

Time dependency of hydrogen - ion concentration and electric conductivity measurements in river water samples of Central Amazonia⁽¹⁾

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ABSTRACT

The hypothesis was tested, whether hydrogen — ion concentration and electric conductivity in river water samples of the Tertiary region of central Amazonia were subject to changes in time and due to nature of storage. Over a period of about two months only changes in pH and conductivity of Rio Negro water samples were found to be significant. The total deviation of both parameters in rain forest stream samples was considered negligible for at least a period of 30 days, independent of the nature of storage (laboratory or icebox). The latter results may be generalized more or less unconditionally for the entire Tertiary formations of Amazonia.

INTRODUCTION

The hydrogen-ion concentration (pH) in natural waters is controlled by chemical reactions and equilibria among the ions in solution. As far as the water samples studied were concerned, the pH was primarily determined by the chemical nature of the watersheds (substrates, soils, vegetation cover, etc), the chemical reactions under way in the river basins (decomposition — and remineralization processes, release of various acids (sulfuric, organic and carbonic), biological processes (photosynthesis, respiration, etc.) and the current (mixing capacity).

Although the hydrogen — ion concentration in river waters is not a main controlling factor in fresh water ecology (Reid,

1961), it should be recognized, that several water organisms have their specific pH tolerance ranges (Welch, 1952).

The electric conductivity is a measure to evaluate the total amount of ionized material in water solutions. The total amount and the composition of dissolved solids in water control up to a certain extent, the variety and abundance of aquatic organisms. Although no exact relationship exists between electric conductivity and total dissolved solids in natural waters, the parameter (electric conductivity) is often used as a first approximation to determine the influence of total dissolved solids on the aquatic environment.

Hydrogen — ion concentration and electric conductivity in water samples are liable to changes during storage between sampling and laboratory measurements, owing to reactions to suspensions, hydrolyses, oxidation-reduction processes, loss of dissolved gases, etc. If samples are collected and stored with care, the early laboratory measurements are supposed to approximate field conditions. If samples reach the laboratory after a two or three months, the reliability of the data is assumed to be dependant on the delay. This hypothesis was tested for several river water samples of central Amazonia.

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MATERIAL AND METHODS

At June 6 th, 1971 four water samples were collected at Paricatuba, the Rio Negro narrows, at about 15 Km upstream of the city of Manaus. Water was sampled in different depths and positions of the Rio Negro cross — section, as.; midstream (surface), midstream (40 m depth), 300 m off right bank (20 m depth) and 300 m off left bank (20 m depth).

At August 8 th, 1971, water samples from four rain forest streams were collected along the BR-174, the Manaus - Caracarai Road at kilometers 61, 35, 32 and 27. These streams drain watersheds of different sizes, but are undisturbed by human activity (slash and burn, cattle breeding, etc.). The areas are covered with a terra firme rain forest, a climax forest of the chapadas of the Tertiary region in central Amazonia. The forest type is closely related to heavy or extremely heavy yellow latosols. Along the river banks hydromorphic soil is common. Several small patches of tropical podzol soils occur scattered on the hill slopes. These soils are covered with "carasco forests" or campinas.

All water samples were stored in pyrex bottles, handled with care and sent back to the laboratory within six hours.

The Rio Negro samples were stored in the laboratory. The BR-174 samples were divided. One set of samples remained under laboratory conditions, the other set of four samples was stored in an icebox.

The hydrogen — ion concentration was measured with a pH — meter, type 390 WTW, Germany. The electric conductivity was read by means of a conductivity meter, type LBR — WTW, Germany. Hydrogen — ion concentration and electric conductivity were repeatedly measured (average of 5 subsamples) for all three sets of samples concurrently up to September 9 th, 1971.

Changes in pH and conductivity during the time between sampling and first laboratory measurements occurred, but these inter-

ferences were disregarded, because field instruments showed an instrumental error of about 5 - 10 percent in duplicated samples.

The Rio Negro samples (midstream-surface) and all four BR-174 samples were analyzed for various constituents of ecological interest (see Table 1).

Sulphur compounds, organics and bacterial and fungal activity were not evaluated, although they are of considerable importance for changes in pH and electric conductivity of the water samples.

RESULTS

For the period measurements (Rio Negro samples : June 6th. — September 15th, 1971; BR-174 samples : August 8th. — September 15th, 1971), hydrogen-ion concentration and electric conductivity data were calculated as the deviation from the initial laboratory readings (0.1 pH and 0.1 uS₂₀ intervals).

I. The Rio Negro samples.

Hydrogen ion concentration and electric, conductivity data obtained, confirmed the significant fluctuations of both parameters, depending on the sampling position in the river cross-section (see Table 2; Table 3). Concerning chemical interactions in the solution, pH and conductivity data proved the lack of homogeneity of the Rio Negro water body. Compared with other river systems in the world, the data are very low with respect to both parameters. The deviation from the first laboratory reading over the period of measurements was significant for pH (range : pH 0.3 - pH 0.7) and electric conductivity (range 0.7 uS₂₀ - 3.8 uS₂₀) respectively. While the pH data displayed no variation from the first laboratory readings, the electric conductivity data, however, increased (samples 1,3 and 4) and decreased (sample 2) with time.

		Rio Negro (surface)	BR-174 (Km 61)	BR-174 (Km 35)	BR-174 (Km 32)	BR-174 (Km 27)
pH		5.2	4.7	4.5	4.6	4.8
uS ₂₀		9.9	5.5	9.2	6.5	5.5
Ca ⁺⁺	ug/1	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0
Mg ⁺⁺	ug/1	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0
SBV	mval/1	< 0.03	< 0.05	< 0.05	< 0.05	< 0.05
N(NH ₄ ⁺)	ug/1	38.4	44.0	59.8	29.4	23.0
N(NO ₂ ⁻)	ug/1	1.0	2.7	2.4	2.3	3.2
N(NO ₃ ⁻)	ug/1	39.7	26.6	27.9	36.1	21.9
N (org.)	ug/1	200.0	495.0	490.5	359.0	331.5
N (total)	ug/1	238.0	539.3	550.3	388.4	354.5
P (total)	ug/1	3.8	.0	.0	.0	.0
Fe (total)	ug/1	39.2	43.9	216.2	135.2	125.1
Mn	ug/1	—	8.7	8.7	7.7	8.7
Si (sol.)	mg/1	1.6	1.6	2.3	2.2	2.1
Cl ⁻	ug/1	448.0	700.0	700.0	700.0	700.0
Color	mgPt/1	69.4	20.8	55.5	30.8	28.5
KMnO ₄	mg/1	54.9	13.9	21.5	20.5	14.0
CO ₂ ⁽¹⁾	mg/1	—	29.7	25.3	20.6	24.2

TABLE 1 — Chemical constituents of 1) the Rio Negro (surface) sample (June 6, 1971) and 2) the BR-174 river samples (August 8, 1971). (1) samples treated with CHCl₃ (5 ml/1).

II. The BR-174 samples.

For all samples, hydrogen-ion concentration and electric conductivity values were considerably low. The conductivity, readings of samples BR-174 Km 61, Km 32 and Km 27 were extremely low (see Table 2; Table 3); The deviation in pH from the first laboratory measurements (range : pH 0.1 - pH 0.3) was insignificant for all samples and independent of storage (laboratory — icebox). Electric conductivity data showed a slight deviation from the first laboratory readings (range : 0.4 uS₂₀ 2.1 uS₂₀).

In sample BR-174 (Km 35) the conductivity decreased with time. Some differences in total deviation from the first laboratory measurements were reported for BR-174 samples (Km 35; Km 32) as far as storage (laboratory — icebox) was concerned (see Table 3).

CONCLUSIONS

Hydrogen - ion concentration and electric, conductivity data of all samples analyzed were extremely low, if compared with equivalent river systems in the world.

The bicarbonate — carbon dioxide system is effective in the control of the pH of natural waters in about the pH 4.5 to pH 8.0 range (Reid, 1961). Calcium and magnesium ion analyzed were below detection in all water samples (see Table 1), i.e. the solution were poorly buffered (Brinkmann and Santos, 1971).

Hidrolyses, the most important type of reaction controlling pH in natural waters must play a part in fixing the low pH as salts of iron and ammonium were present in the samples analyzed (see Table 1). These salts give an acid reaction upon the hydrogen — ion concentration.

As far as Rio Negro samples were concerned, the so-called humic complex of these

	Rio Negro surface (2)	Rio Negro 40m (3)	Fio Negro 2'm right (4)	Rio Negro 20m left (4)	BR 174 Km 61	BR 174 Km 61 (x)	BR 174 Km 35	BR 174 Km 35 (x)	BR 174 Km 32	BR 174 Km 32 (x)	BR 174 Km 27	BR 174 Km 27 (x)
6.7.71	5.2											
15.7.71	- 0.2											
23.7.71	(—)											
28.7.71	+ 0.1											
2.8.71	+ 0.1											
3.8.71	+ 0.5	4.3	4.3	4.8								
9.8.71	+ 0.5	+ 0.2	+ 0.2	+ 0.2	4.7	4.7	4.5	4.5	4.6	4.6	4.8	4.8
16.8.71	+ 0.5	+ 0.4	+ 0.2	+ 0.2	(—)	+ 0.1	(—)	+ 0.1	+ 0.1	+ 0.1	(—)	(—)
20.8.71	+ 0.4	+ 0.2	(—)	+ 0.1	- 0.2	(—)	- 0.3	- 0.2	- 0.2	(—)	- 0.1	(—)
25.8.71	+ 0.6	+ 0.2	+ 0.2	+ 0.1	+ 0.3	+ 0.3	(—)	+ 0.1	+ 0.1	+ 0.1	(—)	(—)
30.8.71	- 0.3	+ 0.2	+ 0.2	- 0.3	(—)	+ 0.1	+ 0.1	- 0.1	+ 0.1	(—)	+ 0.2	- 0.1
6.9.71	- 0.2	+ 0.7	+ 0.1	- 0.3	(—)	+ 0.3	+ 0.1	+ 0.1	(—)	(—)	(—)	- 0.2
9.9.71	- 0.2	+ 0.7	+ 0.1	- 0.3	+ 0.1	+ 0.2	+ 0.1	(—)	+ 0.1	(—)	(—)	(—)
10.9.71	- 0.2	+ 0.7	+ 0.5	+ 0.1	(—)	- 0.1	+ 0.1	+ 0.1	(—)	+ 0.2	- 0.2	(—)
15.9.71	- 0.3	+ 0.7	+ 0.5	+ 0.2	(—)	(—)	+ 0.1	+ 0.2	+ 0.1	+ 0.2	- 0.1	(—)
(1) total deviation	0.7	0.6	0.4	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1

TABLE 2 — pH deviation from the initial pH measurements with time (in 0.1 pH intervals).

(1) Instrumental and individual error calculated

as ± 0.1 pH.

(2) midstream

(3) midstream, 40 mts depth

(4) 300 mts off banks, 20 mts depth

(x) samples stored in a refrigerator.

(—) no deviation.

	Rio Negro surface (2)	Rio Negro 4cm (3)	Rio Negro 20m right (4)	Rio Negro 20m left (4)	BR 174 Km 61	BR 174 Km 61 (x)	BR 174 Km 35	BR 174 Km 35 (x)	BR 174 Km 32	BR 174 Km 32 (x)	BR 174 Km 27	BR 174 Km 27 (2)
6.7.71	9.9											
15.7.71	-1.6											
23.7.71	-2.1											
28.7.71	-2.4											
2.8.71	-2.4											
3.8.71	-0.1	10.7	10.7	7.1								
9.8.71	-0.3	-0.2	-1.1	+0.7	5.5	5.5	9.2	9.2	6.5	6.5	5.5	5.5
16.8.71	-0.6	-1.0	-1.1	+1.6	(-)	-0.1	-0.2	-0.2	-0.1	(-)	-0.3	+0.5
20.8.71	-0.7	-1.1	-1.1	+1.6	-0.2	-0.3	-0.3	-0.2	-0.4	-0.3	-0.5	(-)
25.8.71	-0.5	-0.8	-1.2	+1.6	(-)	-0.3	-0.4	-0.2	-0.5	(-)	-0.4	(-)
30.8.71	-2.3	-0.4	-1.6	+2.3	-0.1	-0.1	-0.9	-0.4	-0.6	+0.1	-0.2	+0.3
6.9.71	-2.6	-0.5	-2.4	+1.3	-0.3	-0.3	-0.9	-0.8	-0.4	+0.3	-0.6	-0.3
9.9.71	-2.6	-0.4	-1.6	+2.1	-0.6	-1.1	-1.6	-1.1	-0.8	-0.5	-1.0	-0.8
10.9.71	-3.3	-0.3	-2.4	+1.2	-0.2	-0.2	-1.6	-1.3	-1.2	-0.5	-1.1	+0.3
15.9.71	-3.9	+0.2	-2.2	+1.3	-0.3	+0.3	-2.2	-1.2	-1.3	-0.5	-0.3	+0.4
(1) total deviation	3.8	0.7	2.3	2.2	0.5	0.4	2.1	1.2	1.2	0.6	1.0	1.1

TABLE 3 — Electric conductivity deviation from the initial conductivity measurements with time (in 0.1 μS_{20} intervals)

(1) Instrumental and individual error calculated

as $\pm 0.1 \mu\text{S}_{20}$.

(2) midstream

(3) midstream, 40 mts depth

(4) 300 mts off banks, 20 mts depth

(x) samples stored in a refrigerator.

(-) no deviation.

waters may have a control function on pH, but the reactions are not understood yet (see Table 1).

According to Schmidt (1968) total carbon dioxide in Rio Negro waters was in about the 5 mg/l range. If compared with free carbon dioxide data obtained for the BR-174 samples (see Table 1), the gas must have a profound effect on the pH of the rain forest stream waters. The high free carbon dioxide content of natural waters of the Tertiary regions of Amazon were also confirmed by other authors (Fittkau, 1964; Sioli, 1957).

As shown in Table 2, the fluctuations of hydrogen — ion concentration in Rio Negro samples with time were significant, while the BR-174 samples were mainly stable, i.e. at least the storage of samples over a period of 30 days was feasible as far as pH was concerned.

The electric conductivity data of the Rio Negro samples displayed significant variations with regard to sampling position in the river

cross — section as well as in total deviation from the first laboratory measurements (see Table 3). It must be understood, that surface samples are not representative for the entire body of river water. As all water samples analyzed (Rio Negro, BR-174 samples), were extremely low in conductivity (ordinary single-distilled water used in the laboratory has a conductivity of 1 to 4 μS_{20}), only the Rio Negro samples (midstream surface, 300 m off right and left bank, 20 m depth) and the BR-174 sample (Km 35) showed a significant change with time (10 - 30 percent). As conductivity data were extremely low, the storage of water samples is practical at least for a period of 30 days. No significant differences were found between samples stored either in the laboratory or the icebox. As similar conductivity data were reported for other Tertiary regions of Amazonia (Fittkau, 1964; Sioli, 1957; Gessner, 1960), the results obtained may be generalized for the entire Tertiary formations of Amazonia.

RESUMO

Algumas vezes não é possível analisar no próprio local amostras d'água com relação aos valores de pH e condutibilidade elétrica, havendo por isso necessidade de posteriores determinações no laboratório.

Foram investigadas as possíveis variações em uma série de 4 amostras colhidas em diversas profundidades no Rio Negro, bem como uma série de 4 amostras de diferentes igarapés da mata tropical úmida ao longo da rodovia BR-174, sendo obtidos os seguintes resultados após um período de armazenamento:

- a) As variações verificadas nas amostras do Rio Negro foram significantes em relação ao período de depósito das mesmas (dois meses);
- b) As amostras dos igarapés mantiveram-se mais ou menos estáveis durante 30 dias. De acordo com os resultados obtidos por outros autores para outras regiões terciárias da Amazônia, os valores analíticos mostram a possibilidade de serem elas analisadas depois de um mês desde a data da coleta;
- c) A natureza da conservação das amostras no laboratório (normal e refrigerador) não mostram variações significativas.

BIBLIOGRAPHY CITED

- BRINKMANN, W. L. F. & SANTOS, A. DOS
1971 — Natural waters in Amazônia. V. Soluble magnesium properties. *Turrialba*, 24 : 95-101.
s/d — Natural waters in Amazônia. VI. Soluble calcium properties. (submitted for publication in *Turrialba*).
- FITTKAU, E. J.
1964 — Remark on limnology of central Amazon rain forest streams. *Vehr. Int. Verein. Limnol.*, XV : 1092-96.
- GESSNER, F.
1960 — Limnologische Untersuchungen am Zusammenfluss des Rio Negro und des Amazonas (Solimões). *Int. Rev. ges. Hydrob.*, 45(1):55-79.
- REID, G. K.
1961 — *Ecology of Inland waters and Estuaries*. New York, Reinhold Pub. corp.; London, Chapman and Hall, Ltd. 375 p.
- SCHMIDT, G. W.
1968 — Zum Problem der Bestimmung der Kohlensäure in kalkarmen tropischen Wassern. *Amazoniana*, 1(4) : 322-26.
- SIOLI, H.
1957 — Valores de pH de águas amazônicas. *Bol. Mus. Pa. Emílio Goeldi. Sér. Geologia*, 1:1-37
- WELCH, P. S.
1952 — *Limnology*. New York-London, McGraw Hill book Comp. inc. 538 p.