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

By William M. Lewis, Jr. and Franz Weibezaehn

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 Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ and relative anion abundances of HCO₃⁻ > SO₄²⁻ > 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⁺ > Ca²⁺ > K⁺ > Mg²⁺; HCO₃⁻ > Cl⁻ > SO₄²⁻). 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 NO₃-N). The Orinoco was much more heavily laden with particulates, of which 95% by weight was elastic material. The Caroni water contained much smaller amounts of particulate material and a lower proportion of elastics (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
possible to obtain information about them from fresh samples, but ana-
lyses 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 solu-
tion. 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
Mann 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.
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.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ca^{2+}</th>
<th>Mg^{2+}</th>
<th>Na^{+}</th>
<th>K^{+}</th>
<th>SO_{4}^{2-}</th>
<th>Cl^{-}</th>
<th>HCO_{3}^{-}</th>
<th>conductances μmho/cm at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orinoco</td>
<td>6.80</td>
<td>2.28</td>
<td>0.64</td>
<td>1.34</td>
<td>0.75</td>
<td>1.3</td>
<td>0.8</td>
<td>10.4</td>
<td>25</td>
</tr>
<tr>
<td>Caroni</td>
<td>6.20</td>
<td>0.57</td>
<td>0.30</td>
<td>0.89</td>
<td>0.41</td>
<td>0.2</td>
<td>0.8</td>
<td>4.6</td>
<td>8</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>PO_{4}-P μg/l</th>
<th>NO_{3}-N μg/l</th>
<th>NO_{2}-N μg/l</th>
<th>NH_{4}-N μg/l</th>
<th>DOP μg/l</th>
<th>DON μg/l</th>
<th>DOC mg/l</th>
<th>SiO_{2} mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orinoco</td>
<td>7.02</td>
<td>122</td>
<td>0.0</td>
<td>0.9</td>
<td>19.0</td>
<td>57</td>
<td>6.5</td>
<td>2.33</td>
</tr>
<tr>
<td>Caroni</td>
<td>3.94</td>
<td>107</td>
<td>0.0</td>
<td>19.9</td>
<td>3.9</td>
<td>21</td>
<td>5.8</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Table 3. Information on particulates in the samples.

<table>
<thead>
<tr>
<th></th>
<th>Total Particulates mg/l</th>
<th>% P</th>
<th>% C</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orinoco</td>
<td>205</td>
<td>0.06</td>
<td>2.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Caroni</td>
<td>7.2</td>
<td>0.07</td>
<td>10.4</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
Table 4. Abundance of phytoplankton, protozoa, and particles in the samples.

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

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 Orinocoufluß 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 $\mu$mho/cm) auf. Die relativen Kationenmengen waren Ca$^{++} > Na^+ > K^+ > Mg^{++}$ und die relativen Anionenmengen $HCO_3^- > SO_4^{=+}$. Der Caroni war etwas sauer (pH 6,2), wies einen viel niedrigeren Ionengehalt (8 $\mu$mho/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 erwartet hohe Mengen an Nitrat (> 100 $\mu m/l$ NO$\textsubscript{3}$-N). Viel stärker als der Caroni 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 $\mu m$), und lebende Organismen waren äußerst selten.

References


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