Arch. Hydrobiol.	91	4	521—528	Stuttgart, Juli 1981

The chemistry and phytoplankton of the Orinoco and Caroni Rivers, Venezuela

By WILLIAM M. LEWIS, Jr. and FRANZ WEIBEZAHN

With 2 figures and 4 tables in the text

Abstract

Chemical and microscopic studies were made of fresh samples from the Orinoco River at Ciudad Bolivar and the Caroni River at Puerto Ordaz, Venezuela. The Orinoco River was slightly acidic (pH 6.8), of low ionic content (25 μmho/cm), showed relative cation abundances by weight of $Ca^{++} > Na^{+} > K^{+} > Mg^{++}$ and relative anion abundances of $HCO_3^{-} > SO_4^{=} > Cl^{-}$. The Caroni is more acidic (pH 6.2), has much lower ionic content (8 μmho/cm) and has greater relative amounts of sodium and chloride ($Na^{+} > Ca^{++} > K^{+} > Mg^{++}$; $HCO_3^{-} > Cl^{-} > SO_4^{=}$). Phosphorus in all forms was present in very small amounts in both rivers and particulates were very poor in nitrogen (< 0.1 %). Both rivers contained unexpectedly high amounts of nitrate (> 100 μg/l NO_3-N). The Orinoco was much more heavily laden with particulates, of which 95 % by weight was clastic material. The Caroni water contained much smaller amounts of particulate material and a lower proportion of clastics (79 %). In both rivers the particle sizes are small (90 % < 20 μm) and living organisms are extremely rare.

Introduction

The chemistry of the major tropical rivers of the world is of interest as an indication of the chemical mass balance of tropical regions, but is still very poorly documented (MEYBECK, 1976). As the watersheds of many of these rivers, including the Orinoco, are changing very rapidly (National Research Council, 1980 a) and impoundments are being added to the main river stems, it will soon become impossible to deduce what the original chemical composition of these rivers must have been prior to disturbance (National Research Council, 1980 b). In many cases, as with the Orinoco, government studies and various other kinds of work have established the total solids content, but other information of interest from a biological viewpoint, including ionic composition, dissolved organic carbon, nitrogen and phosphorus fractions, and particulate carbon load are much less frequently documented (cf. RICHEY et al., 1980). Because of the lability of some of the chemical species of greatest interest, it is only

0003-9136/81/0091-0521 $ 2.00

possible to obtain information about them from fresh samples, but analyses of fresh samples are virtually unavailable. Also, the suspended biota of these large rivers is poorly known. Our objective here is to provide chemical information on fresh samples from the Orinoco system with particular attention to nitrogen, phosphorus, and carbon fractions, and to present some quantitative information on the plankton.

Methods and Sampling Locations

Our samples were taken in two locations: (1) Ciudad Bolivar, on the main stem of the Orinoco above its confluence with the Caroni River, and (2) at Puerto Ordaz, on the lowermost part of the Caroni River. The locations are shown in Fig. 1. The samples were taken on 6 May 1979. This is the time of transition from periods of low to high flow on the Orinoco (Fig. 2) and represents a good choice for a single sampling date because it is a time of median total electrolyte content as indicated by the annual data on electrical conductance published by GESSNER (1965) for Ciudad Bolivar.

The samples were collected in large, clean plastic bottles. Duplicate bottles were collected at each site and the analyses showed negligible difference between these duplicate samples. A 100 ml subsample was preserved with Lugol's solution. The samples were stored in the dark at ambient temperature; analysis was complete by 12 May 1979. In view of the very low biological activity of the samples, and the relatively low pH, the results are assumed to typify river water in situ at the time of sampling.

The particulate and soluble fractions were separated by use of a Whatman GF/C glass fiber paper (effective pore size, ca. 2 μm). Analysis of dissolved constituents was conducted on the filtrate. Particulates remaining on the filter were weighed and analyzed for C, H, N, and P.

In the filtrate, the major cations were analyzed with an atomic absorption spectrophotometer. Lanthanum was added to suppress interference in calcium determinations. Soluble reactive phosphorous, which we shall refer to loosely as orthophosphate, was done by a molybdate method (MURPHY & RILEY, 1962), nitrate was done by cadmium-copper reduction and spectrophotometric determination of the resulting nitrite (WOOD et al., 1967), and ammonia was done by a modified Solorzano method (KOROLEFF, 1976). Silicate was done by a molybdate method (ARMSTRONG & BUTLER, 1962) on an unfiltered portion of the sample. The pH was determined with a pH meter calibrated against buffers of pH 6 and pH 8. Bicarbonate was determined by electrometric titration to pH 4.4. Dissolved organic carbon was determined from the absorbance at 360 nanometers using the equation of LEWIS & CANFIELD (1977). This method has been validated specifically for waters in the Orinoco drainage by infrared gas analysis (LEWIS & CANFIELD, 1977). Dissolved organic nitrogen and dissolved organic phosphorus were determined by ultraviolet combustion using the method of MANNY et al. (1971) followed by reanalysis of the inorganic constituents. Sulfate was analyzed by the barium precipitation method (GOLTERMAN, 1969) and chloride was analyzed by the mercuric thiocyanate method (ANONYMOUS, 1979). Since these two anions were present in relatively small amounts compared to the sensitivity of the tests, samples were first concentrated five-fold in a rotary evaporator at a temperature of 60 °C.

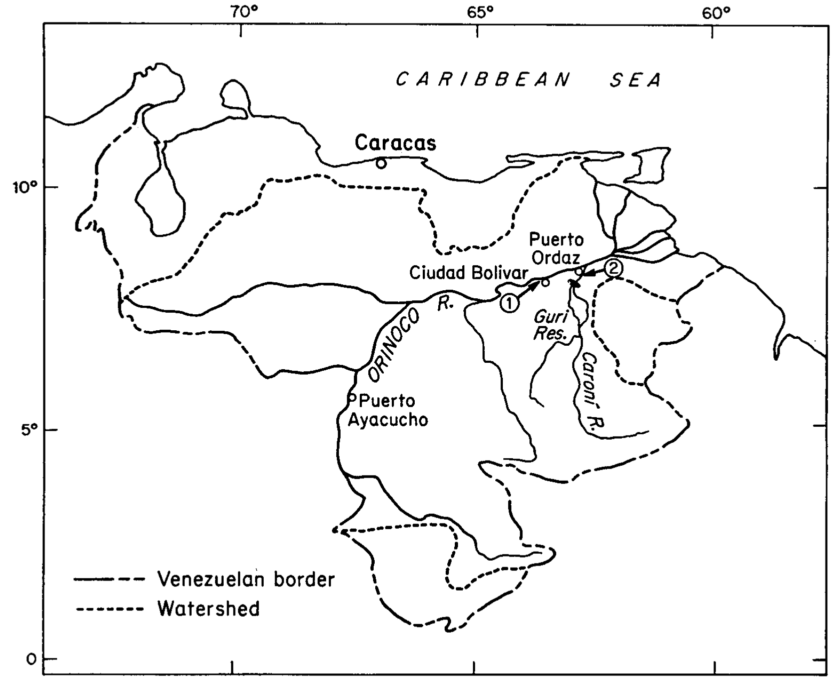

Fig. 1. The Venezuelan Orinoco, showing the sampling sites.

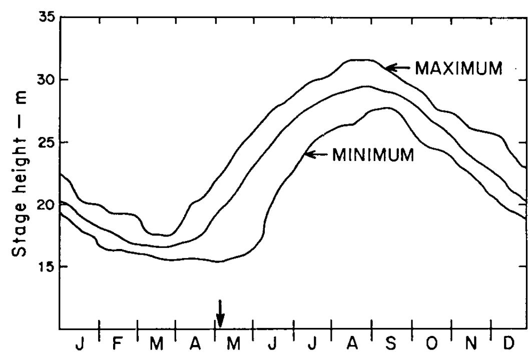

Fig. 2. The cycle of the Orinoco at Ciudad Bolivar, from government records as reported by ZINCK (1977).

The particulate component was analyzed for carbon, hydrogen, and nitrogen by use of a Carlo Erba CHN analyzer. Percent phosphorus was determined by the digestion of particulate material in sulfuric acid and selenium under heat. Recovery as indicated by an orchard leaf standard for this method was over 90 %.

Examination for plankton was made at various magnifications up to 1400× by use of an inverted microscope.

Results

Table 1 gives the pH and major ion composition of the water in the two samples. As these are the main ionic constituents and the main determinants of electrical conductance, a theoretical conductance and a charge balance were computed from the data in Table 1. Cations for the Orinoco sample total 0.242 meq/l, and for the Caroni River the total is 0.101 meq/l. For anions, the corresponding figures are 0.226 meq/l and 0.107 meq/l. The theoretical conductance of the Orinoco sample as computed from the mobilities, sizes, and concentrations of the ions in the sample as determined by the analysis is 25 μmho per centimeter (25 °C) for the Orinoco sample and 11 μmho per centimeter for the Caroni sample. The ion balances match well and the computed conductances correspond very closely with the measured conductances indicated in Table 1, thus indicating good analytical consistency.

Table 2 gives nitrogen and phosphorus fractions plus silicate and dissolved organic carbon. Table 3 shows the total particulates and the phosphorus, carbon, and nitrogen components of the particulates.

Table 1. Major electrolytes of the samples. All concentrations are mg/l.

	pH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	$SO_4^{=}$	Cl^{1-}	HCO_3^{-}	conductances µmho/cm at 25 °C
Orinoco	6.80	2.28	0.64	1.34	0.75	1.3	0.8	10.4	25
Caroni	6.20	0.57	0.30	0.89	0.41	0.2	0.8	4.6	8

Table 2. Soluble nitrogen and phosphorus fractions of the samples, plus dissolved organic carbon and silicate.

	PO_4-P µg/l	NO_3-N µg/l	NO_2-N µg/l	NH_4-N µg/l	DOP µg/l	DON µg/l	DOC mg/l	SiO_2 mg/l
Orinoco	7.02	122	0.0	0.9	19.0	57	6.5	2.33
Caroni	3.94	107	0.0	19.9	3.9	21	5.8	2.03

Table 3. Information on particulates in the samples.

	Total Particulates mg/l	% P	% C	% N
Orinoco	205	0.06	2.5	<0.1
Caroni	7.2	0.07	10.4	<0.1

Table 4. Abundance of phytoplankton, protozoa, and particles in the samples.

Category	Abundance (number/cm^3)
Caroni	
Autotrophs	
Oscillatoria (small)	60
Oscillatoria (large)	25
Chlorella	130
Monoraphidium	135
Unidentified	175
Heterotrophs (> 1 µm)	
Flagellate 1 (2 µm)	60
Flagellate 2 (4 µm)	175
Large Bacterial Rod (1 × 4 µm)	700
Nonliving particles	
Diatom frustules	350
Total visible particles	147,000
Orinoco	
Autotrophs	< 500
Heterotrophs (> 1 µm)	< 500
Nonliving particles	
Diatom frustules	3,500
Total visible particles	1,300,000

An extensive examination was made of the sedimented phytoplankton samples from the Orinoco and Caroni Rivers. The examination on highest power, which is typically required for identification of tropical phytoplankton organisms (Lewis, 1978), showed few living phytoplankton cells (Table 4). Examination of larger amounts of water at lower powers revealed some empty diatom frustules at low concentrations. In the Caroni sample, visible bacterial cells were principally attached to particles rather than free-living. In the Orinoco sample, much larger numbers of unattached bacteria were observed.

Discussion

We conclude from the microscope work that the Orinoco mainstream and the Caroni at the time of year the samples were taken have only very small populations of phytoplankton and small protozoans. At least below the size of 100 μm, the biota is for practical purposes limited to bacterial cells. There are several possible reasons for failure of algae and protozoa to grow well in these waters. The transit time of particles within the Orinoco system is sufficiently long that, if growth conditions were good, substantial populations of plankton should be possible despite the continuous movement downstream, especially in view of potential seeding from backwaters. Although the waters are quite poor in electrolytes, potentially limiting nutrients (N, P) are present in amounts sufficient to support substantial algal growth, so suppression of growth by nutritional inadequacy of the water seems unlikely. The high content of organic matter of these waters has been noted many times and is evident from the relatively high dissolved organic carbon concentrations shown in Table 2. The strong absorbance of these compounds in the blue and violet indicates that they are humic substances or related compounds that are known to be resistant to biological processing. Because of the large amounts of these substances that are present, it is possible that they have some antibiotic effect on the organisms. The importance of this has been emphasized by JANZEN (1974). The physical environment is also quite unfavorable for autotrophs because of the poor light penetration. The depth at which 1 % light is found in the Orinoco on our sampling date was 0.9 m (550 nm); the Orinoco averages well over 10 m deep throughout the main stem. Under these conditions, it would not be expected that ordinary autotrophs could build up biomass. In the Caroni, 1 % light was found at 2.2 m (550 nm).

The information on major ions is of interest because of the very low concentrations of electrolytes, which is well known from existing data on conductance and total dissolved solids. Also noteworthy is the importance of sodium, especially in the Caroni. Although the chemistry of precipitation has received only limited attention in South America (JORDAN et al., 1979; LEWIS, 1981), it would appear that for both the Orinoco and the Caroni, the concentrations of major ions in river water fall near or even below those expected in precipitation, indicating efficient retention of major ions by terrestrial systems.

Soluble inorganic nitrogen and phosphorus are both present in the samples in amounts well in excess of those expected under nutrient limiting conditions. This is explained by the absence of any substantial biotic component which would generate nitrogen and phosphorus demands. Nitrate is particularly high. Retention of inorganic nitrogen by the terrestrial systems is not nearly so efficient as might be expected.

Nitrogen and phosphorus fractions locked up in dissolved organic material are not as high as would be expected in a freshwater system with high biological activity. Furthermore, the organic nitrogen to organic carbon ratio is suggestive of relatively low proportion of nitrogenous compounds in the dissolved organic matter.

The Caroni and the Orinoco differ markedly in their particulate loads. Weathering in the upper reaches of the Orinoco above the Caroni is responsible for the addition of silt; the Caroni drainage is much more thoroughly weathered. The particulate components of both rivers are remarkably low in phosphorus. In the Caroni, 90 % of the particles are $< 20\,\mu m$ in diameter, and 90 % of particles are of a flocculent organic nature. In the Orinoco, the particle sizes are similar (90 % $< 20\,\mu m$), but about 50 % are non-organic clastic materials.

The carbon percentages in Table 3, which have a standard error of less than 0.3 %, indicate that the particulate dry weight of the Orinoco is about 5 % organic material and 95 % clastic. The Caroni particulates are about 21 % organic by weight and 79 % clastic. These findings are consistent with the microscopic observations if the much greater density of clastics than of flocculent organics is considered.

The very low nitrogen content of the organics is remarkable for both rivers and reinforces the impression of very high C : N ratio in the organic matter of these rivers.

The composite picture of nitrogen and phosphorus in particulate and dissolved form in the two rivers is indicative of very efficient sequestering of phosphorus in all forms and surprising mobility of nitrogen in the form of nitrate. The picture of major ion composition from the data differs considerably from the approximations that have been used for world surveys (LIVINGSTONE, 1963; MEYBECK, 1976). The Orinoco appears to contain considerably less total dissolved solids and to have different ion ratios than indicated by world survey data.

Zusammenfassung

Es wurden chemische und mikroskopische Untersuchungen frischer Proben aus dem Orinocofluß bei Cuidad Bolivar und aus dem Caronifluß bei Puerto Ordaz, Venezuela, entnommen. Der Orinoco war schwach sauer (pH 6,8) und wies niedrigen Ionengehalt (25 μmho/cm) auf. Die relativen Kationmengen waren $Ca^{++} > Na^{+} > K^{+} > Mg^{++}$ und die relativen Anionmengen $HCO_3^- > SO_4^= >$ Cl. Der Caroni war etwas saurer (pH 6,2), wies einen viel niedrigeren Ionengehalt (8 μmho/cm) und viel höhere relative Mengen an Natrium und Chlorid auf ($Na^+ > Ca^{++} > K^+ > Mg^{++}$; $HCO_3^- > Cl^- > SO_4^=$). In beiden Flüssen war Phosphor in allen Formen in sehr kleinen Mengen anwesend, Partikel waren sehr arm an Stickstoff ($<$ 0,1 %). Beide Flüsse enthielten unerwartet hohe Mengen an Nitrat ($>$ 100 μm/l NO_3-N). Viel stärker als der Caronin war der Orinoco mit Partikeln beladen, wovon der Anteil an klastischem Material 95 Gew.-% betrug, im Caroni nur 79 %. In beiden Flüssen handelt es sich um kleine Partikelgrößen (90 % $>$ 20 μm), und lebende Organismen waren äußerst selten.

References

ANONYMUS (1979): Methods for chemical analysis of water and waste. — United States Environmental Protection Agency, Publication PA-600/4-79-020. U.S. Government Printing Office, Washington, D.C.

ARMSTRONG, F. A. J. & BUTLER, E. I. (1962): Chemical changes in the sea water off Plymouth during 1960. — Journal of the Marine Biology Association, United Kingdom. **42:** 253—258.

GESSNER, F. (1965): pH and electrolyte content in the Casiquiare. — Int. Revue ges. Hydrobiol. **55:** 431—434.

JANZEN, D. H. (1974): Tropical blackwater rivers, animals, and mass fruiting by the Dipterocarpaceae. — Biotropica. **6:** 69—103.

JORDAN, C. F., GOLLEY, F. B. & HALL, J. (1980): Nutrient scavenging of rainfall by the canopy of an Amazonian rain forest. — Biotropica **12:** 61—66.

KOROLEFF, F. (1976): Determination of ammonia. — In: K. GRASSHOFF (Ed.), Methods of Seawater Analysis: 126—133. — Verlag Chemie, New York, U.S.A.

LEWIS, W. M., Jr. (1978): A compositional, phytogeographical and elementary structural analysis of the phytoplankton in a tropical lake. — Journal of Ecology. 66: 213—226.

— (1981): Precipitation chemistry and nutrient loading in a tropical watershed. — Water Resources Research **17:** 169—181.

LEWIS, W. M., Jr. & CANFIELD, D. (1977): Dissolved organic carbon in some dark Venezuelan waters and a revised equation for spectrophotometric determination of dissolved organic carbon. — Archiv Hydrobiol. **79:** 441—445.

LIVINGSTONE, D. A. (1963): Chapter G. Chemical Composition of Rivers and Lakes. — Sixth Edition, Data of Geochemistry. Geological Survey Professional Paper 440-G. U.S. Government Printing Ofc., Wash. D.C., U.S.A.

MEYBECK, M. (1976): Total mineral dissolved transport by world major rivers. — Hydrological Sciences Bulletin **21:** 265—284.

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

National Research Council (1980 a): Conversion of tropical moist forests. — National Academy of Sciences (Wash., D.C.): 1—205.

— (1980 b): Research priorities in tropical biology. — National Academy of Sciences (Wash., D.C.): 2—116.

RICHEY, J. E., BROCK, J. T., NAIMAN, R. J., WISSMAR, R. C. & STALLARD, R. F. (1980): Organic carbon: oxidation and transport in the Amazon River. — Science **207:** 1348—1351.

WOOD, E. D., ARMSTRONG, F. A. J. & RICHARDS, F. A. (1967): Determination of nitrate in sea water by cadmium-copper reduction to nitrite. — Journal of the Marine Biology Association of the United Kingdom **47:** 23—31.

ZINCK, A. (1977): Rios de Venezuela. Cromotip Publishers, Caracas, Venezuela.

The addresses of the authors:

Dr. WILLIAM M. LEWIS, Jr., Department of E.P.O. Biology, University of Colorado, Boulder, Colorado 80309.

Prof. FRANZ H. WEIBEZAHN, Laboratorio de Limnologia, Escuela de Biologia, Universidad Central de Venezuela, Caracas, Venezuela.