Biogeochemistry 5: 323–342 (1988)

Transport of phosphorus, nitrogen, and carbon by the Apure River, Venezuela

JAMES F. SAUNDERS, III & WILLIAM M. LEWIS, JR.
Center for Limnology, Dept. of Environmental, Population, and Organismic Biology, University of Colorado, Boulder, CO 80309-0334, USA

Key words: tropical river, tropical floodplain, river chemistry, nutrient yield, floodplain–river interaction

Abstract. The concentrations and transport of carbon, nitrogen, and phosphorus were studied in the Apure River, Venezuela, over a period of 21 months. The drainage basin, which is in western Venezuela, encompasses 167,000 km^2, most of which has low relief and supports tropical savanna vegetation. Average runoff for the period of study was 361 mm/year. Discharge-weighted mean concentrations were 188 ug/l for total P, 957 ug/l for total N, and 9.8 mg/l for organic C. Annual transport was 0.68 kg·ha^{-1}·year^{-1} for total P, 3.45 kg·ha^{-1}·year^{-1} for total N, and 35.4 kg·ha^{-1}·year^{-1} for organic C. Particulate matter accounted for 68% of P, 54% of N, and 37% of C transport. The yield of carbon from the Apure watershed agrees well with empirical predictions, based mostly on the temperate zone, for watersheds of similar size and water yield.

Seasonal patterns in chemistry are tied strongly to the hydrologic cycle. When the wet season begins, rising water flushes organic matter from side channels and produces a sharp increase in particulate C and N. Particulate P, which is associated more with mineral material, also increases during rising water. All dissolved constituents except inorganic C also increase over the rising-water phase. As the river inundates the floodplain, the concentration of nitrate declines, whereas the concentrations of dissolved organic C and N continue to rise. At high water the floodplain appears to store sediments that are later remobilized. During low water, all fractions except dissolved inorganic C tend to be at minimum concentration.

Soluble reactive P, total dissolved P, dissolved inorganic C, and dissolved organic C were successfully modelled as hyperbolic functions of discharge. No significant relationships were found between concentration and discharge for any particulate fraction because the flushing and storage mechanisms affecting these fractions occurred within specific hydrologic phases, rather than as a smooth function of discharge. No significant relationships were found for any nitrogen fraction. For nitrate, and thus for total dissolved N, of which nitrate is a major component, poor conformance to standard models is explained by association of key mechanisms (e.g. uptake) with specific hydrologic phases. Particulate components and nitrate in this sense violate the continuity assumptions implicit in the standard models.

Introduction

Weathering, leaching, and erosion contribute to the loss of nutrients from watersheds, while biomass accretion and some abiotic processes cause the retention of nutrients. The relative importance of the two sets of factors may vary seasonally under the influence of environmental variables such as precipitation and temperature (Jordan 1985). From the viewpoint of nutrient export, seasonal tropical watersheds are particularly interesting in that the seasonal variation of some important determinants of biological activity (light and temperature) is small compared to the range of variation that is typical of temperate environments (Lewis 1987). In contrast, precipitation can vary greatly. Alternation of wet and dry seasons is likely to influence the retention and loss of elements, but these effects may not be easily deduced from information on ecosystems of the temperate zone, where light and temperature vary simultaneously with moisture.

In relatively few cases has the export of carbon, nitrogen, and phosphorus been studied in watersheds drained by tropical rivers (Meybeck 1982). Attention has typically been focused on the largest rivers, such as the Amazon (e.g. Richey et al. 1985) or Niger (Martins 1982), which are potentially important to global balances, but are of such great size that processes may be obscured by the complexity of watershed geology and vegetation. Studies of smaller watersheds such as that of the Gambia River, which drains principally a savanna region in Africa (Lesack et al. 1984), or that of the Caura River, which drains a tropical moist forest in Venezuela (Lewis et al. 1986, Lewis 1986), may more readily yield information about processes affecting export.

In this study we examine seasonal patterns of nutrient concentrations and transport for carbon, nitrogen, and phosphorus in the Apure River of Venezuela. The watershed of the Apure River provides an example of tropical environments that are only moderately well watered, and that show strong seasonality in moisture.

Site description

The Apure River drains an area of 167,000 km^2 in western Venezuela (Zinck 1977; Fig. 1). The headwaters of the Apure River are on the eastern flank of the Andes. The river descends rapidly to the Llanos, an alluvial plain that formed during the late Pleistocene over older marine sediments. Erosion on the flat terrain has produced extensive braiding of the river channel. During the wet season, much of the lower part of the watershed is inundated by sheet flooding. The Apure floodplain differs from the typical fringing floodplain in its extent of coverage and in its pattern of flooding (Welcomme 1979).

An internal delta of approximately 5000 km^2 is formed by the Apure and Arauca rivers where these low-gradient tributaries flow into the Orinoco

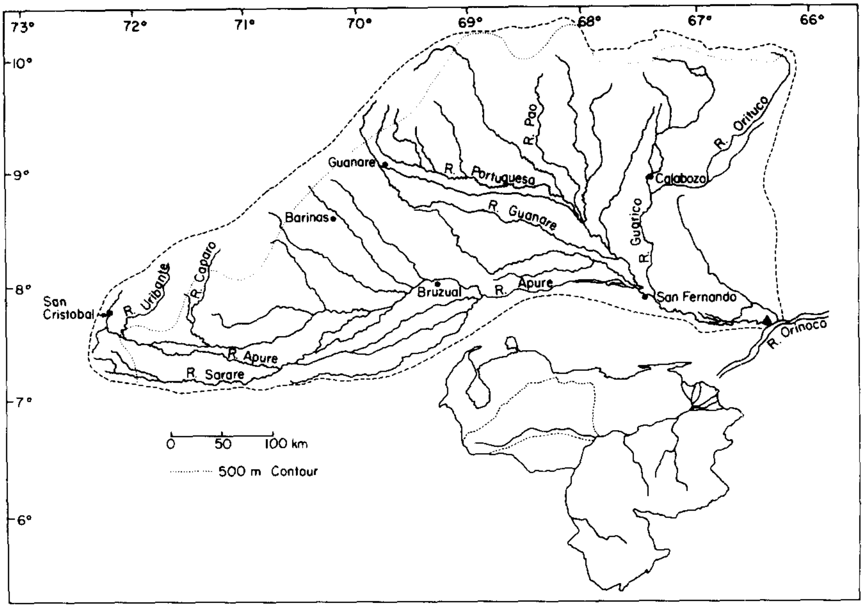

Fig. 1. Map of Apure watershed.

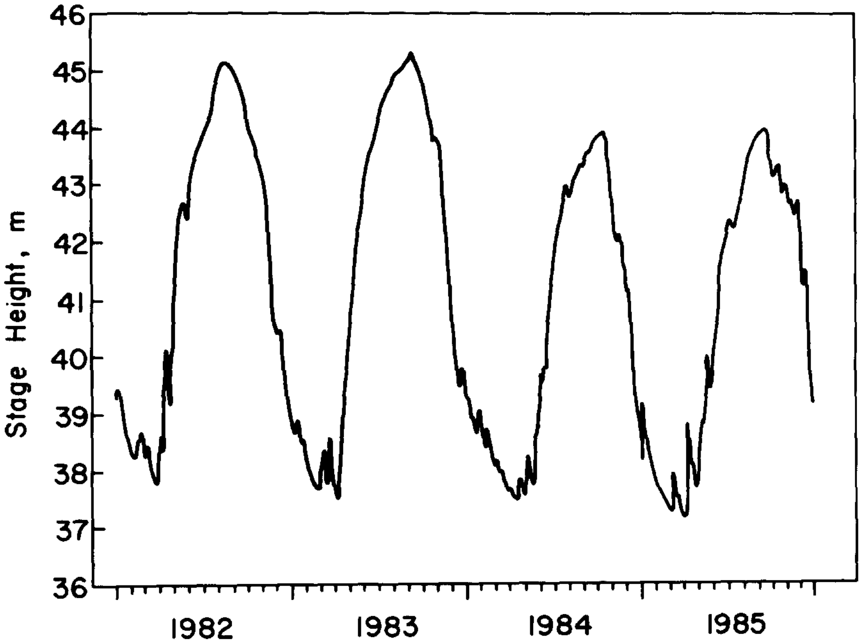

Fig. 2. Hydrograph of Apure River, 1982–1985.

River. When discharge is high in the Orinoco, a large, shallow lake forms in the Orinoco between the mouths of the Capanaparo and Apure rivers that backs up tributary flow (Meade et al. 1983). This partial ponding of the water results in seasonal storage of large amounts of sediment (Meade et al. 1983).

The annual pattern of discharge in the Apure River (Fig. 2) shows the influence of alternating wet seasons (April–November) and dry seasons (December–April). River level changes 6–8 m from low water to high water. A sequence of four hydrologic phases describes the relationship between the river and the floodplain. Approximate temporal boundaries for the phases can be based on the stage height measurements recorded at San Fernando de Apure. During the low-water phase, which corresponds to stage heights below 38 m, the river is not in contact with the floodplain. The wet season brings the rising-water phase, during which the river is still within its banks (38–42m). At stage heights above 42m, the river inundates the floodplain (inundation phase). Inundation begins in July, and peak discharges occur in October or September. The water level then recedes and, when once again within its banks, the river is in the falling-water phase (42–38m).

Precipitation in the basin ranges beteen 900 and 3000 mm/year; the area-weighted mean is 1545 mm/year (1951–70; MARNR 1983). Calabozo, which is in the northern part of the Llanos, and is probably typical of the grasslands, receives about 1300 mm of precipitation each year and loses about 370 mm as runoff (Ewel et al. 1976). The average flow of the Apure is close to 2000 m^3/s and, given a drainage area of 167,000 km^2, water yield from the entire Apure basin would be 378 mm/year. Mean runoff is thus 24% of mean precipitation.

Most of the Apure basin is a savanna with some areas of mixed forest-savanna vegetation (San Jose et al. 1985); above 15% of the watershed is above 500m in elevation and is mountainous. The *Paspalum* savanna (dominated by *P. fasciculatum*) in the lower part of the basin has been used traditionally as dry-season forage for cattle (Ramia 1967). Population density in the Apure basin is relativley low. San Cristobal in the Andes is the only city with a population greater than 150,000, and only 5 other towns have populations in excess of 25,000. Bank stabilization and flood control levees are used near some larger towns to prevent damage. In general, however, human influence is not extensive in the lower part of the drainage and the relationship between river and floodplain is essentially natural.

Methods

Samples were collected near the mouth of the Apure River at 4-week intervals from March 1984 to November 1985. Flow-weighted composite samples were collected over the river cross-section with a sampler of the type described by Nordin & Skinner (1977), (see also Stevens et al. 1980; Nordin et al. 1983). Samples were stored in a dark cooler for transport to a field laboratory at Ciudad Bolivar. Samples were typically filtered within 12 h of collection through Whatman GF/C glass-fiber filters, which have an effective pore size of 0.7 μm (Sheldon et al. 1972).

Soluble reactive phosphorus (SRP) was determined by an acid-molybdate method (Murphy & Riley 1962) and total dissolved phosphorus (TDP) was measured by the same technique after digestion with persulfate in an autoclave at 121°C. The SRP fraction will typically include orthophosphate and some organic phosphorus (Rigler 1968; Levine & Schindler 1980). Particulate phosphorus (PP) was retained on a pre-combusted filter, oxidized to orthophosphate by pyrolysis, and measured by the acid-molybdate method (Solorzano & Sharp 1980a).

Nitrate was reduced to nitrite with a cadmium-copper couple and measured by formation of an azo dye (Bendschneider & Robinson 1952; Wood et al. 1967). Nitrite levels were measured occasionally and were found to be negligible. Ammonium concentrations were measured in triplicate by a modified Solorzano method (Grasshoff 1976). Total dissolved nitrogen (TDN) was oxidized to nitrate with persulfate under alkaline conditions, and nitrate was measured as described above (modified slightly from Solorzano & Sharp 1980b). Particulates were retained on a tared filter, dried at 60°C, and reweighed to the nearest 0.01 mg. Nitrogen content was measured by a modified Pregl & Dumas method with a Carlo Erba Model 1106 Elemental Analyzer. The instrument was calibrated with reagent-grade EDTA and performance was checked against orchard leaves (National Bureau of Standards, Standard Reference Material No. 1571).

Alkalinity was used as a measure of dissolved inorganic carbon (DIC). Unfiltered samples were titrated with 0.02 N H_2SO_4 and the equivalence point was determined potentiometrically by the method of Gran (Stumm & Morgan 1981).

For measurement of dissolved organic carbon (DOC), an aliquot of filtrate was placed in an ashed glass ampule to which potassium persulfate and phosphoric acid were added. Contents of the ampule were bubbled with inert gas to eliminate inorganic carbon. Ampules were then sealed and autoclaved at 121°C. The CO_2 resulting from the digestion was measured on a Hewlett-Packard 5840A gas chromatograph with a thermal conductivity detector. Blanks and standards were prepared by the same procedures. Glucose was used as a standard, and blanks were run with each set of analyses. Particulate carbon on filters was analyzed with the Carlo Erba Elemental Analyzer.

Daily measurements of river stage height at San Fernando de Apure were made available by the Venezuelan Ministerio del Ambiente y de los Recursos Naturales Renovables. The use of a single rating curve was found to be impracticable due to changes in channel characteristics when the river enters the floodplain. smooth curves were fit by eye to calibration measurements of discharge (N = 34) that were available over the range 37.4–45.0 m.

Some interpolation of concentration data was necessary. Discharge esti-

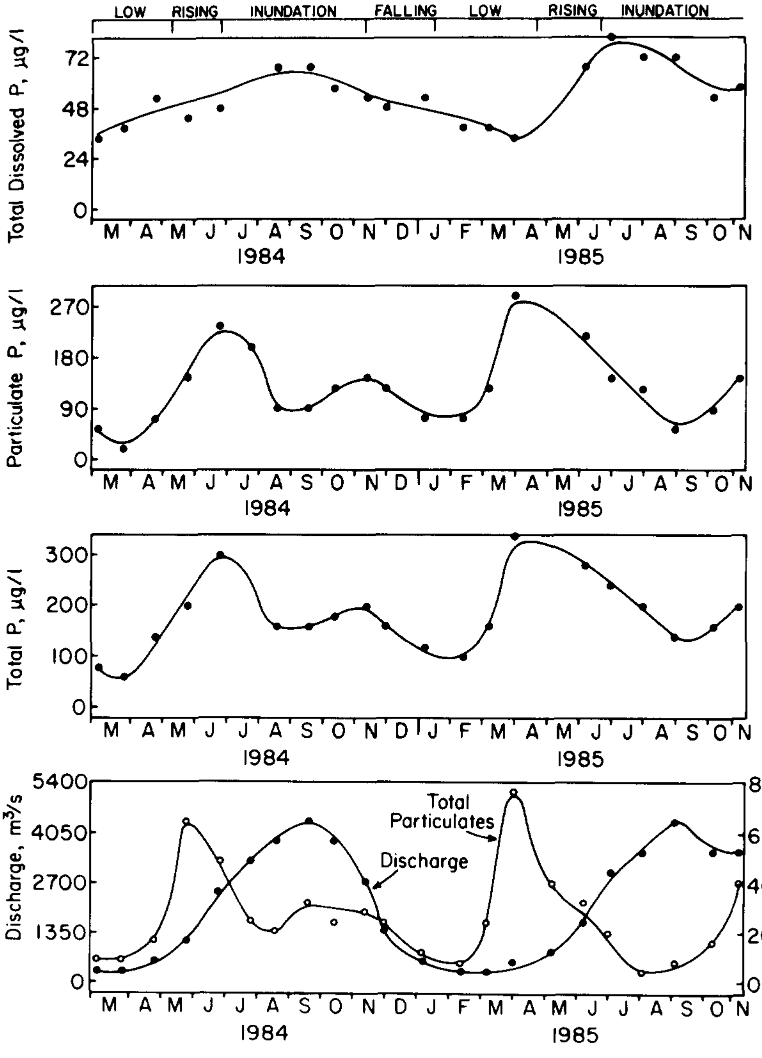

Fig. 3. Concentration vs. time for phosphorus fractions and discharge. Smooth curves fit by eye.

mates were available on each day of both years. For portions of a year not sampled (January and February of 1984; December of 1985) values from the other year were assumed to be representative; these times were just prior to, or early in the low water phase, when chemical conditions are relatively stable. Concentrations for days not sampled were estimated by linear interpolation between sampling dates. Transport was estimated as the product of concentration and discharge on each day; annual transport was estimated as the sum of daily values for each calendar year. Flow-weighted average concentrations were computed as annual transport divided by annual discharge.

Results

Flow regime and suspended load

Discharge of the Apure for the period of study was close to the long-term average of 2000 m^3/s (Table 1), and the two years were quite similar to one another in terms of total discharge. The low-water phase occurred in March and April in 1984 and from February through April in 1985. The start of the

Table 1. Concentrations and yield of P, N, and C for the Apure River, 1984–1985.

	Concentration Time-weighted means*			Concentration Discharge-weighted means*			Annual transport**		
	1984	1985	Both	1984	1985	Both	1984	1985	Both
Soluble reactive P	39.9	36.2	38.1	46.1	41.9	43.9	0.16	0.16	0.16
Total dissolved P	50.5	54.5	52.5	57.0	62.2	59.7	0.20	0.23	0.22
Particulate P	112.0	142.0	127.0	134.0	123.3	128.4	0.47	0.46	0.46
Total P	162.5	196.5	179.5	191.1	185.4	188.1	0.66	0.70	0.68
Ammonia N	37.3	33.5	35.4	42.8	42.2	42.5	0.15	0.16	0.15
Nitrate N	126.0	155.4	140.7	131.0	140.1	135.7	0.45	0.52	0.49
Total dissolved N	401.4	412.5	407.0	440.4	448.8	444.8	1.53	1.69	1.61
Particulate N	583.2	579.3	581.3	609.5	421.9	512.0	2.11	1.58	1.85
Total N	984.6	991.8	988.2	1049.9	870.7	956.8	3.64	3.27	3.45
Dissolved inorganic C	15.2	13.9	14.6	12.6	11.8	12.2	43.57	44.17	43.87
Dissolved organic C	4.9	5.0	5.0	6.2	6.2	6.2	21.35	23.13	22.24
Particulate C	3.9	4.3	4.1	3.7	3.6	3.6	12.98	13.35	13.16
Total organic C	8.9	9.3	9.1	9.9	9.8	9.8	34.32	36.48	35.40
Discharge	1835.7	1986.5	1911.1				347	375	361

* Units are mg/l for C, $\mu g/l$ for N and P, and m^3/s for discharge.

**Units are mm for water yield, $kg \cdot ha^{-1} \cdot yr^{-1}$ for chemical fractions.

rising-water phase was variable because of variation in the start of the rainy season. The period from May through June is designated as the rising-water phase because the river rose continuously during that time. As is apparent from Fig. 2, however, some rise in water level occurred temporarily before this, and such brief rises have considerable bearing on transport.

The concentrations of particulate matter were very sensitive to the initial rise in stage height at the end of the low-water phase (Fig. 3). As soon as stage height rose sharply above 38m, there was a marked rise in concentrations of particulate material. In 1984 this flushing of particulates occurred at the start of the rising-water phase, but in 1985 the increase in particulate concentrations occurred early in April. Fig. 2 shows a sharp rise in stage height in early April 1985 that was not sustained, but that caused the increase of concentrations of particulate material. The rising-water phase began in May, but the major flushing of particulates had already occurred in April.

Inundation occurred in early July of both years. Discharge maxima occurred in October of 1984 and September of 1985. Maximum concentrations of particulate material occurred with the first rise of the river when sediments that had been deposited during the preceding period of lower discharge were resuspended. Concentrations of particulate material also rose near the end of the inundation phase. The bimodal pattern implies storage of particulates at the maximum extent of inundation and remobilization either when the water level falls or during the next rising-water phase. Such a pattern is expected because the internal delta is inundated in response to a partial ponding of the Orinoco, where seasonal storage of particulates occurs (Meade et al. 1983).

The Apure was back within its banks (falling-water phase) in November of both years, and concentrations declined to relatively low levels during the low-water phase.

Means and patterns of concentration and transport

Time-weighted concentrations for most variables were quite similar (within 10%) for the two years of study (Table 1). Nitrate and particulate P were higher in 1985; total P reflects the difference in particulate P. Discharge-weighted concentrations tended to be higher than time-weighted concentrations for fractions except DIC due to the general trend for concentration to increase with discharge (Table 1).

Annual transport for the elements is given in Table 1. Because mean discharge was quite similar in the two years, transport was also similar in the two years. Particulate material accounted for 68% of P, 54% of N, and 37% of C transport.

Total dissolved phosphorus and its principal constituent, soluble reactive phosphorus, showed nearly identical patterns over time. Minima occurred at low water and maxima occurred during the inundation phase (Fig. 3). Particulate phosphorus was mobilized by rising water when the highest concentrations were recorded. Particulate P concentration remained high throughout much of the rising-water phase, but fell during the inundation phase. In general, particulate P followed the pattern of total particulates, and was thus influenced strongly by inundation of the floodplain and by the storage of particulates at high water. The annual pattern for total phos-

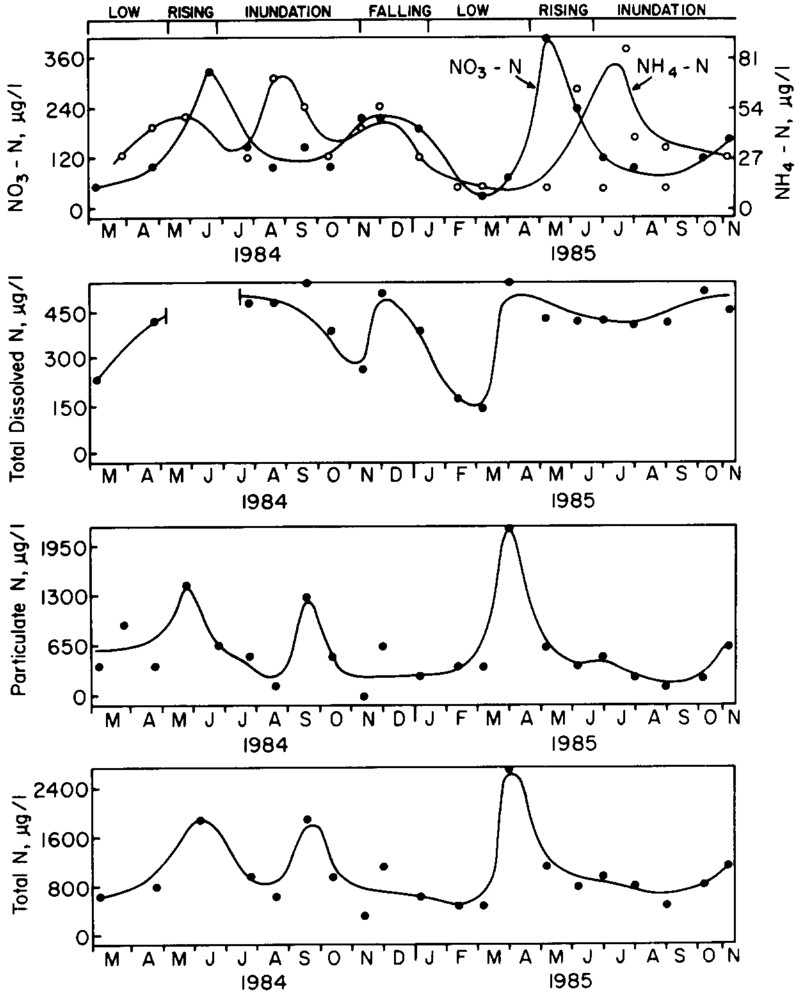

Fig. 4. Concentration vs. time for nitrogen fractions. Gap in panel 2 due to missing data Smooth curves fit by eye.

phorus concentration closely resembled that of its primary constituent, particulate phosphorus.

Ammonia concentrations were low throughout the study (Fig. 4). The pattern, although irregular, suggests minimum concentration at low water and maximum concentration at high water. Nitrate, which was the dominant fraction of inorganic nitrogen, showed a bimodal pattern with peaks at the beginning and at the end of the inundation phase. Concentrations of total dissolved nitrogen were lowest during the low-water phase. The concentration of particulate nitrogen, like that of particulate phosphorus, was highest during rising water, and especially at the beginning of that phase, probably because of the flushing of side channels and low-lying pools as the river began to rise. The pattern for total nitrogen was driven almost entirely by the particulate fraction.

A simple dilution effect appeared to regulate the concentration of dissolved inorganic carbon in the Apure River; minima occurred at high water (Fig. 5). In contrast, dissolved organic carbon showed a purging effect leading to maxima at high water. Particulate carbon followed a pattern similar to that of particulate nitrogen. The bimodal pattern, like that observed for particulate phosphorus, suggests storage of particulate material at highest water levels. Total organic carbon showed mainly a purging effect, which reflects the importance of the soluble fraction, but with superimposed spikes caused by the flushing of particulate carbon from low-lying water bodies at the beginning of the rising-water phase.

A statistical comparison of temporal trends for the various chemical fractions showed the expected significant correlations involving overlapping fractions such as particulate and total, or dissolved inorganic and total dissolved (Table 2). In addition, however, the analysis showed strong correlations between phosphorus fractions and dissolved carbon fractions. The dissolved fractions of both elements are strongly related to discharge. In fact, the strong associations between dissolved phosphorus and dissolved carbon fractions disappear when the effect of discharge is controlled by partial correlation analysis, and the relationship between particulate P and DIC is weakened substantially with control for discharge. Thus there is no evidence for causal connection between P and C in the Apure River.

Seasonal chemical patterns can be summarized from a hydrologic perspective. With the onset of the rainy season, the river rises, flushing sluggish side channels and low-lying pools, and producing a sharp rise in the levels of total particulates, including particulate C and N associated with organic matter. Particulate P is also affected by rising water, but high concentrations persist as the water level continues to rise during the inundation phase, whereas the concentrations of particulate C and N fall. Particulate P is

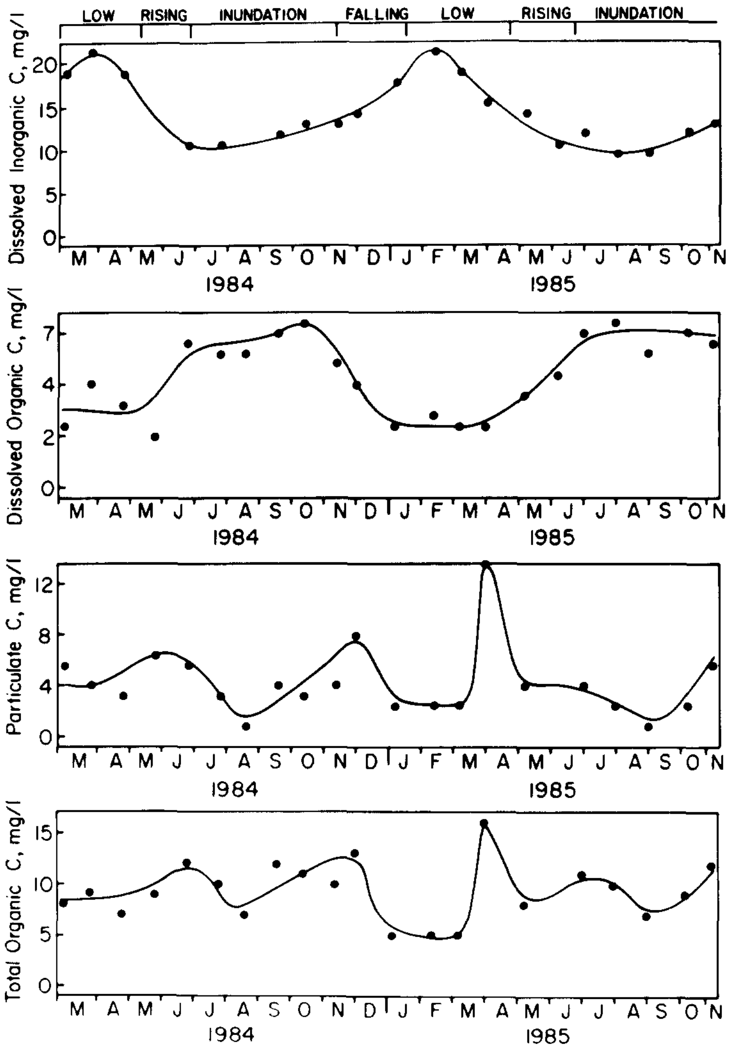

Fig. 5. Concentration vs. time for carbon fractions. Smooth curves fit by eye.

associated primarily with suspended mineral matter and secondarily with organic matter, but particulate C and N are associated almost exclusively with organic matter. Statistical analysis supports the view that particulate C and N are transported together and apart from particulate P (Table 2). Moreover, the strength of the relationship between particulate C and particulate N is not reduced by controlling for the influence of discharge or total particulates.

All of the dissolved components except inorganic C increase in concentra-

Table 2. Pearson product-moment correlations among chemical fractions and discharge, and for transport with discharge and total particulates following logarithmic transformation of all variables. Coefficients are shown for pairs with $p \leqslant 0.05$ and $p \leqslant 0.01(*)$.

Concentration														Transport	
	SRP	TDP	PP	TP	NH_4	NO_3	TDN	PN	TN	DIC	DOC	PC	TOC	Partic	Discharge	Partic
Discharge	0.72*	0.82*	NS	0.52	0.50	NS	0.63*	NS	NS	−0.92*	0.84*	NS	0.49	NS	—	NS
Soluble reactive P		0.78*	NS	NS	NS	NS	NS	NS	NS	−0.68*	0.74*	NS	NS	NS	0.99*	NS
Total dissolved P			NS	NS	NS	NS	0.55	NS	NS	−0.80*	0.77*	−0.46	NS	NS	0.99*	NS
Particulate P				0.98*	NS	NS	NS	NS	0.47	−0.59*	NS	NS	0.56	0.75*	0.93*	NS
Total P					NS	NS	NS	NS	NS	−0.68*	NS	NS	0.61*	0.70*	0.97*	NS
NH_4-N						NS	0.52	NS	NS	NS	NS	NS	NS	NS	0.94*	NS
NO_3-N							0.62*	NS	NS	NS	NS	NS	NS	NS	0.87*	NS
Total dissolved N								NS	0.61*	−0.61*	0.53	NS	0.61*	NS	0.98*	NS
Particulate N									0.92*	NS	NS	0.72*	0.48	0.48	0.74*	0.46
Total N										NS	NS	0.63*	0.68*	0.59*	0.92*	NS
Dissolved inorganic C											−0.80*	NS	−0.54	NS	0.99*	NS
Dissolved organic C												NS	0.44	NS	0.99*	NS
Particulate C													0.67*	0.59*	0.85*	0.64
Total organic C														0.50	0.98*	NS

tion over the rising-water phase. During the inundation phase, the concentration of nitrate declines while concentrations of dissolved organic C and N continue to rise. Hamilton & Lewis (1987) found that nitrate disappeared rapidly as waters of the lower Orinoco entered the floodplain, probably because of biological transformations, which would occur on the Apure floodplain as well. At high water, the flooded internal delta appears to act as a sediment trap. Sediments are mobilized again as the water level falls when there are brief rises in particulate C and, to a lesser extent, particulate N. Stored sediments may also be remobilized during the next rising-water phase. During the low-water phase, all fractions of N, P, and C reach minima except dissolved inorganic C.

Relationship between concentration and discharge

The relationship between concentration and discharge was found to be nonlinear by inspection and by statistical analysis for all fractions of C, N, and P. The data were analyzed for relationships based on concentration versus the logarithm of discharge, the logarithm of concentration versus logarithm of discharge, and concentration versus a hyperbolic function of discharge. The log–log relationship provided the best fit for TDN. For the other chemical variables, their relationships cannot truly be distinguished from each other. Further analysis focused primarily on the hyperbolic model, which was developed by Johnson et al. (1969, see also Hall 1970) to represent concentration as the mixing of base flow with storm flow.

According to the hyperbolic model, the mixed concentration, C, is defined as:

$$C = (C_0V_0 + C_\alpha V_\alpha)/(V_0 + V_\alpha)$$

where V_0 is the initial volume, V_α is the added volume, and C_0 and C_α are the corresponding concentrations (Lesack et al. 1984). Added volume is proportional to discharge (Q): $V_\alpha = rQ$, where r is the residence time of water in the system. By substituting S for $C_0 - C_\alpha$ and β for the ratio r/V_0, one obtains:

$$C = (1/(1 + \beta Q))S + C_\alpha$$

Normally, the parameters S and C_α are estimated with a linear regression model after selecting a value for the parameter β. The estimates are improved iteratively by substituting new values for β. We have instead used a nonlinear analysis because all parameters (β, S, C_α) should be estimated

Table 3. Parameter means for a mixing model and standard error (S.E.) for β. Standard error estimates were based on Tukey's Jackknife procedure. R^2 was derived from linear model (see text).

Variable	C_0–C_x	C_x	β	S.E. of β	R^2
SRP	−36.9	60.6	4.72×10^{-4}	6.00×10^{-4}	0.554
TDP	−49.7	83.1	4.48×10^{-4}	5.68×10^{-4}	0.631
DIC	20.0	9.8	38.28×10^{-4}	22.80×10^{-4}	0.897
DOC	−10.6	13.3	1.80×10^{-4}	2.10×10^{-4}	0.803

simultaneously and because nonlinear analysis facilitates use of the Jackknife procedure described below. After the parameters were estimated, β was fixed and the level of significance was approximated with a linear regression model.

Relationships between concentration and discharge are significant for four fractions (Table 3). Concentrations of the two fractions of dissolved P, which were strongly correlated with one another, increased with discharge. The two fractions of dissolved carbon also showed a significant relationship to discharge. Dissolved organic C concentration increased with discharge (purging effect), whereas dissolved inorganic C concentration decreased with increasing discharge (dilution effect). For all four fractions, Tukey's Jackknife procedure (Sokal & Rohlf 1981) was employed to determine standard errors for the parameter β (Table 3). Confidence intervals are quite broad for the estimates of β (the 95% confidence interval can be approximated from Table 3 as twice the S.E.).

No significant relationships were found between concentration and discharge for any particulate fraction because the flushing and storage mechanisms affecting these fractions occurred within specific hydrologic phases, rather than as a smooth function of discharge. No significant relationships were found for any nitrogen fraction. For nitrate, and thus for TDN, of which nitrate is a major component, poor conformance to standard models is explained by association of key mechanisms (e.g. uptake) with specific hydrologic phases. Particulate components and nitrate in this sense violate the continuity assumptions implicit in the standard models.

Seasonal patterns of transport

A statistically significant relationship existed between discharge (Q) and the transport (T) of each of the elemental fractions when a power curve was used ($T = aQ^b$; Table 2). Both variables were log-transformed so that a linear regression model could be used. In most instances, more than 80% of the variance in log transport is explained by log discharge. Discharge is thus a good predictor of transport. Of greatest interest are those variables for which the least variance is explained. These relationships, which include nitrate (complex relationship to discharge), and particulate N and C (pronounced flushing effect limited to the early rising-water phase) confirm that inundation of the floodplain exerts a strong influence on the behavior of certain constituents.

Discussion

The parameters in the hyperbolic mixing model characterize features of a watershed that are typically considered constant. Previous studies have reported considerable variability among solutes in estimates of β, but have established no basis for interpreting the observed variability. In the Hubbard Brook watershed, Johnson et al. (1969) found differences in β associated with the relationship between C_0 and C_α. β converged on 10^{-4} where $C_0 > C_\alpha$ (dilution effect) and on 10^{-5} where $C_0 < C_\alpha$ (purging effect). In the Gambia, Lesack et al. (1984) found that, for solute concentrations governed by dilution effects, β varied over an order of magnitude. In neither case, however, were confidence intervals reported for the estimates of β. If we apply the Jackknife procedure to the Gambia data to estimate the variance in β for TDP, the resulting 95% confidence interval encompasses 5 of the other 6 estimates of β reported by Lesack et al. (1984). This illustrates the need to establish a perspective on variability. There is too much uncertainty in the estimates of β from our study to attribute differences in β to differences in chemical control processes, although this is clearly a desirable objective (cf. Johnson et al. 1969).

A comparison with other tropical rivers shows that the Apure River exhibits some unusual features in its temporal patterns of concentration. The Caura River in Venezuela, which is also a major tributary to the Orinoco River, differs substantially from the Apure in terms of geology, vegetation, and the amount of runoff (Lewis 1986; Lewis et al. 1986). The Gambia River of West Africa drains a savanna and thus more closely resembles the Apure watershed (Lesack et al. 1984). Mean runoff as a percent of mean precipitation is also quite similar for the Apure (24%) and the Gambia (21%). The Gambia was studied in a year that was drier than average, however (Lesack et al. 1984). In all three rivers, rising water flushes particulate matter and increases concentrations of particulate P. Flushing is not a major mechanism for the transport of particulate N and C in the Caura, but concentrations of particulate N and C rise due to flushing in the Apure and, to a lesser extent, in the Gambia. Variations among the rivers in the transport of particulate organic matter containing N and C depend mainly on the seasonality of the environment and the nature of the floodplain. Seasonal environments that prevail along the Gambia and the Apure accumulate litter during the dry season that can be washed out with the advent of the wet season. Tropical forests like those of the Caura basin are much less seasonal in this respect. The Caura and the Gambia have narrow, fringing floodplains, in contrast to the broad internal delta of the Apure. The seasonal storage of sediments in such a large floodplain may explain the greater range in concentrations of particulate fractions in the Apure.

Dissolved phosphorus rises with increasing discharge in the Apure and the Gambia, but no pattern is apparent in the Caura. Total soluble P in the Gambia seems to increase consistently with discharge, as it also does in the Apure. Dissolved nitrogen tends to increase during the rising-water phase in all three rivers, but the relationships between concentration and discharge do not conform to standard models. Dissolved organic C changes relatively little while water rises in the Caura or the Gambia, but increases in the Apure. During the inundation phase, concentrations of most fractions decline in the Apure, but not in the Caura or the Gambia. As water levels recede in the rivers (late inundation phase and falling-water phase), the most conspicuous changes occur in the Apure, where concentrations of particulate fractions and some dissolved inorganic fractions rise. In the Gambia, the concentration of dissolved organic C rises only as the river falls (counterclockwise hysteresis effect), which Lesack et al. (1984) attribute to bank-storage water that drains into the river.

That there is so little uniformity among the rivers in patterns of concentration underscores the importance of contact between river and floodplain. The Apure and Gambia are remarkably similar in terms of climate, vegetation, and basin morphology, but differ sharply with respect to floodplain type. Although the period of inundation is of comparable duration for the two rivers, a much greater volume of Apure water is in prolonged contact

Table 4. Nutrient yields ($kg \cdot ha^{-1} \cdot year^{-1}$) and runoff (mm/year) from three tropical watersheds.

	Carbon	Nitrogen	Phosphorus	Runoff	Source
Apure	35.4	3.45	0.678	361	This study
Caura	123	9.98	0.461	2423	Lewis et al. 1986; Lewis 1986
Gambia	3.83	1.26	0.077	110	Lesack et al. 1984
Global average	72	3.10	1.85	370	Schlesinger & Melack 1981; Meybeck 1982
Tropical forest	50	—	—	—	Schlesinger & Melack 1981
Tropical grassland	10	—	—	—	Schlesinger & Melack 1981

Table 5. Molar C:N:P ratios from selected sources.

	C:N:P	Source
River ratios		
Apure	135:11:1	This study
Caura	772:47:1	Lewis 1986 and unpubl. data
Gambia	128:36:1	Lesack et al. 1984
Biomass ratios		
Protoplasm (Redfield)	106:16:1	Redfield 1958
Land plants	2041:17:1	Likens et al. 1981
Tropical humid forest litterfall	2545:58:1	Cuevas & Medina 1986 (average of 15 sites)
Tropical savanna forest leaves	772:39:1	Hase & Folster 1982
Tropical savanna grass (*Paspalum fasciculatum*)	1157:23:1	Howard-Williams & Junk 1977

with its floodplain than is the case for the Gambia. When the Apure River inundates its floodplain, a vast body of standing water is created that serves as a trap for sediments, and in which biological activity is pronounced.

The three rivers also differ with respect to the magnitude of transport (Table 4) and the relative abundance of C, N, and P (Table 5). Carbon yield from the Apure watershed is higher than expected for tropical grasslands, but it agrees closely with predictions based on empirical relationships between carbon yield and water yield, and between carbon yield and watershed area (Schlesinger & Melack 1981). The explanation for this apparent discrepancy is not clear. Since so few data are available for carbon yield from tropical grasslands, it is difficult to place the Apure in perspective with regard to watershed area or water yield. Furthermore, the Apure watershed may be unusual among tropical grasslands because such a large area is subject to seasonal inundation. The prolonged contact between the floodplain and the river may augment carbon yield either by increased leaching or by enhanced aquatic productivity. Yield from the Gambia, although low, is probably more typical of tropical savannas. Carbon yield for the Caura is high, even among tropical rain forests, and far exceeds that of the Apure.

The annual yield of phosphorus from the Apure River is below the global average reported by Meybeck (1982), but is probably high in comparison to many watersheds (Table 4). Phosphorus is not strongly retained in the Apure watershed. The high load of suspended matter contributes greatly to phosphorus transport (68%). Nitrogen yield from the Apure watershed is much lower than the yield from the forested watershed of the Caura River.

Molar ratios of the transported elements reveal differences among the rivers in source materials (Table 5). Carbon:phosphorus ratios are similar in the two savanna rivers and resemble the Redfield ratio, but the similarity may be misleading because much of the phosphorus is associated with inorganic material. The C:P ratio for transport in the Caura River is lower than would be expected for litterfall in tropical humid forests (Table 5), but comparable to that of leaf material (see also Likens et al. 1981). The C:N ratios for the Apure (12:1) and the Caura (16:1) are similar to one another and are much higher than the ratio in the Gambia (4:1). At the same time, the C:N ratios for particulate fractions in all three rivers are nearly the same (8–9:1). We interpret this as evidence that the particulate organic material carried in these rivers is quite similar in composition despite major differences in vegetation. The C:N ratio for particulates in the Caura is surprisingly low in view of ratios reported for tropical humid forest litterfall, and the same ratio in the Apure is quite low compared to the composition of the dominant grass in most of the savanna (Table 5). Both ratios are, nevertheless, quite similar to that reported for fine ($< 63\,\mu$m) particulate matter in the Amazon (11:1; Hedges et al. 1986).

The areal extent of seasonal inundation appears to enhance nutrient yield from the Apure, especially in the particulate organic fractions, in a manner that would not be expected in grassland watersheds with only a fringing floodplain. The creation of a shallow lake over a large area of the watershed stores sediments seasonally and is likely to stimulate fixation of C and N from the atmosphere. Sediment storage also derives temporal patterns for nutrient concentrations in the river by uncoupling discharge and sediment concentration during inundation. The resulting bimodal pattern of concentration over time may be peculiar to rivers with large, undistrubed floodplains.

Acknowledgements

This work is a contribution to a collaborative Venezuelan-North American ecological investigation of the Orinoco River. Logistical support was provided by the Venezuelan Ministerio del Ambiente y de los Recursos Naturales Renovables and funding was provided by the US National Science Foundation (Grants DEB 8116725, BSR 8315410.

We thank Michael Grant for statistical advice and Stephen Hamilton for helpful comments on the manuscript. L. Lesack, J. Melack, D.W. Kinsey, and one anonymous reviewer provided numerous constructive criticisms of the original manuscript.

References

Bendschneider, K. & R.J. Robinson (1952) A new spectrophotometric method for the determination of nitrate in sea water. J. Mar. Res. 11: 87–96

Cuevas, E. & E. Medina (1986) Nutrient dynamics within amazonian forest ecosystems. I. Nutrient flux in the litter fall and efficiency of nutrient utilization. Oecol. 68: 466–472

Ewel, J.J., A. Madriz & J.A. Tosi, Jr. (1976) Zonas de Vida de Venezuela. Sucre, Caracas.

Grasshoff, K. 1976. Methods of Sea Water Analysis. Verlag Chemie, Weinheim

Hall, F.R. (1970) Dissolved solids-discharge relationships. 1. Mixing Models. Water Resources Res. 6: 845–850

Hamilton, S.K. & W.M. Lewis, Jr. (1987) Chemistry and nutrient mass balance of a floodplain lake on the Orinoco River floodplain, Venezuela. Limnol. Oceanogr. 32: 1277–1290

Hase, H. & H. Folster (1982) Bioelement inventory of a tropical (semi-) evergreen seasonal forest on eutrophic alluvial soils, western Llanos, Venezuela. Acta Oecol./Oecol. Plant. 3: 331–346

Hedges, J.I., W.A. Clark, P.D. Quay, J.E. Richey, A.H. Devol & U. de M. Santos (1986) Compositions and fluxes of particulate organic material in the Amazon River. Limnol. Oceanogr. 31: 717–738

Howard-Williams, C. & W.J. Junk (1977) The chemical composition of Central Amazonian aquatic macrophytes with special reference to their role in the ecosystem. Arch. Hydrobiol. 79: 446–464

Johnson, N.M., G.E. Likens, F.H. Bormann, D.W. Fisher & R.S. Pierce (1969) A working model for the variation in streamwater chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources Res. 5: 1353–1363

Jordan, C.F. (1985) Nutrient Cycling in Tropical Forest Ecosystems. Wiley, New York

Lesack, L.R., R.E. Hecky & J.M. Melack (1984) Transport of carbon, nitrogen, phosphorus, and major solutes in the Gambia River, West Africa. Limnol. Oceanogr. 29: 816–830

Levine, S.N. & D.W. Schindler (1980) Radiochemical analysis of orthophosphate concentration and seasonal changes in the flux of orthophosphate to seston in Canadian Shield lakes. Can. J. Fish. Aquat. Sci. 37: 479–487

Lewis, W.M., Jr. (1986) Nitrogen and phosphorus runoff losses from a nutrient-poor tropical moist forest. Ecol. 67: 1275–1282

Lewis, W.M., Jr. (1987) Tropical Limnology. Ann. Rev. Ecol. Syst. 18: 159–184

Lewis, W.M. Jr., J.F. Saunders III, F.H. Weibezahn, & S.N. Levine (1986) Organic carbon in the Caura River, Venezuela. Limnol. Oceanogr. 31: 653–656

Likens, G.E., F.H. Bormann & N.M. Johnson (1981) Interactions between major biogeochemical cycles in terrestrial ecosystems. In: G.E. Likens (Ed) Some Perspectives of the Major Biogeochemical Cycles pp. 93–112. Scope 17. Wiley, New York

MARNR. (1983) Venezuela en Mapas. Ministerio del Ambiente y de los Recursos Naturales Renovables. Caracas

Martins, O. (1982) Geochemistry of the Niger River. In: E.T. Degens (Ed) Transport of Carbon and Minerals in Major World Rivers. Part I. Mitt. Geol.-Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderbd. 52: 397–418

Meade, R.H., C.F. Nordin, Jr., D. Perez Hernandez, A. Mejia & J.M. Perez Godoy (1983) Sediment and water discharge in Rio Orinoco, Venezuela and Colombia. In: Proc. Second Internat. Symposium on River Sedimentation, 11–16 October, 1983, Nanjing, China (pp. 1134–1144). Water Resources and Electric Power Press, Beijing

Meybeck, M. (1982) Carbon, nitrogen, and phosphorus transport by world rivers. Amer. Jour. Sci. 282: 401–450

Murphy, J. & J.P. Riley (1962) A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27: 31–36

Nordin, C.F., Jr. & J.V. Skinner (1977) Sediment sampling equipment for deep fast currents. Proc. Internat. Assoc. Hydraul. Res. 6: 606–609

Nordin, C.F., Jr., C.C. Cranston & A. Mejia. (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

Ramia, M. (1967) Tipos de sabanas en los Llanos de Venezuela. Bol. Soc. Venezolana Cien. Nat. 112: 262–288

Redfield, A.C. (1958) The biological control of chemical factors in the environment. Am. Scientist 46: 205–221

Richey, J.E., E. Salati & V. Dos Santos (1985) Biochemistry of the Amazon River: an update. In: E.T. Degens & S. Kempe (Eds), Transport of Carbon and Minerals in Major World Rivers. Part 3. Mitt. Geol. Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderbd. 58: 245–257

Rigler, F.H. (1968) Further observations inconsistent with the hypothesis that the molybdenum blue method measures orthophosphate in lake water. Limnol. Oceanogr. 13: 7–13

San Jose, J.J., R. Montes, J. Garcia-Miragaya & B.E. Orihuela (1985) Bioproduction of trachypogon savannas in a latitudinal cross-section of the Orinoco Llanos, Venezuela. Acta Oecol./Oecol. Gener. 67: 25–43

Schlesinger, W.H. & J.M. Melack (1981) Transport of organic carbon in world's rivers. Tellus 33: 172–187

Sheldon, R.W. (1972) Size separations of marine seston by membrane and glass-fiber filters. Limnol. Oceanogr. 17: 494–498

Sokal, R.R. & R.J. Rohlf (1981) Biometry, second ed. Freeman, San Francisco

Solorzano, L. & J. Sharp (1980a) Determination of total dissolved phosphorus and particulate phosphorus in natural waters. Limnol. Oceanogr. 25: 754–758

Solorzano, L. & J. Sharp (1980b) Determination of total dissolved nitrogen in natural waters. Limnol. Oceanogr. 25: 751–754

Stevens, H.H., Jr., G.A. Lutz & D.W. Hubbell (1980) Collapsible-bag suspended-sediment sampler. American Society of Civil Engineers Proceedings 106: 611–616

Stumm, W. & J.J. Morgan (1981) Aquatic Chemistry, second ed. Wiley, New York

Welcomme, R. (1979) Fisheries Ecology of Floodplain Rivers. Longman, London

Wood, E.D., F.A.J. Armstrong & F.A. Richards (1967) Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Assoc. UK 47: 23–31

Zinck, A. (1977) Rios de Venezuela. Cuadernos Lagoven. Caracas