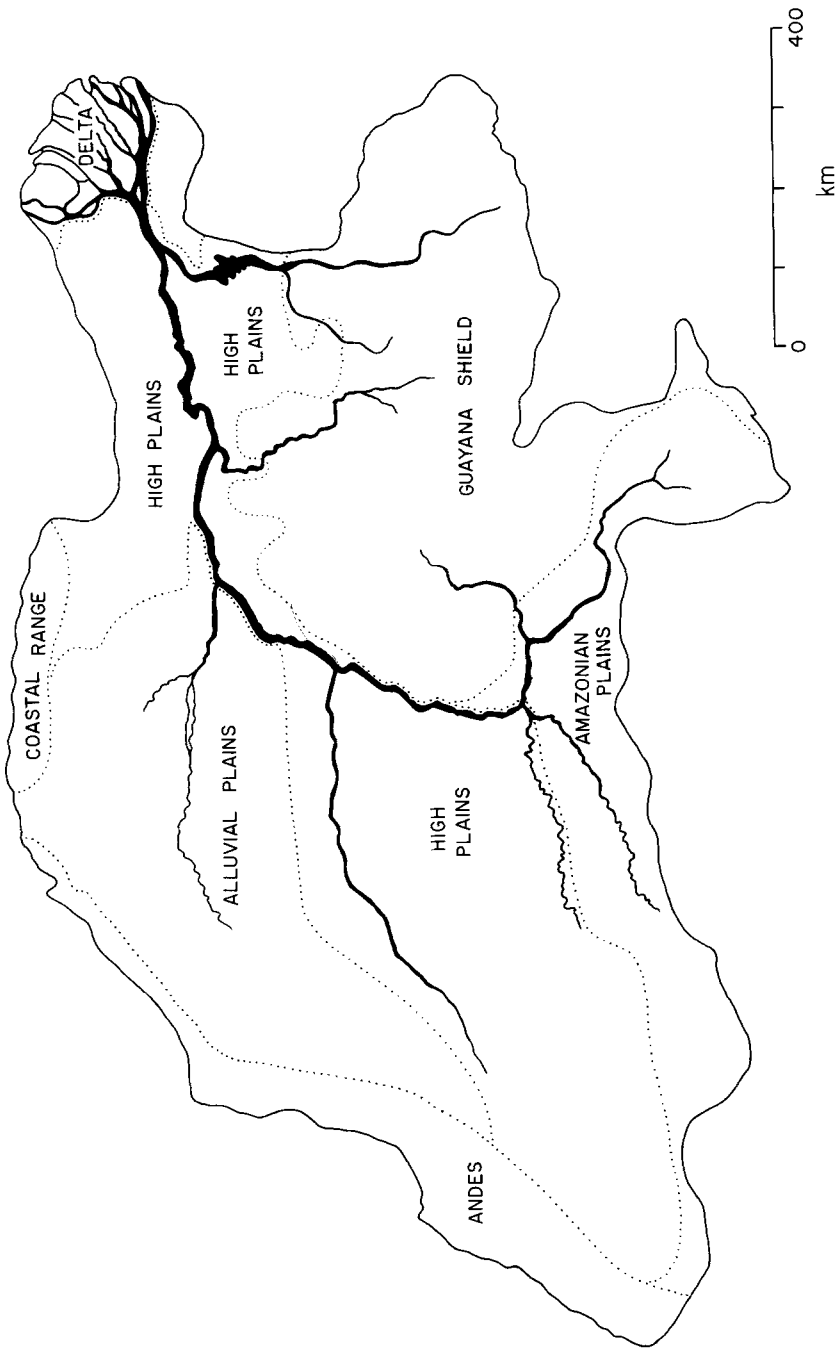


Fig. 2. Major physiographic provinces of the Orinoco watershed (composite of several sources: Sarmiento 1983, MARNR 1983, TGAC 1977).

within Venezuela and 30% within Colombia. The west and northwest portions of the watershed are occupied by the Andes and the Cordillea de la Costa (Fig. 2). Rivers descending from the mountains traverse vast plains on the north and west sides of the Orinoco. These can be subdivided into alluvial plains, which are subject to flooding during the wet season, and high plains, which are less subject to flooding (Sarmiento 1983). The Amazonian plains to the South are very similar to and probably of common origin with the alluvium supporting tropical moist forest of the adjoining Amazon basin, but presently drain into the Orinoco basin. The high plains, as designated by Sarmiento (1983), include high plateaus that may be dissected and hilly, as they are to the south of the Orinoco. The southeastern portion of the drainage is occupied by the Guayana Shield (Case et al. 1984). Although Sarmiento classifies the area east of the Caura River as high plains, this portion of the drainage is also underlain by the shield, which extends to the southern margin of the Orinoco channel. Within the Orinoco drainage, the rocks of the shield are mostly of early or middle Proterozoic origin ($1.5\text{--}2.25 \times 10^9$ y), but the shield adjacent to the river near Ciudad Bolivar is Archaean ($> 2.7 \times 10^9$ y; Gibbs & Barron 1983). Although much of the shield is of low relief, it also contains terrain of high relief, particularly near the Brazilian border, as well as numerous large mesas (tepuys).

There is a pronounced moisture gradient in the Orinoco watershed (Fig. 3). Precipitation in the northern lowlands can be as low as 1000 mm per year. Precipitation in the immediate vicinity of the lower Orinoco main stem is closer to 1200 mm per year, and the amount of precipitation increases upstream to more than 3500 mm per year in the southernmost portion of the Guayana Shield. Although not reflected by Fig. 3, precipitation as high as 6000–8000 mm may be typical in southern areas of high relief (Ewel et al. 1976). The area-weighted mean precipitation derived from Fig. 3 is 2270 mm/y. However, Fig. 3 may understate average precipitation because moister upland areas are not well represented among the gauging stations.

The vegetation of the northern and western mountainous portion of the Orinoco watershed is complex because of the uneven distribution of precipitation in this region (Ewel et al. 1976). Some limited areas of high paramo are found in the Andean zone. Most of the vegetation is dry, moist, or very moist premontane or montane forest. At the base of the mountains, these zones give way to dry tropical forest and savanna, which occupy most of the area between the mountains and the north bank of the Orinoco River. However, there is a zone of moist forest near the coast to the east and near the Andes to the west. To the south of the Orinoco, the vegetation is primarily moist and very moist tropical forest. There is also a substantial

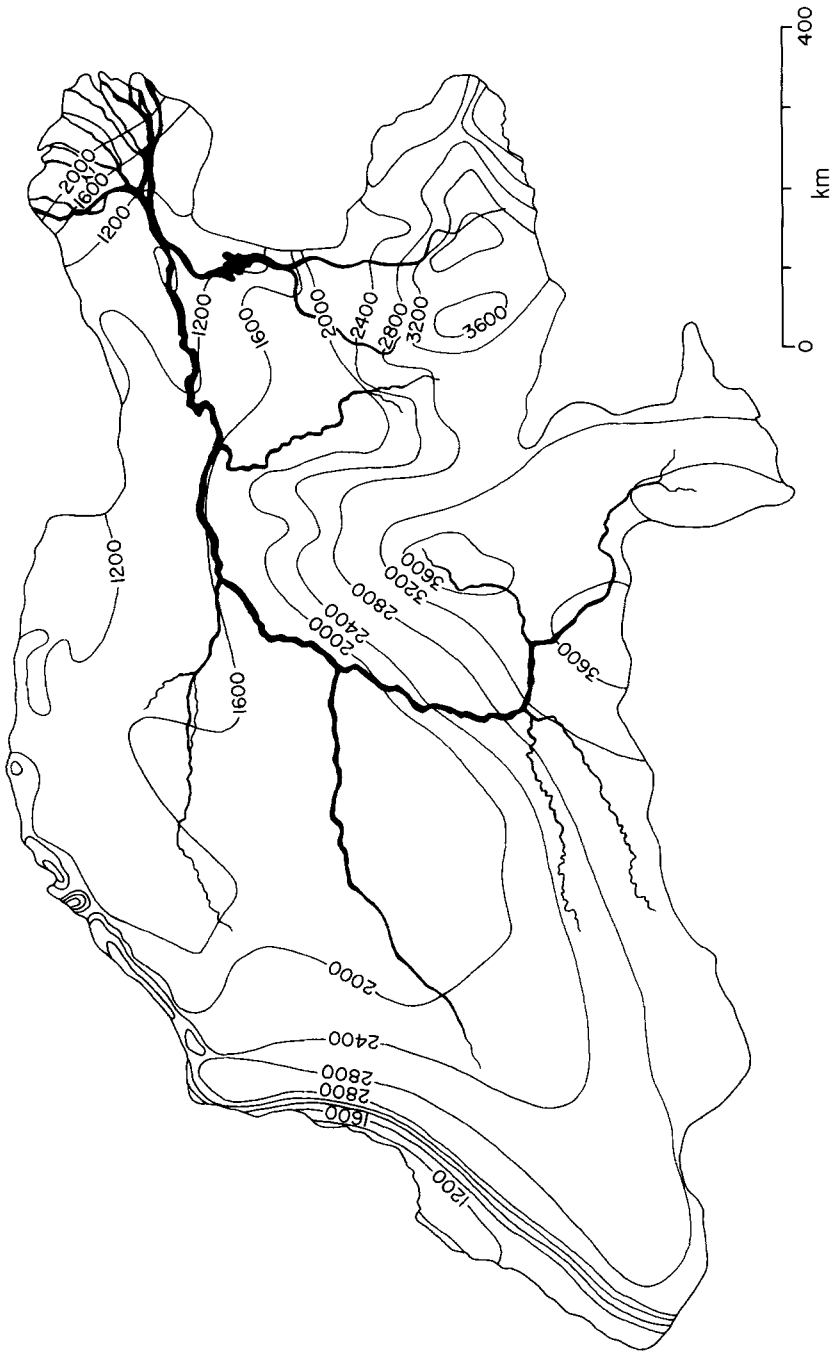


Fig. 3. Rainfall distribution within Venezuela (based on a composite of information from MARNR 1983 and IGAC 1977).

component of upland rain forest and very humid premontane forest in the areas of higher relief. These forests have not yet been significantly disturbed.

The Orinoco has extensive floodplains. A linear floodplain of 6940 km² occupied mostly by floodplain forest extends upstream along the river from the delta to the Meta. The Orinoco enters this floodplain typically during late May or June and drains from it during November. The area of standing water on the floodplain drops to 470 km² by the end of the dry season. In addition, a large internal delta forms on the savanna (Llanos) to the north side of the Orinoco between the Arauca and Apure rivers. The area of this internal delta has been estimated as 70,000 km² (Welcomme 1979). Although a vast portion of the area below 100 m a.s.l. (117,000 km²) does become very wet due to poor drainage, our estimate of the area that is actually in direct contact with river water at maximum discharge is 4920 km² (S. Hamilton & W. Lewis, unpubl.). Smaller flooded areas are found near the mouths of major tributaries. Discharge phasing is very nearly synchronous (i.e., \pm one week) throughout the system (Lewis 1988).

Water draining from the alluvial areas, and particularly from the plains between the Meta and the Apure Rivers, carries a high load of suspended solids (200–700 mg/l) and dissolved solids (100–150 mg/l). These waters are comparable to the so-called white waters of the Amazon drainage (Sioli 1984). Waters draining from the shield area to the south contain very small amounts of suspended solids (5–15 mg/l) and dissolved solids (20–25 mg/l). Most of these waters are darkly colored by dissolved organic carbon, and can thus be classified as black waters according to the system that is used for the Amazon. In addition, however, some of the waters draining from the Guayana Shield area are clear waters, i.e., they contain minimal amounts of colored organic solids.

The Orinoco receives almost half of its water from the Guayana Shield to the south, which occupies only a third of the watershed but has high average precipitation. However, the waters draining from the northern and western portions of the watershed have exceptional influence on water chemistry because of their higher concentrations of dissolved and suspended solids.

There is only one major impoundment on the entire Orinoco system (the Guri Reservoir on the Caroni River: Fig. 1). Floodplain disturbance and control of flooding are minimal, and most of the forested areas retain their natural vegetative cover. Although there is some agricultural development, particularly to the north of the Orinoco main stem and in the Apure River basin, and some mining, principally to the south of the Orinoco main stem, the overall influence of human intervention on water chemistry and element transport is still very small (Zinck 1980).

Methods

The lower Orinoco was sampled between the beginning of 1982 and the end of 1985. The key sampling point for present purposes was near Barrancas, just above the Orinoco delta (Fig. 1). The Orinoco was also sampled upstream (Fig. 1); these samples were taken prior to the sample at Barrancas by an amount of time approximately equal to the travel time of the water between the stations (Lewis 1988). The data for the Orinoco at Ciudad Bolívar, after appropriate correction for the chemistry and volume of flow of the Caroni River (average, 11% of main stem flow), is the basis for establishing the confidence limits for weighted mean concentrations and transport of the Orinoco River at Barrancas. The calculation of these confidence limits is described at the end of this section.

Samples were taken bi-weekly during the first two years of the study and monthly during the second two years. As a means of avoiding biases that may be introduced by uneven horizontal or vertical distribution of dissolved or suspended materials in the river (Lewis & Saunders 1984; cf. Curtis et al. 1979), samples were always taken with a depth-integrating sampler (Nordin & Skinner 1977; Nordin et al. 1983) at several points across the river. The sampler collects water through a nozzle at a rate proportional to flow in front of the nozzle; the composite of a steady vertical traverse of the water column is thus integrated with respect to velocity over the range of depths. The processing and analysis of samples has been described in detail elsewhere (Lewis et al. 1986, 1987; Lewis 1986, 1988) and will be given here only briefly.

Particulate material was separated from soluble material by filtration of water through a Whatman GF/C filter (effective pore size $\pm 0.7 \mu\text{m}$; Sheldon 1972). The amounts of carbon and nitrogen in particulate material on the filters were determined by use of an elemental analyzer. Additional filters were used for analysis of particulate phosphorus by pyrolysis followed by orthophosphate determination (Solorzano & Sharp 1980). An additional portion of particulate material was obtained by sedimentation of water over a period of 7 days. This material was decomposed chemically and analyzed for major elements other than carbon, nitrogen, and phosphorus as described by Lewis et al. (1987).

Particulate material is defined functionally on the basis of filtration. The Orinoco River, like other rivers, contains colloids that may pass the most commonly used filters. Some of the methods used for the analysis of the soluble fraction decompose the sample as it is analyzed (major metal ions, organic fractions). The colloidal portion of these constituents thus will not be lost because it will be represented in the dissolved fraction, even though

it is not truly in solution. However, colloidal silica may not be decomposed fully in the analysis of the soluble fraction, and thus may partly escape detection. These losses are expected to be small because the size spectra for inorganic particles in the Orinoco are not unusual (mean size, 4–6 μm ; Kranck & Milligan 1983). However, two estimates were made of these potential losses. First, samples that had been filtered through GF/C filters were refiltered through membrane filters of 0.22 μm pore size. On two separate occasions (June and September of 1984), refiltrations resulted in the capture of a mean additional 5.6% of solids. A significant portion of these refiltered solids would have been represented in the analysis because of the use of destructive analytical methods for some dissolved constituents. Thus the refiltration procedures indicate that the colloidal material passing through the filter could not account for an error any greater than 6%, at least down to particle sizes of 0.2 μm (and probably smaller, given inevitable clogging of the filters).

The second type of test was based on the evaporation of aliquots of the filtered river water that was used in the analysis of dissolved constituents. The residue was dried in a tared crucible and weighed. The residue determined directly in this manner would have included all filterable solids, whether truly dissolved or colloidal. This direct determination of filterable material by evaporation was then compared with the sum of the individual components as determined by the analyses of individual fractions. The difference between these two sets of estimates is a measure of the amount of material that did not appear in the analyses of specific constituents.

The discharge-weighted mean for total filterable solids as determined by evaporation was 37.3 mg/l. The discharge-weighted mean for analytical components was 34.2 mg/l. However, a small amount of bound water can be expected in the residue, which could not be dried at a very high temperature (60 °C) because of the need to retain the organic material. Thus the mass that cannot be accounted for by the analytical procedures is almost certainly less than the gap between the direct and the indirect estimates, i.e., less than 10%.

Because two separate estimates indicate that material escaping analysis was below 10% (and probably 5% or less), the estimates of dissolved and suspended materials will be assumed to account for all of the transport in the water column of the Orinoco River. However, it should be noted that the dissolved component actually includes some colloidal materials.

Conductance and pH were determined on unfiltered water, and inorganic carbon was estimated by fixed endpoint titration standardized against Gran titrations (Lewis et al. 1987). The amounts of major metal cations were determined by atomic absorption analysis on acidified subsamples of filtered

water. Unacidified portions of filtered water were used in the analysis of sulfate and chloride by ion chromatography. Nitrate, ammonium, total soluble nitrogen, total soluble phosphorus, and soluble reactive phosphorus were all determined by wet chemical methods as given by Lewis (1986). Dissolved organic carbon was measured by gas chromatography following persulfate digestion (Lewis et al. 1986).

For the soluble components, anions totaled 0.267 meq/l as an average over the study period and cations totalled 0.268 meq/l. This agreement is well within the limits of analytical error and uncertainties related to anion contributions of organic acids (here assumed to be 5 μ eq per mg C: Lewis et al. 1987).

The daily discharge of the Orinoco at Barrancas was calculated as the sum of the Orinoco's discharge at Ciudad Bolivar and the discharge of the Caroni River. The discharge of the Caroni River was obtained from the records for the Guri Reservoir, an impoundment of the Caroni River, and the discharge of the Orinoco at Ciudad Bolivar was obtained from daily stage height records and empirical curves relating discharge and stage height (Lewis 1988).

For all water chemistry variables, the concentration data were interpolated linearly between sampling dates as a means of reducing error in the discharge-weighted mean concentrations for the year. Such error would result primarily from invalid extension of discharge peaks over the entire interval between samples. Discharge-weighted mean concentrations were then calculated as the sum of the products of discharges and concentrations over all days of the year divided by the annual discharge. The discharge-weighted means were expressed as total transport and as specific transport (transport per unit of watershed area: kg/ha/y).

Discharge-weighted means and transport estimates for rivers are typically reported in the literature without any estimate of confidence limits. For the Orinoco study, a method was developed for calculating confidence limits that quantify the sampling and analytical errors leading to estimates of discharge-weighted mean concentrations, total transport, and specific transport. This method is based on a comparison of samples taken at two separate locations. Concentrations of soluble and suspended materials in the Orinoco at Ciudad Bolivar, after a small correction for entry of the Caroni River, should be essentially identical to those observed at Barrancas; differences in these two estimates are explained by measurement error (including both sampling and analysis). Metabolic rates of organisms in the river are very low in relation to the rate of transport between these two points (Lewis 1988), and therefore do not affect significantly the concentrations of carbon, nitrogen, or other biologically labile elements. Floodplain effects are

also likely to be small over such a short distance. Even if biological or floodplain effects were quantifiable, they would amplify the differences between stations, leading to an overestimate rather than an underestimate of the measurement error, and in this sense would be conservative.

In establishing the confidence limits, it is necessary to deal only with the discharge-weighted mean concentrations, because the errors in the estimates of transport follow linearly from errors in the discharge-weighted mean concentrations. This excludes from consideration any bias that may be present in the discharge estimates as a result of errors in curves that relate stage height to discharge (the stochastic error in actual reading of stage heights is trivial). If such bias exists, it will tend to cause fixed errors in the estimates rather than variance. Thus for each variable and each year, the absolute differences are obtained between the discharge-weighted mean concentrations for all constituents at the two sampling locations. Because these absolute deviations of concentrations at the two stations bear a known relationship to the standard deviation of an infinite population of samples (Dixon & Massey 1957), they can be used in estimating the standard deviation due to sampling and analytical error for the discharge-weighted mean concentrations, and from this the corresponding standard deviations can be calculated for absolute transport and specific transport.

For the calculation of specific transport (transport per unit area), it is essential to know the watershed area above the point where concentrations and discharges are estimated. Estimates for the Orinoco vary considerably (Weibezahn 1985). Although Zinck (1977), from government sources, cites an area of $1.1 \times 10^6 \text{ km}^2$, this is on the high end of all available estimates. Our own most recent estimate from planimetry of maps ($1:1 \times 10^6$) is $1.02 \times 10^6 \text{ km}^2$ for the entire drainage, including the delta. We estimate the drainage above Barrancas, our key downstream site, as $0.95 \times 10^6 \text{ km}^2$. This estimate is in the midrange of other reported values. Therefore we will use $0.95 \times 10^6 \text{ km}^2$ in calculating specific transport for the basin, as estimated from sampling at Barrancas.

Results

Figure 4 shows the discharge of the Orinoco River at Barrancas over the period of study. The seasonal patterns and the annual discharges were similar across years, although the discharge was 10 to 15% higher for the first two years than for the second two years of the study. The date of peak discharge was slightly delayed in years of lower discharge (Aug 21, Aug 15, Sept 4, Sept 13 for 1982–1985). The mean discharge over the entire study

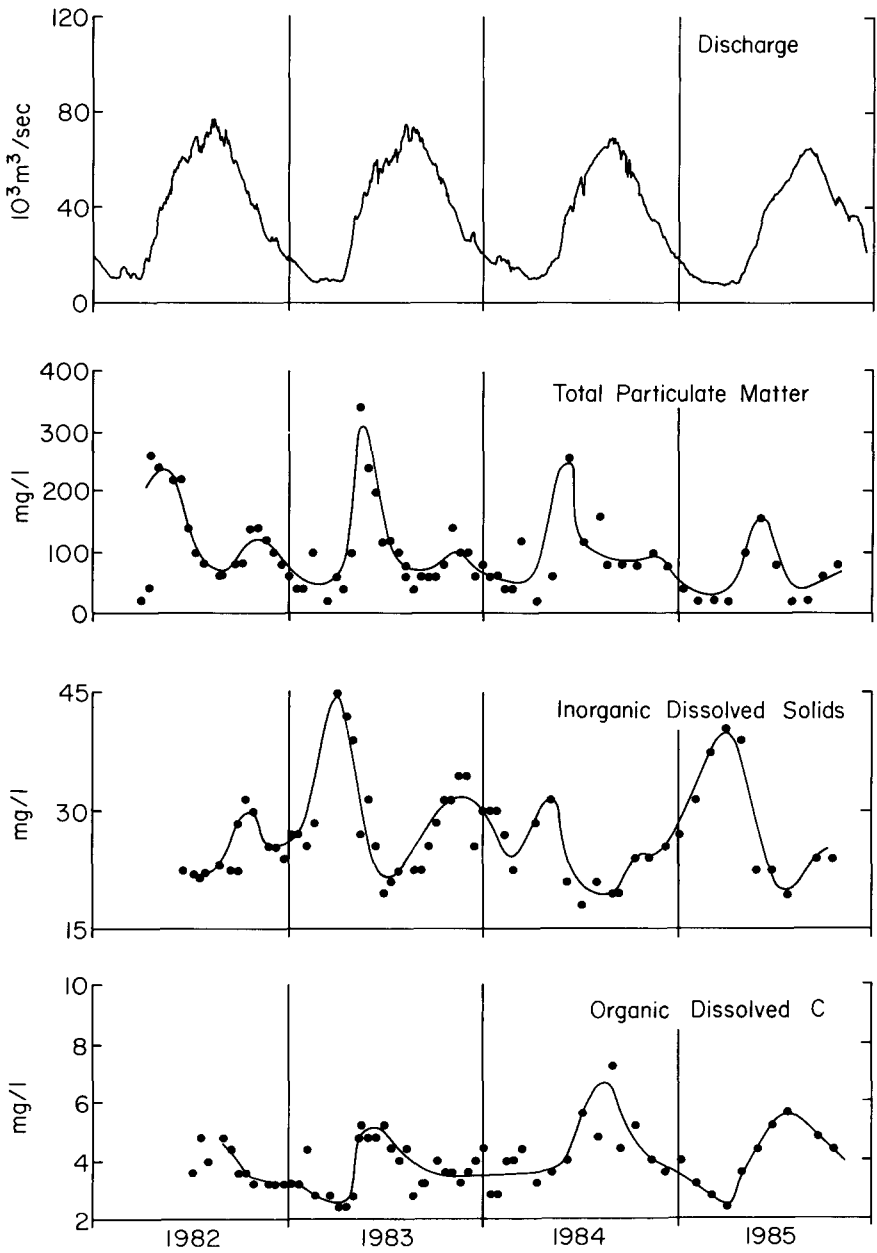


Fig. 4. Records of discharge, suspended solids, dissolved organic matter, and dissolved inorganic solids for the Orinoco River at Barrancas over the four years of study.

Table 1. Dissolved materials in the Orinoco River at Barrancas, 1982–1985. Concentrations are given as discharge-weighted means.

Variable	Discharge-weighted concentrations, mg/l		Mean as meq/l	Total transport thousands of metric tons/yr	Transport kg/ha/yr
	Mean	Error variation, as std. deviation			
Major cations					
Ca ⁺⁺	2.59	0.01	0.129	2,934	30.88
Mg ⁺⁺	0.66	0.00	0.055	751	7.91
Na ⁺	1.47	0.04	0.064	1,668	17.55
K ⁺	0.66	0.00	0.017	742	7.82
Total	5.38	–	0.268	6,095	64.16
Major anions and carbon					
HCO ₃ [–]	9.99	0.18	0.164	11,299	118.84
SO ₄ ⁼	2.31	0.07	0.048	2,619	27.57
Cl [–]	0.86	0.02	0.024	976	10.28
DOC	4.40	0.05	0.022	4,978	52.41
Total	17.56	–	0.258	19,872	209.18
Phosphorus fractions					
Reactive P, µg/l	9.56	0.74	–	11	0.11
Organic P, µg/l	10.88	–	–	12	0.13
Total soluble P, µg/l	20.44	0.29	–	23	0.24
Nitrogen fractions					
NH ₄ ⁺ –N, µg/l	35.01	0.86	0.003	40	0.41
NO ₃ [–] –N, µg/l	79.96	0.75	0.006	90	0.95
Organic N, µg/l	160.17	–	–	181	1.92
Total soluble N, µg/l	275.14	1.14	–	311	3.28
Other variables					
pH ¹	6.77	–	0.00017	0.28	0.003
Conductivity, µS/cm	25.82	0.10	–	–	–
Soluble SiO ₂ , as Si	3.01	0.02	–	3,121	32.85
Total dissolved solids	34.20	0.02	–	38,690	407.26

¹ pH of average H⁺ concentration, yields given as H⁺

period was $1.13 \times 10^{12} \text{ m}^3/\text{y}$ ($36\,000 \text{ m}^3/\text{sec}$), which corresponds to an annual runoff of 1190 mm/y (381 sec/km^2) for the entire Orinoco drainage. Our estimate of the average discharge for 1982–85 is the same as the long-term average discharge as estimated by Meade et al. (1983).

The lower three panels of Fig. 4 give an overview of variations in dissolved and suspended load for the Orinoco River over the four-year study interval. The total suspended load and the concentrations of dissolved inorganic and organic solids show clear seasonal changes. Consistent seasonal phasing favors statistical analysis of the relationships between discharge and con-

Table 2. Concentrations and transport of suspended particulate materials and transport of particulate plus dissolved materials for the Orinoco River at Barrancas, 1982–1985. Concentrations are given as discharge-weighted means.

Variable	Particulate			Particulate plus dissolved		
	Concentration mean, mg/l	Error variation, as std dev	Total transport thousands of metric tons/yr	Transport kg/ha/yr	Transport as thousands of metric tons/yr	Transport as kg/ha/yr
Ca	0.41	—	459	4.17	3,393	35.72
Mg	0.36	—	411	3.70	1,162	12.23
Na	0.48	—	546	4.93	2,214	23.31
K	0.96	—	1,086	9.88	1,828	19.24
Si	24.57	—	27,793	251.06	30,914	325.41
Al	5.98	—	6,760	61.42	6,760	71.16
Fe	1.54	—	1,748	15.87	1,748	18.40
Mn	0.04	—	49	0.46	49	0.52
P, $\mu\text{g/l}$	44.32	0.27	45	0.45	68	0.72
Cl	0.03	—	39	0.37	1,016	10.69
S	0.03	—	39	0.37	913	9.61
C (organic)	1.45	0.09	1,641	14.92	6,619	69.67
N, $\mu\text{g/l}$	184.86	9.55	209	1.90	520	5.47
Total organic	2.90	—	3,282	29.84	13,238	139.35
Total ¹	79.84	3.93	90,320	821.09	132,563	1,395.40

¹ Includes 10% bound water in the particulate fraction.

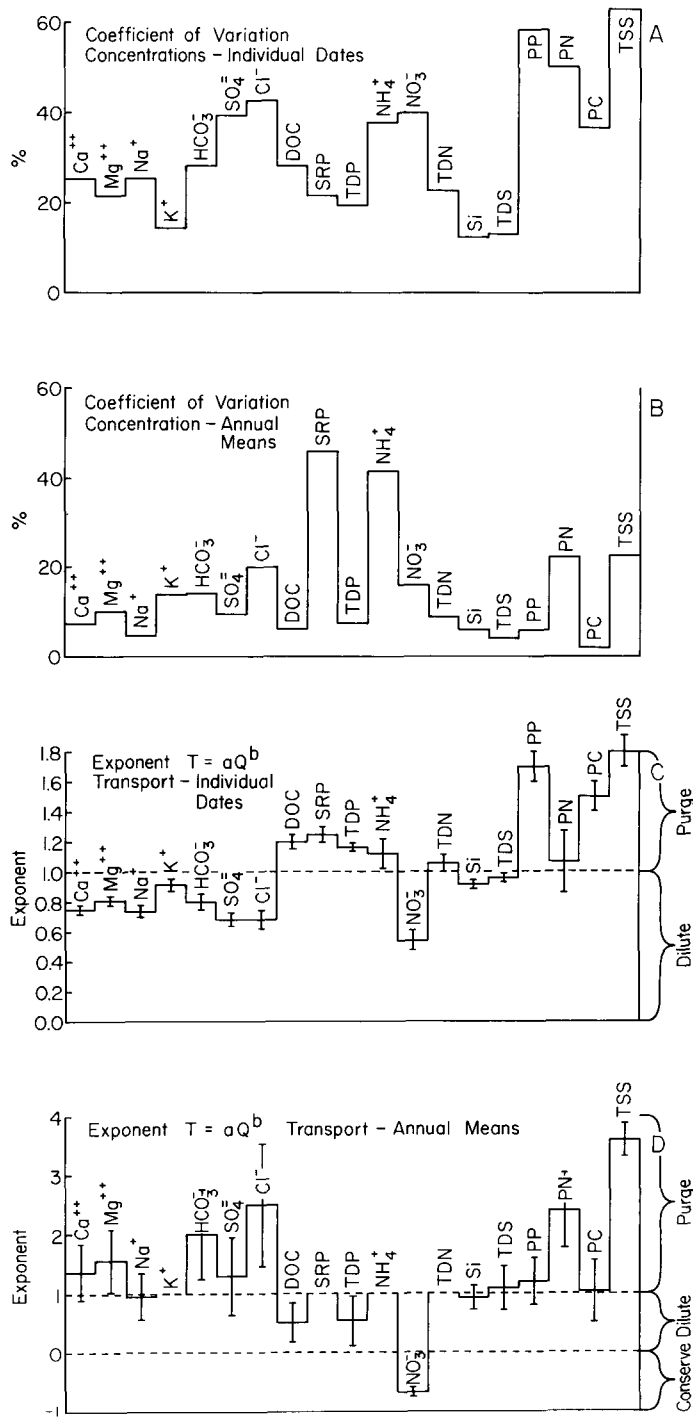
centration, as developed below through combination of the four annual data sets.

Table 1 summarizes the concentration and transport of the soluble constituents in the Orinoco River. Table 2 provides similar information for particulate materials, and also summarizes the total transport of the combined particulate and dissolved fractions for each element. As shown in Table 1, the error variance, determined by the simultaneous sampling of two stations as indicated in the methods section, is extremely low for all variables. Error variance is also extremely low for the components of particulate matter, although only some of the fractions were analyzed at both stations.

The top two panels of Fig. 5 show the true variation (i.e., with error variance removed) of concentrations measured on each of the individual sampling dates and of the annual average concentrations. The coefficients of variation for individual dates reflect the amplitude of seasonal change in concentration. Relative variability is highest for total suspended solids and for individual components of total suspended solids (particulate phosphorus, nitrogen, and carbon). Within this group, seasonal variation is higher for components that are primarily inorganic (total suspended solids, particulate phosphorus) than for components that primarily derive from organic matter (particulate nitrogen, particulate carbon). Among the soluble substances, major ions that originate primarily from the atmosphere (sulfate, chloride) have higher seasonal variability than major ions that originate primarily from weathering (calcium, magnesium, sodium) or a combination of weathering and gas exchange (bicarbonate). The relative variability of potassium concentrations is extraordinarily low. Concentrations of soluble silicon are much more stable seasonally than concentrations of other products of weathering except for potassium. Total dissolved solids have much lower relative variability than most of the individual constituents of dissolved solids, indicating different phasing of major components. Soluble organic fractions of nitrogen, phosphorus, and carbon have variabilities equal to or slightly lower than those of major ions originating from weathering. Nitrate has a notably higher seasonal variability than other nitrogen or phosphorus fractions.

Variability across years is much lower than variability across seasons for most constituents. Exceptions include soluble reactive phosphorus and ammonium nitrogen, both of which are present in very small amounts (Table 1). Concentrations of particulate carbon are especially stable across years, and annual variability in the concentrations of other particulate constituents is remarkably low in relation to the seasonal variation in the same constituents.

The relationship between transport and discharge can be represented



generally as a power function: $T = aQ^b$ where T is transport and Q is water discharge. The exponent in this equation (b) will be 1.0 for a constituent whose concentration remains constant. However, three kinds of deviation from an exponent of 1.0 are possible:

- exponent greater than 1, which indicates concentrations increasing as discharge increases (purging effect);
- exponent greater than 0 and less than 1, indicating that concentrations decrease as discharge increases, but at a rate less rapid than the increase in discharge (dilution effect); and
- exponent less than 0, indicating that concentrations decrease at a rate faster than the corresponding increase in discharge, so that transport actually declines as discharge increases (conservation effect).

Purging, dilution, or conservation of individual constituents can be identified on either a seasonal time scale (based on individual samples) or on an annual time scale (based on annual means). The coefficients can be determined empirically by regression analysis of the relationship between transport and discharge following logarithmic transformation of both variables. The slope of the linear relationship between the transformed variables provides an estimate of the exponent b . Complexities in the relationship of transport to discharge, such as differences in concentration at equal discharges on the rising and falling limbs of the hydrograph (hysteresis), are not reflected in the power function; the importance of these irregularities is indicated by the standard error of the exponent (b). Constituents with high hysteresis have a high standard error caused by the separation of concentrations on the ascending and descending phases of the hydrograph.

Sometimes concentrations can be modelled effectively by use of a hyperbolic equation that assumes mixing of varying volumes of water from two sources of fixed but different concentration (Johnson et al. 1969; Lesack et al. 1984; Saunders & Lewis 1988a), or by other models involving compartments (Hall 1970). The specific assumptions underlying these models may not be appropriate, even if a reasonable fit can be obtained (which is likely, given the use of more than one parameter). For example, the hyperbolic model could be most reasonably applied to major inorganic solids in the Orinoco, but the heterogeneity of the watershed is inconsistent with the underlying rationale because the assumption of two compartments is not

Fig. 5. Statistical characteristics of water chemistry variables for the Orinoco River at Barrancas. (A) Coefficients of variation for specific water chemistry variables across individual dates, after removal of analytical error variance. (B) The same across years (annual means). (C) Relationship between transport and discharge for specific water chemistry variables across individual dates. (D) The same across years (annual means).

even approximately correct. Thus we rely here on a descriptive model (power function on transport), which may point to mechanisms, but which does not require knowledge of mechanisms.

Panel C of Fig. 5 gives the results of the determinations of the exponent b across seasons (individual data points). The proportion of variance accounted for by the relationships represented in panel C exceeds 60% for all variables except nitrate (41%), particulate nitrogen (42%), and total suspended solids (46%). In general, all particulate constituents and nitrate show the combination of highest standard error and lowest r^2 , indicating that complexities causing departure from a monotonic relationship are greatest for these fractions. All of the major ions show dilution effects ($b < 1$) across seasons (consistent with a conductance trend noted by Paolini et al. 1983), whereas all particulate constituents show purging effects across seasons ($b > 1$). All soluble organic constituents also show purging effects across seasons, but these effects are smaller than the ones that are typical of particulate materials. Silicon, like the major ionic solids, shows a dilution effect, and total dissolved solids, which are a composite of the organic and inorganic constituents, show an exponent very close to 1.0, indicating very limited response to changes in discharge. Nitrate shows an exceptionally high dilution effect.

Panel D of Fig. 5 shows the relationship of transport and discharge across years rather than seasons. Estimates of the exponents for equations accounting for less than 35% of the variance in transport are not shown because these estimates are not sufficiently reliable to be informative. The relationship accounts for more than 35% of variance in most of the major soluble and particulate constituents (mean, $r^2 = 74\%$ for individual dates, 75% for annual means). The exponents for major ionic constituents in panel D are the inverse of the exponents for the same constituents in panel C. The same is also true for dissolved organic carbon, which shows a purging effect on a seasonal basis but a dilution effect on an annual basis. However, particulate constituents are consistent within and between years in showing a purging effect in relation to discharge. Nitrate is exceptional in showing even stronger reductions of concentration on an annual basis than on a seasonal basis; it is the only constituent on either an annual or seasonal basis that is conserved in relation to increasing discharge. Patterns of concentration and discharge for total organic C, total N, and total P are the composite of differing patterns for specific fractions contributing to the totals. As shown by Table 3, all three of the totals show purging ($b > 1$) on a seasonal basis, although degree of purging differs substantially among the three. On an annual basis, carbon shows a strong dilution effect, but the exponents for total N and total P are not distinguishable from 1.0 because of their high

Table 3. Statistics for total organic carbon, total nitrogen, and total phosphorus across seasons (individual data points) and across years (annual means). The exponent b , its standard error, and the r^2 value are shown for the equation relating transport to discharge. The coefficient of variation is calculated as $100 s/\bar{x}$, where s is true variation (error variance removed: see text).

Statistic	Element		
	C	N	P
Seasonal variation			
b	1.26	1.16	1.47
SE_b	0.04	0.10	0.06
r^2 , %	94	70	89
C.V., %	27	42	44
Annual variation			
b	0.64	1.35	0.99
SE_b	0.14	0.83	0.38
r^2 , %	92	57	77
C.V., %	5	12	5

standard errors. For all three elements, the variation across years is much lower than across seasons.

Figures 6 through 11 illustrate the mean concentrations for the annual cycle across the range of constituents. The figures also show for selected constituents the standard deviation for true variation (i.e., with error variance removed) in concentration between years on all dates. Three seasonal patterns in concentration can be identified, as summarized in Table 4. The soluble inorganic constituents show a common pattern that is essentially opposite to that of soluble organic constituents. The particulate constituents show a common pattern that is distinct from those of the soluble constituents.

Erosion rates can be calculated from Table 2. The total transport of

Table 4. Summary of concentrations in relation to hydrologic phasing (R = rising concentration; FP = falling to a plateau; RP = rising to a plateau).

Pattern	Hydrologic phase (water discharge)			Constituents
	Low	Rising	Falling	
1	R	FP	RP	Major cations and anions; nitrate; soluble Si; TDS
2	F	RP	FP	Soluble organic C, N*, P*; hydrogen ion**
3	P	RF	RF	All particulate fractions

* Patterns are weaker for these constituents.

** Does not show plateaus shown by other constituents.

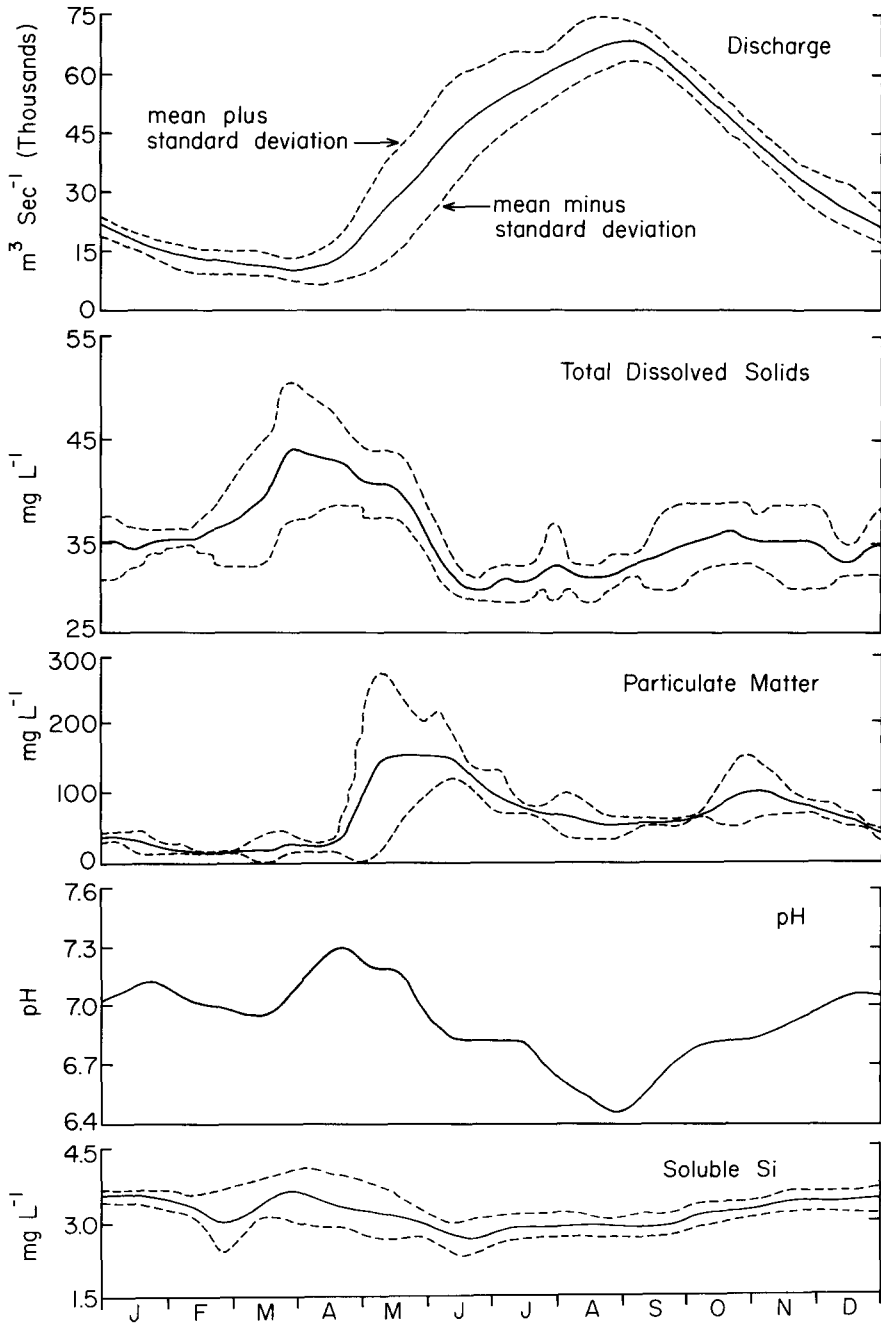


Fig. 6. Mean concentrations for dissolved and suspended solids, pH, and soluble Si for the Orinoco River at Barrancas over the seasonal cycle across the four years, with indications of the true standard deviation among years (i.e., after removal of error variance) for selected variables.

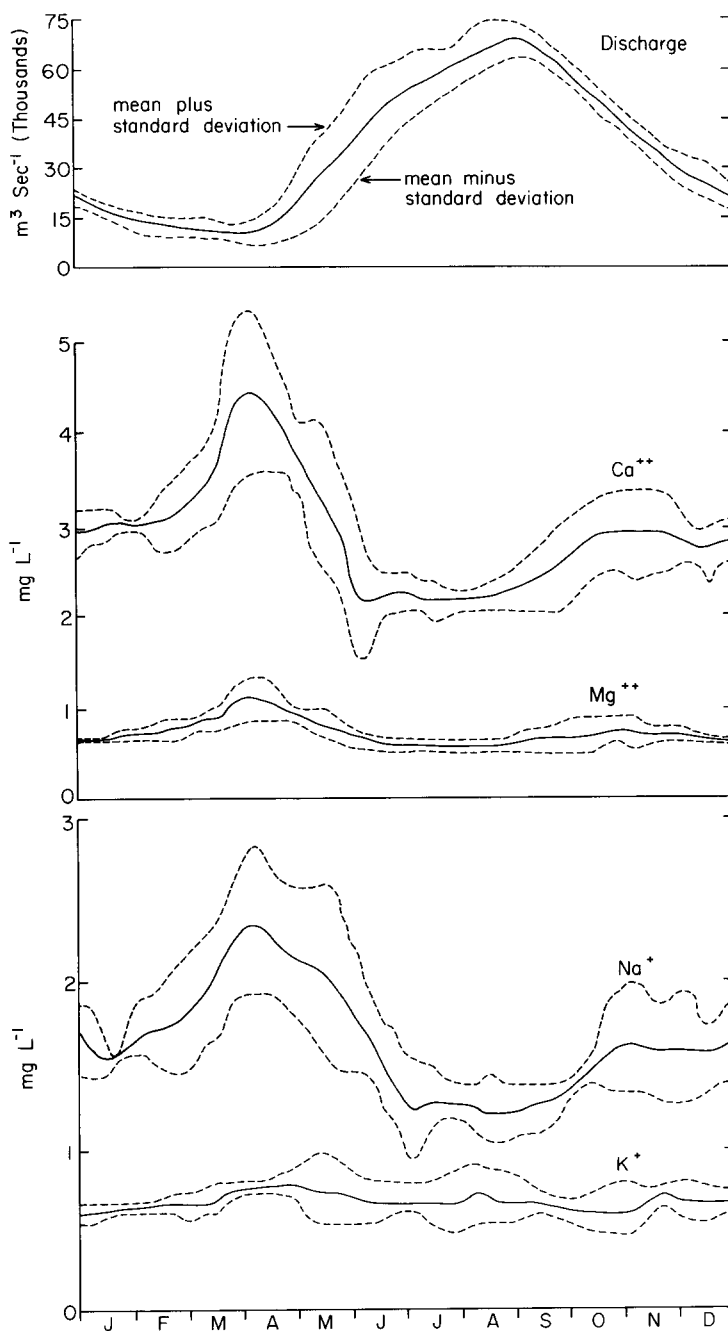


Fig. 7. Mean concentrations for major cations of the Orinoco River at Barrancas over the seasonal cycle across the four years, with indications of the true standard deviation among years (after removal of error variance).

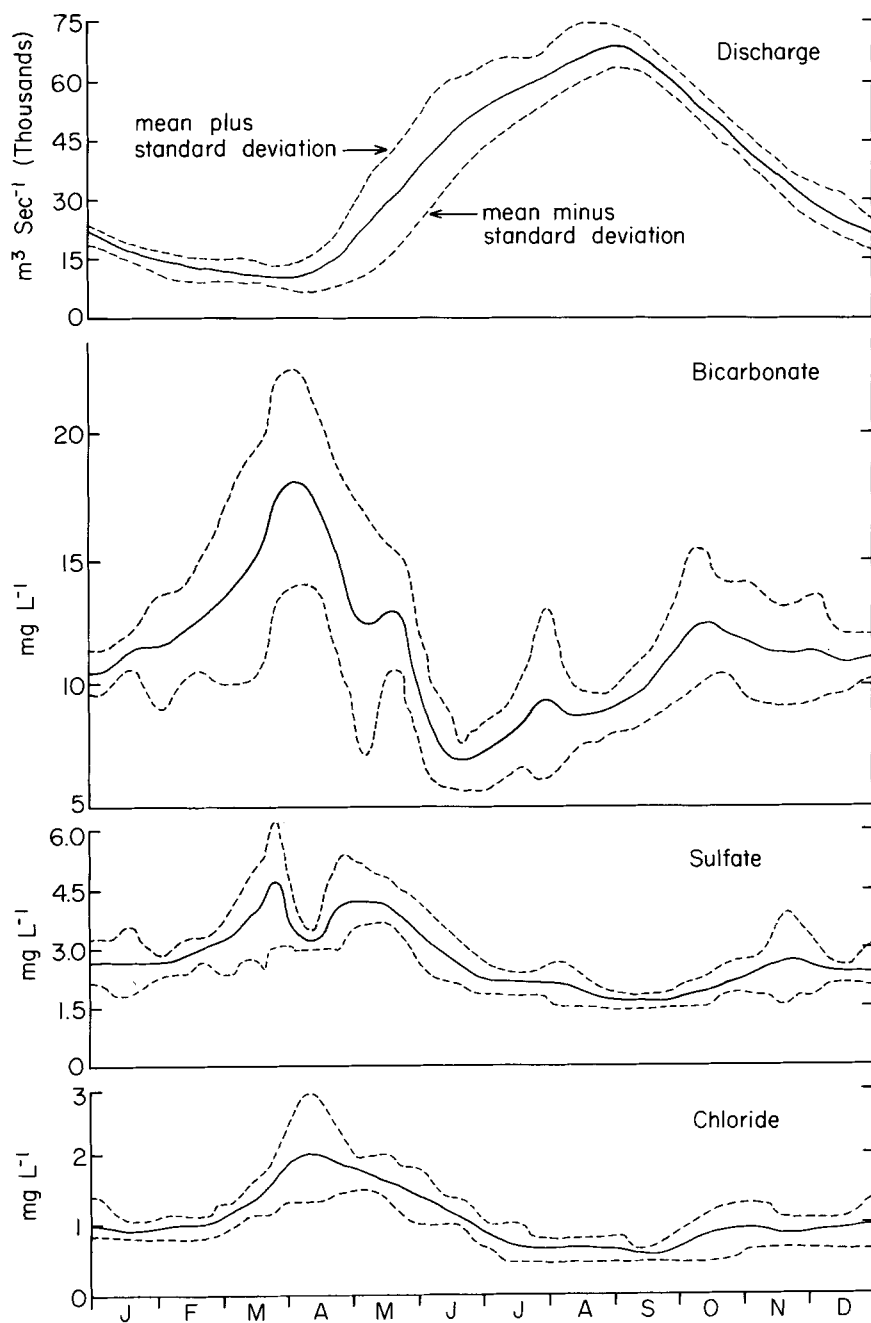


Fig. 8. Mean concentrations for major anions of the Orinoco River at Barrancas over the seasonal cycle across the four years, with indications of the true standard deviation among years (after removal of error variance).

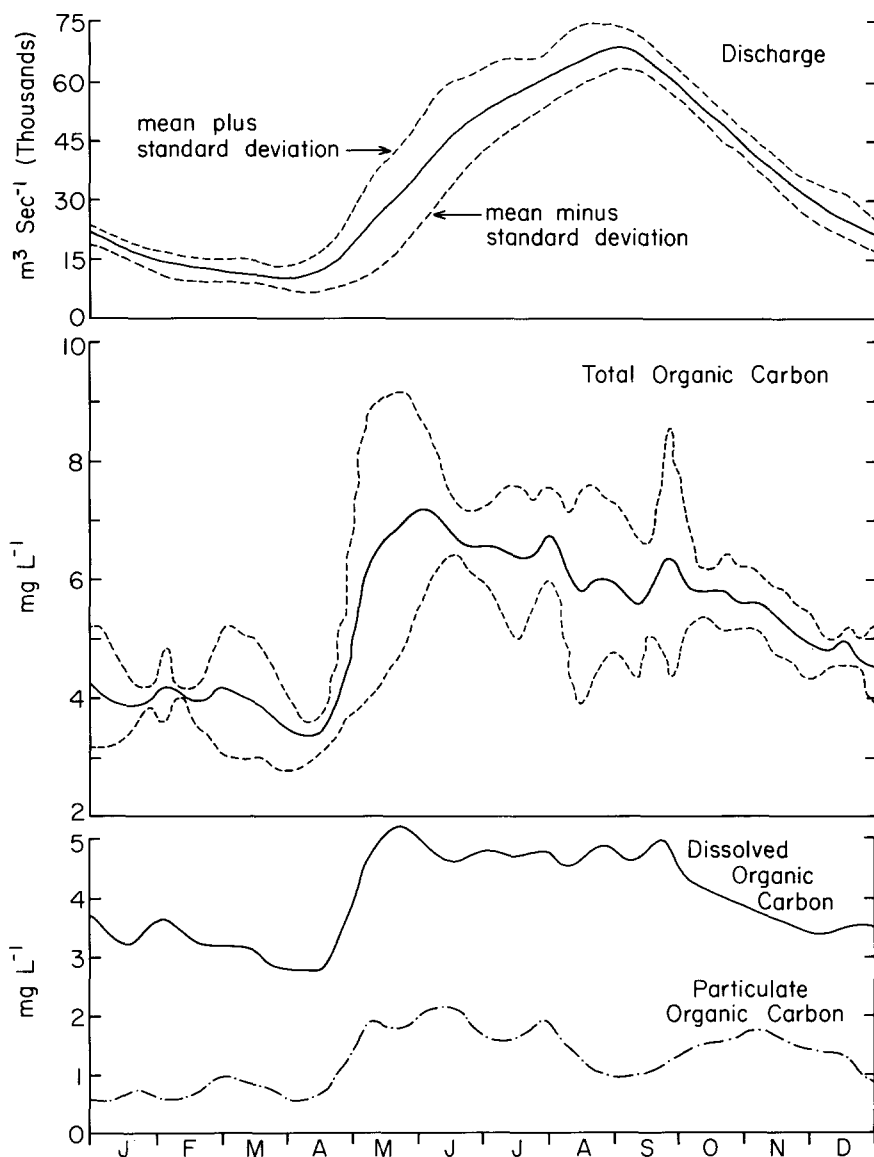


Fig. 9. Mean concentrations of organic carbon fractions in the Orinoco River at Barrancas over the seasonal cycle across the four years, with indication of the true standard deviation of total organic carbon among years (after removal of error variance).

inorganic material from the Orinoco River watershed as calculated from Table 2 is $119 \times 10^6 \text{ t/y}$. However, this does not include bedload, which is likely to be 10% or less of particulate transport (Meade et al. 1988). If 10% of particulate transport is allowed for bedload, the total transport of inor-

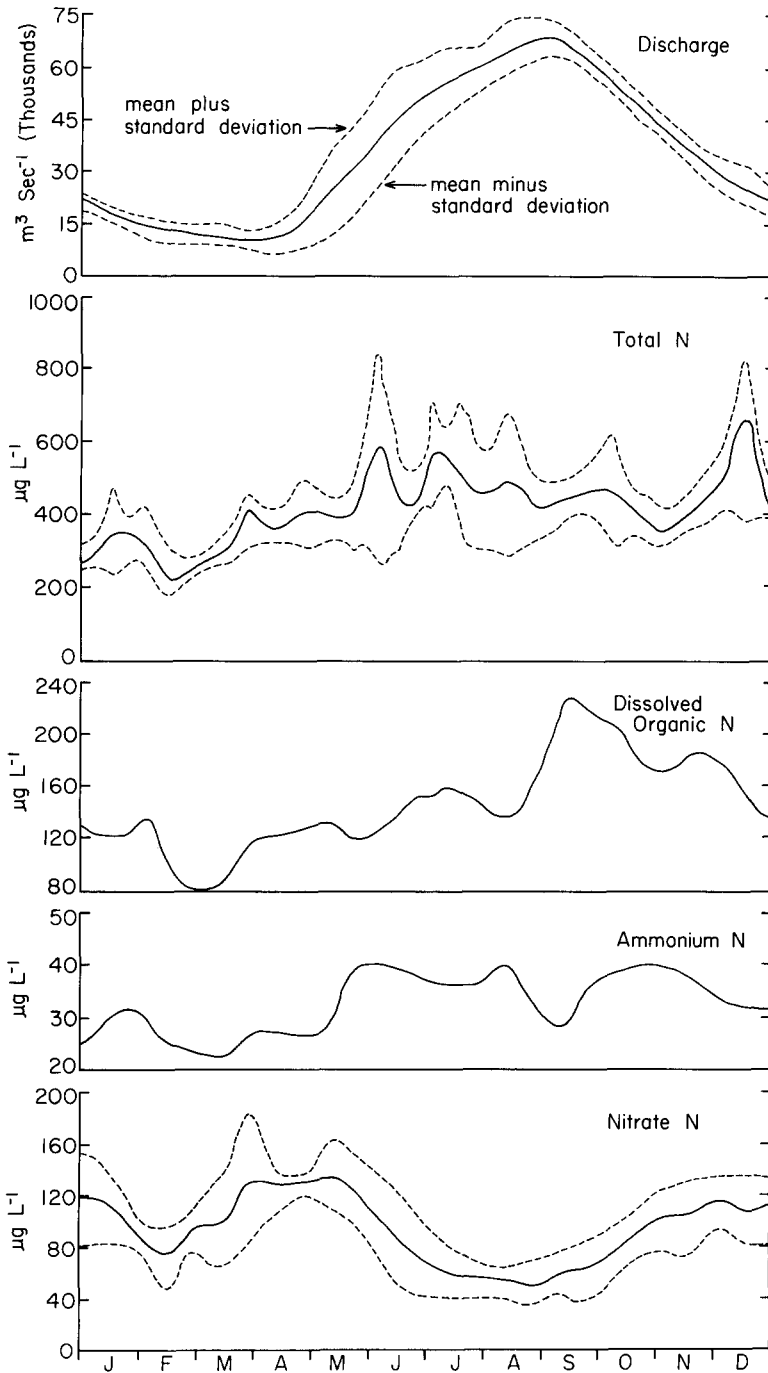


Fig. 10. Mean concentrations of nitrogen fractions in the Orinoco River at Barrancas over the seasonal cycle across the four years, with indication of the true standard deviation of total nitrogen among years (after removal of error variance).

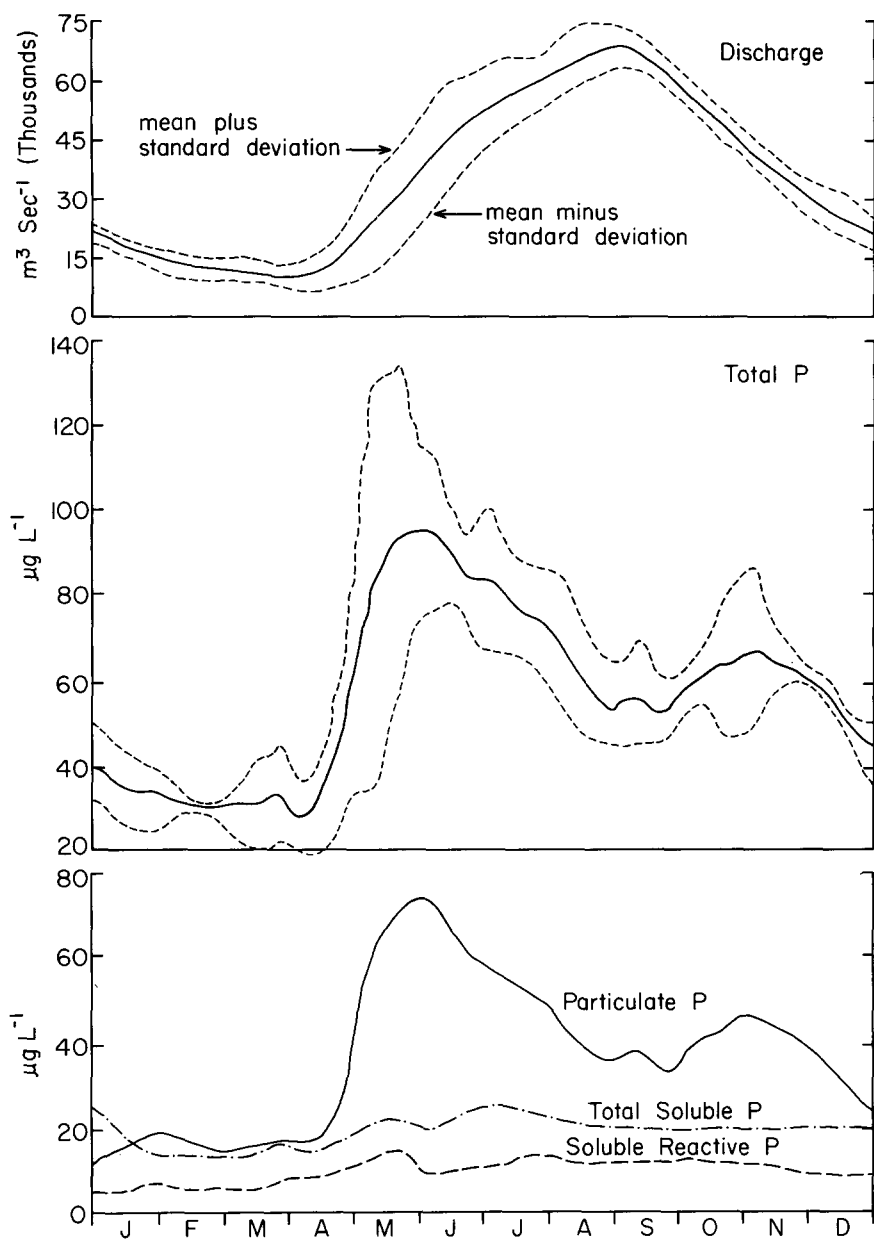


Fig. 11. Mean concentrations of phosphorus fractions in the Orinoco River at Barrancas over the seasonal cycle across the four years, with indication of the true standard deviation of total phosphorus among years (after removal of error variance).

ganic materials is 128×10^6 t/y, or 1350 kg/ha/y (340 kg/ha/y dissolved, 1010 kg/ha/y suspended).

The total transport of inorganic material from the Orinoco basin to the delta corresponds to an erosion rate of 4.3 cm/1000 y, given a rock density of 2.7 g/cm³. The dissolved component of total inorganic transport includes substances that originate mostly from the atmosphere (chlorine, sulfur, nitrogen), partly from the atmosphere (bicarbonate), or to a minor extent from the atmosphere (metal cations: Lewis et al. 1987). Given that the erosion rate is overrepresented by the amount of atmospheric transport, all chlorine, sulfur, nitrogen, and bicarbonate can be subtracted to provide a lower bound for the estimate: 3.8 cm/1000 y. Thus the true basin-wide erosion rate is between 3.8 and 4.3 cm/1000 y, or very close to 4 cm/1000 y.

Discussion

Total suspended and dissolved solids

Seasonal patterns in the concentration of total particulate material can be explained partly by seasonal changes in kinetic energy applied to the suspension and transport of solids (Webster et al. 1987). In addition, however, there are important seasonal changes in the storage or release of suspended material on the river banks or floodplain (Meade et al. 1985). The initial abrupt increase in concentration and transport of particulate material just as the river level begins to rise (Fig. 4) is accounted for jointly by the increase in mechanical erosion rates that accompanies increased runoff, and by the rise in water level within the channel, which causes resuspension of fine material that was deposited during the interval of declining discharges the previous year. A steep rise in concentration of suspended material with rising discharge is typical of many rivers (Meade et al. 1988). After discharge has risen substantially in the Orinoco, but before it has begun to decline, there is a decrease in concentration of suspended solids. This decrease is probably explained jointly by the previous removal of much of the easily resuspended fine material in the channel, and by the entry of waters into the floodplain, where storage of a substantial amount of particulate material can occur through sedimentation (Meade et al. 1983). The rapid clarification of waters that enter the floodplain (Hamilton & Lewis 1987) clearly demonstrates the storage of particulate material by this mechanism.

A small secondary rise in the concentration of particulate material occurs during the falling-water phase of each hydrologic cycle (Fig. 4). This probably reflects the separation of the river from the floodplain, which eliminates

the sedimentation losses to the floodplain, as well as return of some portion of stored material to the channel (Meade et al. 1983).

The concentrations of suspended solids in the Orinoco River are very low by comparison with those of most other major rivers of the world. The worldwide average suspended load is 400–500 mg/l (Meybeck 1976), or several times the load of the Orinoco. The suspended load of the Orinoco would appear to be similar to that of the Amazon as reported by Gibbs (1967: 90 mg/l). However, Meade et al. (1985) have reestimated the load of the Amazon as 190 mg/l. The reason for this large discrepancy is probably underestimation of the vertical concentration gradient by Gibbs (R. Meade, pers. comm.). Meade et al. (1983) also provisionally estimated the transport of suspended matter by the Orinoco as 200×10^6 t/y. More recently, Meade et al. (1988) have used the seasonal resolution of the data set reported here, but corrected upward to match the mean concentrations obtained on cruises by Meade and collaborators. This resulted in an estimate of 150×10^6 t/yr. For consistency we use here the estimate of 90×10^6 t/y from our own sampling, but a truly secure value cannot be given until the causes of discrepancies among measurements are better known. If the estimates of Meade et al. (1988) ultimately prove to be more accurate, the transport of suspended solids reported here will be too low. For general comparison of the Orinoco data with the literature on element transport by large rivers, it should be noted that virtually all existing information is based on surface samples rather than integrated samples, and will therefore be biased toward underestimate of actual transport.

The low concentrations of suspended solids in the Orinoco River can be explained by the large proportion of water in the Orinoco main stem that originates from the Guayana Shield. The rivers of the Guayana Shield carry very low amounts of suspended solids (5–15 mg/l: Lewis et al. 1987). In addition, the minimal disturbance of vegetative cover throughout the watershed is probably also partly responsible for the low concentrations of suspended solids.

Organic matter accounts for only a small proportion of the total particulate matter in the Orinoco River. The ratio of organic carbon to total suspended solids is 2.0%, which is below the trend line developed by Meybeck (1982) for rivers of the world. However, the Orinoco does lie within the cluster of points from which Meybeck's trend line was derived. Deviation of the Orinoco from the trend line is mainly explained by the large influence of waters draining from the Guayana Shield. These waters do not carry as much suspended organic carbon as would be predicted from Meybeck's trend line.

Seasonal variation in total dissolved solids is far lower than seasonal

variation in suspended solids. In part this is explained by complementary seasonal phasing of organic and inorganic dissolved solids. Because the concentrations of dissolved inorganic solids are low in the Orinoco River, the concentrations of total dissolved solids are strongly influenced by dissolved organic matter, which would not be such an important component of dissolved solids in rivers carrying higher amounts of inorganic solids. Thus the complementary phasing of organic and inorganic fractions damps the variability in total solids much more effectively than it would in rivers with higher total solids content. The moderating effect of complementary phasing for inorganic and organic solids on total dissolved solids is illustrated by the ratios of maximum to minimum concentrations. The mean ratio of annual maximum to annual minimum total dissolved solids for the Orinoco is 1.46. For inorganic solids alone, the ratio is 1.86.

The discharge-weighted mean for dissolved inorganic solids in the Orinoco is 25 mg/l, which is well below the amount that would be predicted on the basis of the equation obtained by Meybeck (1976) for specific transport of worldwide continental waters (50 mg/l). Also, the dissolved inorganic solids of the Orinoco are substantially lower than those of the Amazon. Furch (1984) estimates the inorganic solids content of the Solimoes as 65 mg/l and the inorganic solids content of the Rio Negro as 19 mg/l. The mixture of these concentrations in proportion to the relative flows of these two rivers that make up the Amazon main stem would produce an average very similar to that reported by Gibbs for the Amazon (1967, 1972: 53 mg/l). The low concentrations of inorganic dissolved solids in the Orinoco drainage are explained by a combination of high dilution rates, lack of watershed disturbance, and high proportionate yield of water from the Guayana Shield, where chemical weathering proceeds slowly. The Orinoco River probably has the lowest concentrations of inorganic dissolved solids of the world's major non-tributary rivers.

Soluble silicon

The mean concentration of soluble silicon, expressed as SiO_2 , is 6 mg/l. This concentration agrees well with the estimates reported by Nemeth et al. (1982). Also, the concentrations appear to be very similar to those reported recently for the Amazon. Furch (1984) gives an average of 8.6 mg/l for the Solimoes and 4.3 mg/l for the Rio Negro. The mixture of these two waters in the main stem would give an intermediate concentration, which would be very similar to that of the Orinoco; the 12 monthly data points shown in Kempe (1982) for the Amazon at Obidos have a median of 5 mg/l.

Meybeck (1979) made an extensive summary of the SiO_2 concentrations

for rivers of the world, including South America. The concentrations shown by Meybeck for South America range between 10 and 15 mg/l. Meybeck attributes these high concentrations to a temperature effect on the silica content of surface waters. However, Meybeck's summary appears to be in conflict with the most recent analyses for the Amazon and the Orinoco.

Mineralogical analysis (Emeis & Stoffer 1982; Irion 1983; Jones 1987) shows that the main mineral constituents of the Orinoco main stem are kaolinite and illite (80%), quartz (19%), and feldspars (6%). Application of equilibrium modelling to the mixture of dissolved and mineral constituents of the Orinoco River for selected discharge stages indicates that the water is probably oversaturated with respect to kaolinite, but that feldspars may tend to dissolve (Jones 1987).

The concentrations of soluble silica in the Orinoco River are much more stable than the concentrations of any other component of dissolved or suspended solids except potassium (Fig. 5), which may be stabilized by vegetation (Meybeck 1984). However, there is a detectable seasonal cycle; the concentration of soluble Si decreases by about 0.5 mg/l as discharge rises. Dilution probably explains the decrease. Temperature, which strongly affects the solubility of silicate minerals (Hem 1970), varies little with season. The pH of soil water may vary seasonally, but the effect of pH on solubility of silicate is small when the pH is below 8.0 (Stumm & Morgan 1981).

Ionic dissolved solids

Detailed studies of the Caura River drainage on the Guayana Shield have shown that approximately 20% of the sodium in surface waters draining from the shield originates from the atmosphere (Lewis et al. 1987). Also, approximately 7% of calcium in shield waters originates from the atmosphere, as well as most of the sulfate and chloride. The shield waters should provide an extreme example of the influence of precipitation on water chemistry, given the very high amounts of precipitation and the general resistance of the shield material to chemical weathering. Even so, the vast majority of anions and cations in solution originate from weathering, and not from precipitation.

In waters originating from the north of the Orinoco, the contribution of precipitation to ionic solids has not been estimated, but it must be a great deal smaller than in waters draining from the Guayana Shield. Thus for the Orinoco as a whole, the contribution of precipitation to the transport of ionic solids must be very small; the water chemistry of the Orinoco is rock-dominated.

Organic carbon

In the Orinoco, 75% of the organic carbon is dissolved and 25% is particulate. Of the particulate organic carbon, only a small portion is living. Phytoplankton account for 0.036% of the total carbon transport (2.4×10^6 kgC/y: Lewis 1988), zooplankton account for 0.0048% (0.32×10^6 kgC/y: Saunders & Lewis 1988b), and bacteria account for 0.43% (28×10^6 kgC/y). The low transport of phytoplankton in particular reflects the tendency of the floodplain to retain phytoplankton biomass and the failure of phytoplankton to grow in transit within the channel because of low light exposure in the deep, turbid water column (Lewis 1988).

For rivers in general, the ratio of dissolved to particulate organic carbon is related inversely to the amount of inorganic dissolved solids (Meybeck 1982). The ratio of dissolved to particulate organic carbon in the Orinoco falls within the range expected from the relationships developed by Meybeck, and is higher than in the Amazon, as would be predicted from the higher amounts of dissolved inorganic solids in the Amazon.

Even though waters draining from the Guayana Shield are typically darkly colored, their concentrations of dissolved organic carbon (DOC) are relatively low (Lewis & Canfield 1977; Lewis & Weibezahn 1981; Lewis et al. 1986). None of the major rivers draining from the Guayana Shield carry concentrations of DOC as high as those of the Rio Negro (8.8 mg/l: Furch 1984). Thus the concentrations of dissolved organic carbon in the Orinoco River, which is strongly influenced by shield waters, are not especially high. However, the concentrations of the Orinoco are only slightly lower than those of the Solimoes (6.8 mg/l: Furch 1984).

Across the individual sampling dates for the Orinoco, concentrations of DOC are inversely related to concentrations of ionic solids ($r = -0.55$ for DOC vs. meq/l ionic solids: $p < 0.001$). This reflects the opposing trends for substances that show purging (soluble organics) and substances that show dilution (dissolved inorganic solids). In fact the purging of DOC could be in part determined by dilution of ionic solids, which may affect the solubility of organic matter, or by coincident changes in pH that affect sorption processes (Thurman 1985). However, a second possible explanation for the purging phenomenon is the accumulation of soluble organic carbon in terrestrial systems during the season of low water, when flushing of the system is minimal. The onset of seasonal runoff may then remove this accumulated soluble organic matter, and thus produce a seasonal rise in concentration as high discharges return. A rise in rates of water column respiration just as the hydrograph rises is found in many rivers and seems to be explained by movement of labile carbon into the channel at this time

(Kempe 1982), which would be consistent with the seasonal accumulation of organic carbon. The purging effect, although as yet poorly documented, may be widespread in large rivers; it apparently occurs in the Amazon (Klinge 1972) and the Niger (Martins 1982, 1983). The mechanisms that might explain purging cannot yet be distinguished, however.

The transport of organic carbon from the Orinoco drainage is 72 kg/ha/y (Table 2 plus the bedload allowance, which may be inappropriate for C, but adds only 2 kg/ha/y). This corresponds to 6.8×10^6 t/y (lower than the 8.8×10^6 t/y estimated by Paolini et al. 1983), or approximately 1.6% of the carbon flow to the world's oceans based on global estimates of Schlesinger and Melack (1981) or Meybeck (1982). The specific carbon yield of the Orinoco drainage is considerably above what might be expected from the review by Schlesinger and Melack, but is consistent with the trend line developed by Lugo (1983) for rivers in Puerto Rico. High transport can be mostly explained by the very high contributions from the Guayana Shield.

Nitrogen

The concentrations of ammonium in the Orinoco River (30–40 $\mu\text{g/l}$) are higher than might have been expected. The rate of decomposition for organic matter in transit is so low (1–2% per day of the organic carbon) that it can scarcely account for any accumulation of ammonium. Growth of autotrophs in transit is negligible, and the low substrate concentrations would not encourage the development of large populations of nitrifiers. Thus the ammonium concentrations may to a large degree reflect the persistence of ammonium originating from terrestrial systems in the absence of significant ammonium demand. Data for ammonium concentrations in uncontaminated waters are relatively scarce (Meybeck 1982), and it is thus difficult to put the concentrations of ammonium in the Orinoco into perspective with those of other uncontaminated rivers.

Nitrate is the most abundant form of inorganic fixed nitrogen in the Orinoco. The concentrations that are typical of the Orinoco main stem are near the world averages estimated by Meybeck (1982: 100 $\mu\text{g/l}$ as N). Although the concentrations of nitrate in the Orinoco are well below those that are typical of disturbed ecosystems, they are still well in excess of limiting concentrations for aquatic autotrophs. The persistence of high concentrations of inorganic nitrogen in the Orinoco River water reflects the negligible autotrophic demand on the nitrogen pool (Lewis 1988). In this sense, the flowing waters of the Orinoco contrast with those of the floodplain, in which there is substantial autotrophic nitrogen demand. In the

floodplain waters, complete depletion of inorganic nitrogen occurs in response to phytoplankton growth (Hamilton & Lewis 1987).

Dissolved organic nitrogen has been studied only poorly for flowing waters in general, but Meybeck (1982) provides a good summary of the existing information. Dissolved organic nitrogen accounts for 58% of the total fixed nitrogen in the Orinoco. This proportion is higher than for the small unpolluted rivers listed by Meybeck. However, it is very near the ratio given by Meybeck for the Solimoes (62%). Meybeck (1982) gives the median mass ratio of soluble organic carbon to soluble organic nitrogen as 20 for unpolluted rivers; the ratio for the Orinoco is 21. The ratio of organic carbon to organic nitrogen appears to be conservative and is centered around a mean of approximately 8.5 (Meybeck 1982: for comparison, the Redfield Ratio is 5.7). The ratio for the Orinoco main stem is 8.1, and the ratio for the Solimoes is 8.6.

The seasonal concentration pattern for nitrate in the Orinoco drainage is unusual among the dissolved solids in showing a high degree of dilution at peak flow, despite persistence of high concentrations well into the phase of rising water (Figs. 5, 10). High concentrations at rising water have been documented elsewhere (Mekong: Carbonnell & Meybeck 1975, Parana: Maglianesi 1973). However, it is not clear whether the extreme peak-flow dilution or interannual conservation features of nitrate in relation to discharge are typical of large undisturbed rivers in general. In the Orinoco system, nitrate differs from all fractions of carbon and phosphorus in its relation to discharge. Because the interannual conservation phenomenon is difficult to explain by strictly physical mechanisms, exceptional biological effects are implicated for nitrate. The strong depletion of nitrate in river water entering the floodplain suggests that the floodplain may cause the peculiarities in seasonality of nitrate concentrations.

The Orinoco transports 0.54×10^6 t/y of fixed nitrogen (Table 2 plus bedload estimate of 0.02×10^6 t/y), which is approximately 1.5% of the global nitrogen flux through rivers (Meybeck 1982). The high specific transport of nitrogen (5.7 kg/ha/y) is to a large degree explained by high contributions of the Guayana Shield (10 kg/ha/y: Lewis 1986). The high transport of nitrogen implies high rates of nitrogen fixation within the drainage because atmospheric deposition in the Shield watersheds is unlikely to exceed 1 to 2 kg/ha/y (Lewis et al. 1987).

Phosphorus

Meybeck has estimated that the global average for soluble reactive phosphorus is $8 \mu\text{g/l}$ in undisturbed river systems. This is very close to the

discharge-weighted mean concentration for the Orinoco River (Table 1). Close to 50% of the total soluble phosphorus in the Orinoco is organic. The concentrations of total soluble phosphorus in the Orinoco River fall within the mid-range of values reported by Meybeck (1982) for uncontaminated waters. Conclusive comparisons with the concentrations in the Amazon do not appear to be possible at the present time.

The amount of phosphorus in particulate material in the Orinoco River averages 0.055%, which is only half of the worldwide average derived by Martin & Meybeck (1979). The concentrations of particulate phosphorus in waters draining from the Guayana Shield are extraordinarily low because of the low amounts of total particulate material as well as the low amount of phosphorus per unit weight for particulate material originating on the Shield.

The concentrations of total phosphorus in the Orinoco are low by comparison with those of world rivers, and appear to be even lower than those of the Solimoes ($105 \mu\text{g/l}$; Furch 1984). Because of their low particulate phosphorus load, the waters draining from the Guayana Shield have total phosphorus concentrations that rank among the lowest measured in large rivers. The addition of large quantities of water from the Shield lowers the concentration of total phosphorus in the Orinoco main stem.

The Orinoco carries $0.074 \times 10^6 \text{ t/y}$ of phosphorus, which is 0.35% of the global phosphorus transport by rivers as calculated by Meybeck (1982). The specific transport is 0.75 kg/ha/y . The specific transport rates from the Guayana Shield are, counter-intuitively, essentially identical to those from the savannas and mountains to the north of the Orinoco (Lewis et al. 1987; Saunders & Lewis 1988a), although the concentrations of phosphorus are very low in waters draining from the Shield because of the high yield of water from the Shield. As demonstrated by calculations for the Caura River drainage (Lewis et al. 1987), the weathering and erosion rates, even for shield rock, are easily sufficient to account for the total transport of phosphorus from the Orinoco drainage.

Erosion and weathering rates

The composite chemical and mechanical erosion rate for the Orinoco drainage as estimated from the data in Tables 1 and 2 (4 cm/1000 y) is very similar to a rate estimated for the Amazon by Gibbs (1967: 4.6 cm/1000 y). However, the estimate by Gibbs is closer to 7 cm/1000 y when revised on the basis of the more comprehensive sediment estimates from Meade et al. (1985). The erosion rate for the Guayana Shield is lower than the basin-wide average for the Orinoco (ca. 1.8 cm/1000 y ; Lewis et al. 1987). Thus the

erosion rates for portions of the drainage to the north and west must be considerably above 4 cm/1000 y in order to account for the basin-wide average. Higher erosion rates are expected north of the Orinoco because of the alluvial nature of the lower portion of the watershed and the association of higher weathering rates with areas of high relief, such as the Andes (Gibbs 1967). It should also be noted that basin-wide rates obscure internal discontinuities, such as translocation of sediment material from mountains to floodplains (Meade et al. 1988).

Conclusions

Inorganic suspended solids, soluble silica, major ionic solids, and one of the two key nutrient elements (phosphorus) in the Orinoco River originate from mechanical or chemical erosion. The concentrations of these constituents are extremely low by comparison with concentrations that are typical of large rivers of the world. This unusual feature of the Orinoco River is explained jointly by two factors. First, the runoff per unit area from the Orinoco drainage as a whole is extremely high; it may exceed that of any major non-tributary river in the world (that of the Rio Negro is slightly higher). Thus to a large extent the low concentrations are simply a product of dilution. In addition, however, an exceptionally large portion of the Orinoco watershed is underlain by resistant shield rock covered with undisturbed forest. Because a large portion of the Orinoco's flow drains from this area, the waters of the main stem reflect the low rates of mechanical and chemical erosion from the shield.

In contrast to the geologically-derived constituents, concentrations of substances that originate biologically (i.e., nitrogen and organic carbon through biological fixation) are not exceptionally low in the Orinoco River. The dilution effects are not so pronounced for these substances; the high rates of runoff from the Orinoco drainage are matched by high specific transport rates. Thus the biogenic substances are generally compensatory for high runoff (i.e., they maintain concentrations similar to those of drier watersheds, thus offsetting dilution), whereas the geologic substances are not.

The Orinoco River demonstrates clear seasonal phasing in concentration and transport for most major suspended and dissolved constituents. Even though the concentrations change rapidly across the seasons, the degree of consistency in the pattern from one year to the next and the smoothness of the trends illustrate the great homeostasis of a large, undisturbed watershed. Predictable phasing for dissolved and suspended constituents reflects the

operation of biological and geochemical mechanisms that control concentration and transport at the interface between the terrestrial system and flowing water. The data demonstrate that these mechanisms extend well beyond simple dilution. For particulate constituents, storage and remobilization influence concentration and transport, and these phenomena are in turn dependent on the large amplitude of river discharge and annual contact of the river with its extensive floodplain. For dissolved organic carbon and the organic fractions of nitrogen and phosphorus, the purging phenomenon associated with rising discharge indicates regulation of concentration through mechanisms other than dilution. Still different factors must affect nitrate, which shows exceptional decline in concentration with increasing discharge.

Despite the extraordinarily low concentrations of ionic and suspended solids in the Orinoco River, the water of the Orinoco easily supports the development of abundant plankton, as demonstrated both by the concentrations of inorganic nutrients in the river and by the ultimate growth of large plankton populations in the Orinoco floodplain at the time of inundation. However, biological effects on water chemistry in transit are minimal, despite the fact that the transit time is as much as two weeks from the upper to the lower end of the Orinoco system. Physical conditions in the river (primarily light limitation) prevent the growth of autotrophs, which would otherwise remove the inorganic nutrients and raise the concentrations of organic carbon in the river.

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References

- Carbonnel JP & Meybeck M (1975) Quality variation of the Mekong River at Phnom Penh, Cambodia, and chemical transport in the Mekong basin. *J. Hydrol.*, 27: 249–265
- Case JE, Holcombe TL & Martin RG (1984) Map of geologic provinces in the Caribbean

- region. In: Bonini WE, Hargraves RB & Shagam (Eds) (pp. 1–30) *The Caribbean-South American Plate Boundary and Regional Tectonics*. Geological Society of America Memoir 162
- Curtis WFR, Meade RH, Nordin CF, Jr, Price NB & Sholkovitz ER (1979) Non-uniform vertical distribution of fine sediment in the Amazon River. *Nature* 280: 381–383
- Degens ET & Kempe S (1982) Riverine carbon—an outlook. *Mitt. Geol. Palaont. Inst. SCOPE/UNEP Sonderband* 52: 757–765
- Dixon WJ & Massey FJ, Jr (1957) *Introduction to statistical analysis*. McGraw-Hill, New York
- Emeis K & Stoffers P (1982) Particulate suspended matter in the major world rivers: EDAX analysis, scanning electromicroscopy and X-ray diffraction study of filters. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 52: 529–554
- Ewel JJ, Madriz A & Tosi JA, Jr (1976) *Zonas de Vida de Venezuela*. Sucre, Caracas
- Furch K (1984) Water chemistry of the Amazon basin: the distribution of chemical elements among fresh waters. In Sioli H (Ed) *The Amazon. Limnology and Landscape Ecology of a Mighty Tropical River and its Basin*. (pp 167–199) Dr. W Junk, The Hague
- Gibbs AK & Barron CN (1983) The Guiana Shield reviewed. *Episodes* 1983: 7–14
- Gibbs RJ (1967) The geochemistry of the Amazon river system. I: The factors that control the salinity and the composition and concentration of the suspended solids. *Geological Society of America Bulletin* 78: 1203–1232
- Hall FR (1970) Dissolved Solids—Discharge Relationships. I. Mixing Models. *Water Resources Research* 6(3): 845–850
- Hamilton SK & Lewis WM, Jr (1987) Causes of seasonality in the chemistry of a lake on the Orinoco River floodplain, Venezuela. *Limnol. Oceanogr.* 32: 1277–1290
- Hem JD (1970) *Study and Interpretation of the Chemical Characteristics of Natural Water*. Geological Survey Water-Supply Paper 1473. US Government Printing Office, Washington
- IGAC (1977) *Atlas de Colombia*. Instituto Geografico Augustin Codazzi, Bogota
- Irion G (1983) Clay mineralogy of the suspended load of the Amazon and of rivers in the Papua-New Guinea mainland. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 55: 483–504
- Johnson NM, Likens GE, Bormann FH, Fisher DW & Pierce RS (1969) A working model for the variation of stream-water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resour. Res.* 5: 1353–1363
- Jones SL (1987) Modeling of aqueous equilibria and sediment/water interactions, Orinoco River, Venezuela. MS thesis, University of Colorado, Boulder
- Kempe S (1982) Long-term records of CO₂ pressure fluctuations in fresh waters. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 52: 91–332
- Kempe S (1985) Compilation of carbon and nutrient discharge from major world rivers. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 58: 29–32
- Klinge H (1972) Die Ionenfracht des Rio Negro, Staat Amazonas, Brasilien, nach Untersuchungen von Dr. Harald Ungemach. *Amazoniana* 2–3: 175–185
- Kranck K & Milligan TG (1983) Grain size distributions of inorganic suspended river sediment. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 55: 525–534
- Lesack LFW, Hecky RE & Melack JM (1984) Transport of carbon, nitrogen, phosphorus, and major solutes in the Gambia River, West Africa. *Limnology and Oceanography* 29: 816–830
- Lewis WM, Jr (1986) Nitrogen and phosphorus runoff losses from a nutrient-poor tropical moist forest. *Ecology* 67(5): 1275–1282
- Lewis WM, Jr (1988) Primary production in the Orinoco River. *Ecology* 69: 679–692
- Lewis WM, Jr & Canfield D (1977) Dissolved organic carbon in some dark Venezuelan waters

- and a revised equation for spectrophotometric determination of dissolved organic carbon. *Archiv fur Hydrobiologie* 79(4): 441–445
- Lewis WM, Jr & Weibezahn (1981) The chemistry and phytoplankton of the Orinoco and Caroni Rivers, Venezuela. *Archiv fur Hydrobiologie* 91: 521–528
- Lewis WM, Jr & Saunders III JF (1984) Cross-sectional variation in the chemistry and suspended sediment load of the Orinoco River at Ciudad Bolivar. *Acta Cientifica Venezolana* 35: 382–385
- Lewis WM, Jr, Saunders JF, Weibezahn & Levine SN (1986) Organic carbon in the Caura River, Venezuela. *Limnology and Oceanography* 31: 653–656
- Lewis WM, Jr, Hamilton S, Jones S & Runnells D (1987) Major element chemistry, weathering and element yields for the Caura River drainage, Venezuela. *Biogeochemistry* 4: 159–181
- Lugo AE & Quinones F (1983) Organic carbon export from intensively used watersheds in Puerto Rico. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 55: 237–242
- Maglianesi R (1973) Principales características químicas y físicas de las aguas del Alto Parana y Paraguay Inferior. *Physis* 32(85): 185–197
- Martin JM & Meybeck J (1979) Elemental mass-balance of material carried by world major rivers. *Marine Chemistry* 7: 173–206
- Martins O (1982) Geochemistry of the Niger River. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 52: 397–418
- Martins O (1983) Transport of carbon in the Niger River. *Mitt. Geol. Palaont. Inst., SCOPE/UNEP Sonderband* 55: 435–449
- MARNR (1983) Venezuela en mapas. MARNR Direccion de Cartografia Nacional, 1st edn. Caracas
- Meade RH, Nordin CF, Jr, Perez Hernandez D, Mejia AB & Perez Godoy JM (1983) Sediment and water discharge in Rio Orinoco, Venezuela and Colombia. In: *Proceedings of the Second International Symposium on River Sedimentation, Water Resources and Electric Power Press* (pp 1134–1144) Beijing, China
- Meade RH, Dunne T, Richey JE, de M. Santos U & Salati E (1985) Storage and remobilization of suspended sediment in the lower Amazon River of Brazil. *Science* 288: 488–490
- Meade RH, Yuzyk TR & Day TJ (1988) Movement and storage of sediment in rivers of the United States and Canada. In: *The Geology of North America. Vol 0–1. Surface Water Hydrology* (in press)
- Meade RH, Weibezahn FH, Lewis WM, Jr & Perez Hernandez D (1988) Suspended-sediment budget for the Orinoco River. In: Weibezahn FH, Alvarez H & Lewis WM, Jr (Eds) *The Orinoco River. Assoc. Venez. AV. Cien.* (in press)
- Meybeck M (1976) Total dissolved transport by world major rivers. *Hydrological Science Bulletin* 21: 265–284
- Meybeck M (1979) Concentrations des eaux fluviales en elements majeurs et apports en solution aux oceans. *Rev. Geol. Dyn. Geogr. Phys.* 21: 215–246
- Meybeck M (1982) Carbon, nitrogen and phosphorus transport by world rivers. *American Journal of Science* 282: 401–450
- Meybeck M (1984) Variabilite géographique de la composition chimique naturelle des eaux courantes. *Verh. Internat. Verein. Limnol.* 22: 1766–1774
- Nemeth A, Paolini J & Herrera R (1982) Carbon transport in the Orinoco River: preliminary results. *Mitteilungen aus dem Geologisch-Palaontologischen Institut der Universitat Hamburg. SCOPE/UNEP Sonderband* 52: 357–364
- Nordin CF, Jr & Skinner JV (1977) Sediment sampling equipment for deep fast currents. *Proc. Internat. Assoc. Hydraul. Res.* 6: 606–609
- Nordin CF, Jr, Cranston CC & Mejia AB (1983) New technology for measuring water and suspended-sediment discharge of large rivers. In: *Proc. Second Internat. Symposium on*

- River Sedimentation, 11–16 October, 1983, Nanjing, China. (pp 1145–1158) Water Resources and Electric Power Press, Beijing, China
- Paolini J, Herrera R & Nemeth A (1983) Hydrochemistry of the Orinoco and Caroni Rivers. *Mitt. Geol. Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband* 55(2): 223–236
- Sarmiento G (1983) The savannas of tropical America. In: Bourliere, F (Ed) *Tropical Savannas. Ecosystems of the World*. 13. (pp 245–288) Elsevier, Amsterdam
- Saunders JF, III & Lewis WM, Jr (1988a) Transport of phosphorus, nitrogen and carbon by the Apure River, Venezuela. *Biogeochemistry* 5: 323–342
- Saunders JF, III & Lewis WM, Jr (1988b) Zooplankton abundance in the lower Orinoco River, Venezuela. *Arch. Hydrobiol.* (in press)
- Schlesinger WH & Melack JM (1981) Transport of organic carbon in the world's rivers. *Tellus* 31: 172–187
- Sheldon RW (1972) Size separation of marine seston by membrane and glass fibre filters. *Limnology and Oceanography* 17: 494–498
- Sioli H (1984) The Amazon and its main affluents: hydrography, morphology of the river courses, and river types. In: Sioli H (Ed) *The Amazon. Limnology and Landscape Ecology of a Mighty Tropical River and its Basin* (pp 127–166) Junk, The Hague
- Solorzano L and Sharp J (1980) Determination of total dissolved phosphorus and particulate phosphorus in natural waters. *Limnology and Oceanography* 25: 754–758
- Stumm W & Morgan JJ (1981) *Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters*. Second edition. John Wiley and Sons, New York, NY. 780 p
- Thurman EM (1985) *Organic Geochemistry of Natural Waters*. Junk, Dordrecht
- Webster JR, Benfield EF, Golladay SW, Hill BH, Hornick LE, Kazmierczak RF, Jr & Perry WB (1987) Experimental studies of physical factors affecting seston transport in streams. *Limnol. Oceanogr.* 32(4): 848–863
- Weibezahn F (1985) Concentraciones de especies químicas disueltas y transporte de sólidos suspendidos en el alto y medio Orinoco y sus variaciones estacionales. Universidad Simon Bolívar, Informe, MARNR
- Welcomme R (1979) *Fisheries Ecology of Floodplain Rivers*. Longman, London
- Zinck A (1977) *Rios de Venezuela. Cuadernos Lagoven*, Caracas
- Zinck A (1980) *Valles de Venezuela. Cuadernos Lagoven*, Caracas