ECOTROPICOS, Vol. 6 (2): 30-42. 1993
Sociedad Venezolana de Ecología

DIEL VARIATIONS IN SOME CHEMICAL VARIABLES OF THE ORITUCO RIVER, VENEZUELA

VARIACIONES DIARIAS EN ALGUNOS PARAMETROS QUIMICOS DEL RIO ORITUCO, VENEZUELA

by

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ABSTRACT

Diel changes of several chemical variables were measured on three ocassions during 1986 in Orituco River, Venezuela. Dissolved oxygen was the only variable to show a regular diel variation. Sodium, dissolved reactive phosphorus, nitrite, nitrate and ammonium showed irregular variations of some magnitud but not statistically significant. Calcium, magnesium, and potassium did not show any fluctuation in their diel concentrations.

Key Words: Diel changes, concentration, hydrochemistry

RESUMEN

Las variaciones diarias de varios parámetros químicos fueron cuantificadas en tres ocasiones 1986 en el Río Orituco, Venezuela. El oxígeno disuelto fué la única variable que mostró una variación regular. Sodio, fósforo disuelto reactivo, nitritos, nitratos y amonio presentaron fluctuaciones irregulares de cierta magnitud pero no estadisticamente significativas. Calcio, magnesio y potasio no mostraron fluctuaciones diarias.

Palabras Claves: cambios diarios, concentración, hidroquímica

INTRODUCTION

Several chemical variables have been used to quantify and characterize seasonal variations in aquatic systems. On the other hand, diel changes on dissolved oxygen, pH and alkalinity has been related to diurnal biological activities. Therefore, measurements of photosynthesis and respiration of the whole aquatic biota have been used as estimators of community metabolism (Bush and Fisher 1981, Odum 1956, Verduin 1956, Wylie and Jones 1987).

It has long been recognize that water chemistry of rivers are an expression of the environment through which they are flowing (Hynes 1975). Then, their temporal variation should reflect their geological nature or could be associated with climatic processes such as snow accumulation which afterwards melts resulting in changes in the water chemistry (Lewis and Grant 1979, Loranger and Brakke 1988). However, diel fluctuations are more difficult to be associated with a particular process. First, they could reflect internal activities, mainly metabolic, such as diel changes in oxygen which are pronounced and common in tropical and subtropical waters but few have been reported (Whitton and Rother 1988). Second, they might be the product of activities external to the system such as human use of the watershed through logging, agriculture and farming. Then, monitoring the fluctuation in concentration of chemical variables around 24 h-cycles could increase our understanding on the functioning of aquatic systems as well as aim to implement sound management practices.

The Orituco river has been subject to a comprehensive study since 1983 and routinely sampled during day light hours. Therefore, it was important to determine if any daily periodicity in the stream chemistry does exist and should have been of consideration in the design of a regular sampling program.

The objective of this study is to report diel changes in water chemistry variables, the degree and importance of this irregular variation, and the relationship between the variables measured.

Study Site and Methods

Three twenty-four hour studies were undertaken in the Orituco river on the following dates: January 25-26, 1986; April 15-16 and April 29-30, 1986. The sample taken in January represent conditions under rainy season since precipitation for that month (306.7 mm) was higher that the mean average for the main rainy season for the area (May-August 197.1 mm). The other two sampling dates correspond to the dry season (Cressa and Senior 1987). The sample site was the Hacienda Uverito (Fig. 1) where the river had an annual average mean width, depth and water velocity of 7.05 m, 0.22 m and 1.08 m/sec, respectively. The substrate is uniform with cobbles of approximate 6 cm mean diameter. Preliminary data on the chemistry is given in Cressa and Senior (1987).

The water-chemistry analysis used are described in Cressa and Senior (1987, 1990) with the following exceptions. Dissolved oxygen was determined with an oxygen electrode (Orion Model 97-08). The electrode was tested by two procedures: (i) several days before the experiment several samples of water were taken, to one batch the concentration of oxygen was determined with the electrode and the other batch was processed according to the Winkler method (Wetzel and Likens 1979), (ii) in the laboratory, against determination of dissolved oxygen concentration by the Winkler method the day before its use on the field. Ammonia was determined with an electrode (Orion Model 95-12). Calcium, magnesium, sodium and potassium were determined by atomic absorption.

Results and Discussion

A summary of the descriptive analysis on the three sampling dates are presented in Table 1. In general, all variables tested have a coefficient of variation less than 50 %, except for soluble reactive phosphorus (PO_4-P).

Diel fluctuations in oxygen and pH are expected since both parameters are linked to the metabolic activity of the biota. Thus, in this case the interest was centered on the magnitud of those fluctuations. The diel changes for dissolved oxygen are presented in Fig 2. It is evident from the figure that a higher concentration of dissolved oxygen was found during light hours. Furthermore, the range of diel fluctuations was greater during the dry season that for the rainy seasons (8.6-5.0 mg/L compare with 7.6 - 5.5 mg/L). The smaller variation observed on April 29-30 (6.9 - 5.3 mg/L) could be explained beçause it was a cloudy day.

Comparisons with other systems are difficult to made since data are scarce for the tropics as well as for the temperate region. However, some analysis could be worthwhile with the data at hand. Bush and Fisher (1981) reported a diel variation of 8.7 mg/L of dissolved oxygen (17.3 - 8.6 mg/L) for Sycamore Creek (USA). The diel changes on dissolved oxygen

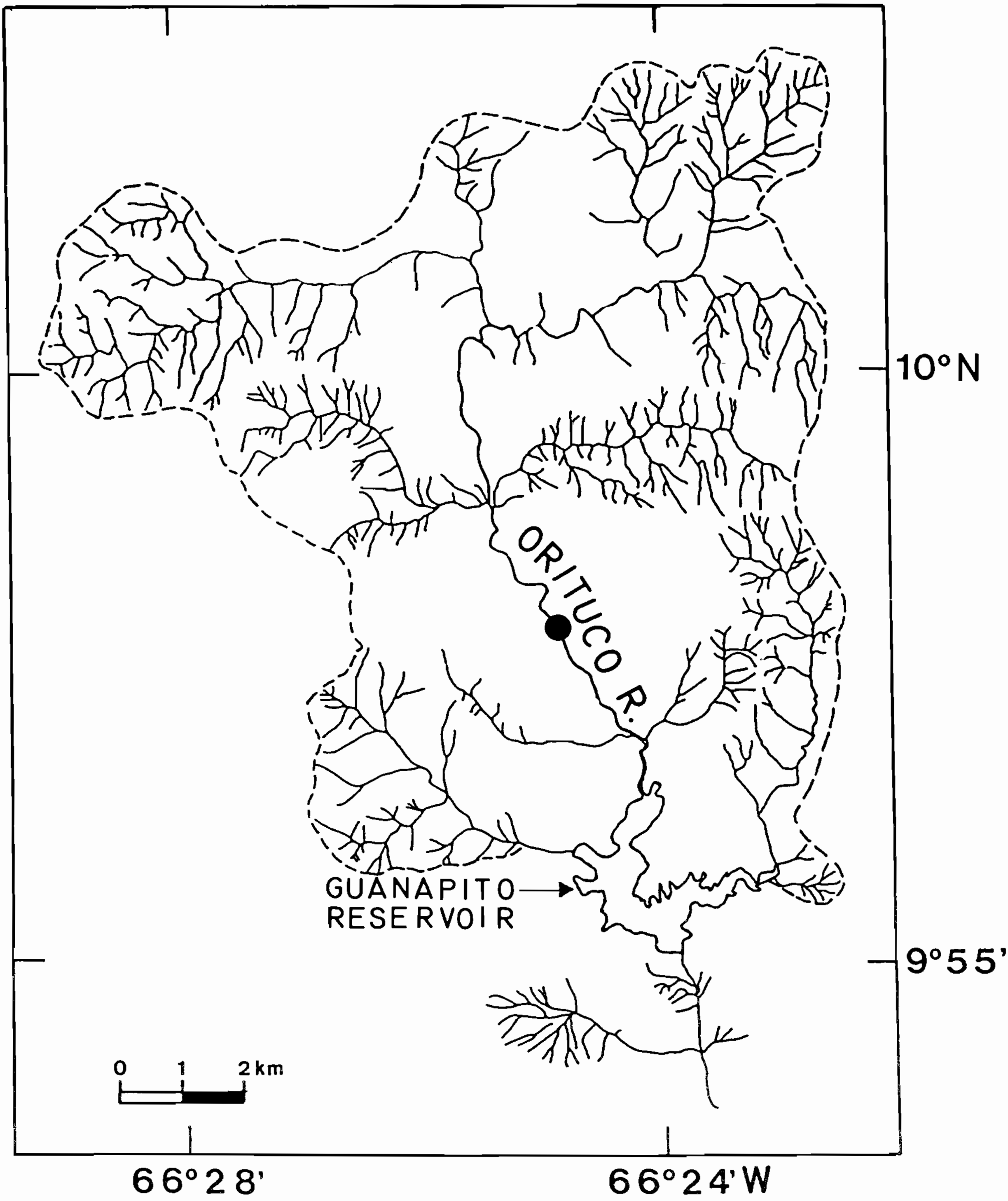

Figure 1. The Orituco river watershed showing the sampling station.

Table 1. Mean ($\bar{X}$), Standard deviations (SD) and Coefficient of variation (CV = SD x 100 / $\bar{X}$) for the four 24-h sampling series.

Date		NO_2-N (µg/L)	NO_3-N (µg/L)	NH_4-N (µg/L)	PO_4-P (µg/L)	O_2 (mg/L)	pH (mg/L)	Alkalinity (mg/L)	Ca^{++} (mg/L) ($CaCO_3$)	Mg^{++} (mg/L)	Na^+ (mg/L)	K^+
25-26 January 1986	$\bar{X}$	1.49	74.51	23.53	3.46	6.51	7.75	73.00	12.97	6.61	4.97	0.37
	SD	0.59	15.69	7.38	3.43	0.69	0.10	6.37	0.98	1.07	0.42	0.07
	CV	39..60	21.06	31.37	99.25	10.55	1.28	8.73	7.56	16.19	8.45	18.94
15-16 April 1986	$\bar{X}$	4.32	401.86	21.66	9.50	7.07	7.90	90.64	22.60	10.33	9.03	1.71
	SD	0.92	135.44	3.81	4.13	1.12	0.17	4.70	1.10	0.50	0.89	0.12
	CV	21.30	33.70	17.59	43.50	15.88	2.14	5.19	4.87	4.84	9.94	6.90
29-30 April 1986	$\bar{X}$	6.63	200.00	93.43	18.78	5.88	8.11	88.76				
	SD	2.61	24.78	30.23	4.17	0.55	0.13	1.85				
	CV	39.40	12.39	32.36	22.21	9.27	1.64	2.08				

for the Orituco river are small (the highest was 3.6 mg/L) when compared with Sycamore Creek. Nevertheless, the small variation found on the Orituco river is surprising since the determination were made at low water level (dry season) when 85 % of the river bed was covered with algae (*Cladophora*, *Cloniophora* and a high density of periphyton). The system at this time of the year should have its highest metabolic activity which in turn should produce the greatest diel fluctuation. Therefore, it will be interesting to pursue this investigation in order to determine not only oxygen diel fluctuations but also primary production and see how they compare with temperate regions.

Diel changes on pH were low, rarely exceding 0.5 units (Fig. 2). It is interesting to note that the diel changes during the cloudy days are markedly different from the others which correspond with low daily variation on dissolved oxygen.

Total alkalinity (Fig. 2) also showed some decrease during night hours however, the coefficient of variation is low and do not follow a particular pattern. The major ions Ca^{++}, Mg^{++}, K^+ (Fig. 3) showed very slight variations that cannot be considered significant. Since the concentration of these ions are mainly product of weathering it is not surprising to find these results because there is no reason to have a different rate of weathering on a daily basis. It is surprising that Na^+ does not follow the same patron and an explanation for this difference is not possible at the moment.

The greatest CV were obtained for dissolved reactive phosphorus, NO_2-N, NO_3-N and NH_4-N (Table 1). Fig. 4 depicts the water chemistry changes for each of these variables on each of the 24-h studies and from it several conclusions could be drawn. First of all, even though some fluctuation is evident this is small, not statistically significant and irregular. Second, on the sampling date where the dry season is more pronounced a diel variation is observed on all variables. It is particularly interesting to note the correlation between the variation on dissolved oxygen, NO_2-N, and NH_4-N (Figs. 2 and 4). Finally, soluble reactive phosphorus showed the most pronounced and diel irregular-timed fluctuation. Similar randomly timed irregularities were obtained by Lewis et al. (1984) in his study on several affluents of Lake Dillon (USA).

The descriptive analysis of the data up to this point indicated that even though some variables showed a diel fluctuation they were irregularly timed and a predictable pattern was non-existent. Furthermore, the average mean concentration obtained for each variable during the sampling dates do not differ

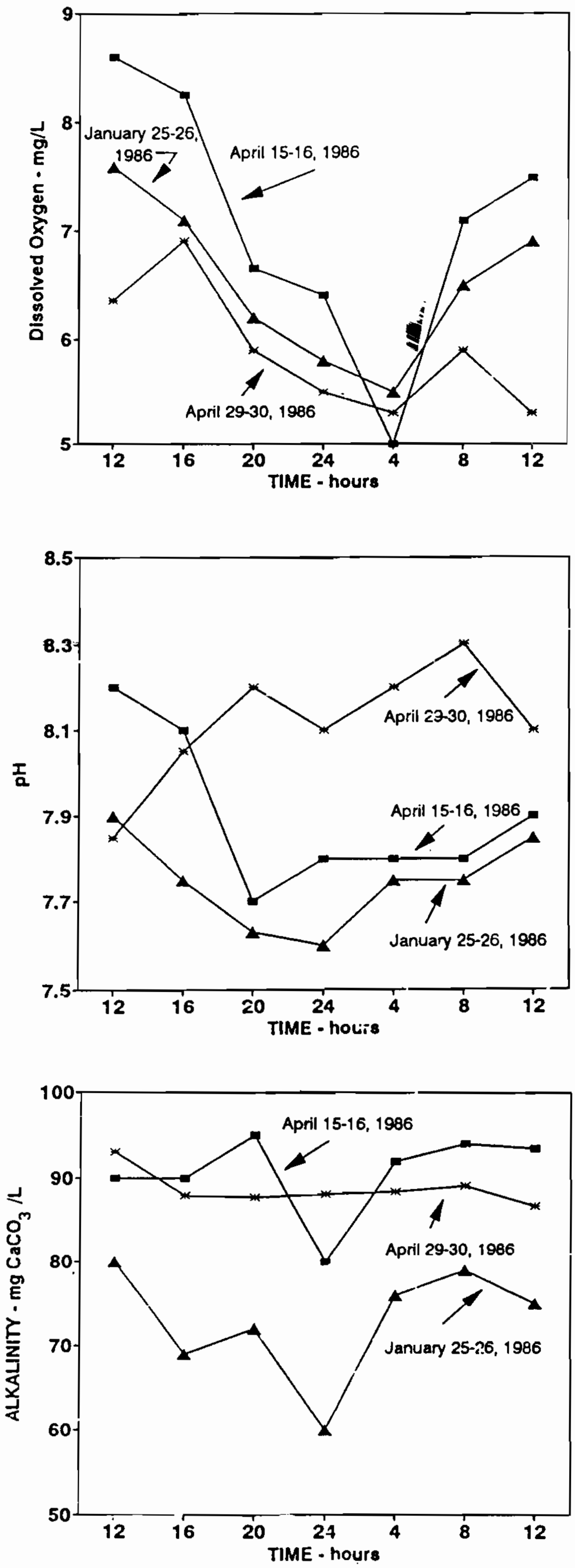

Figure 2. Diel changes in dissolved oxygen, pH and total alkalinity (mg/L of $CaCO_3$) in the Orituco River.

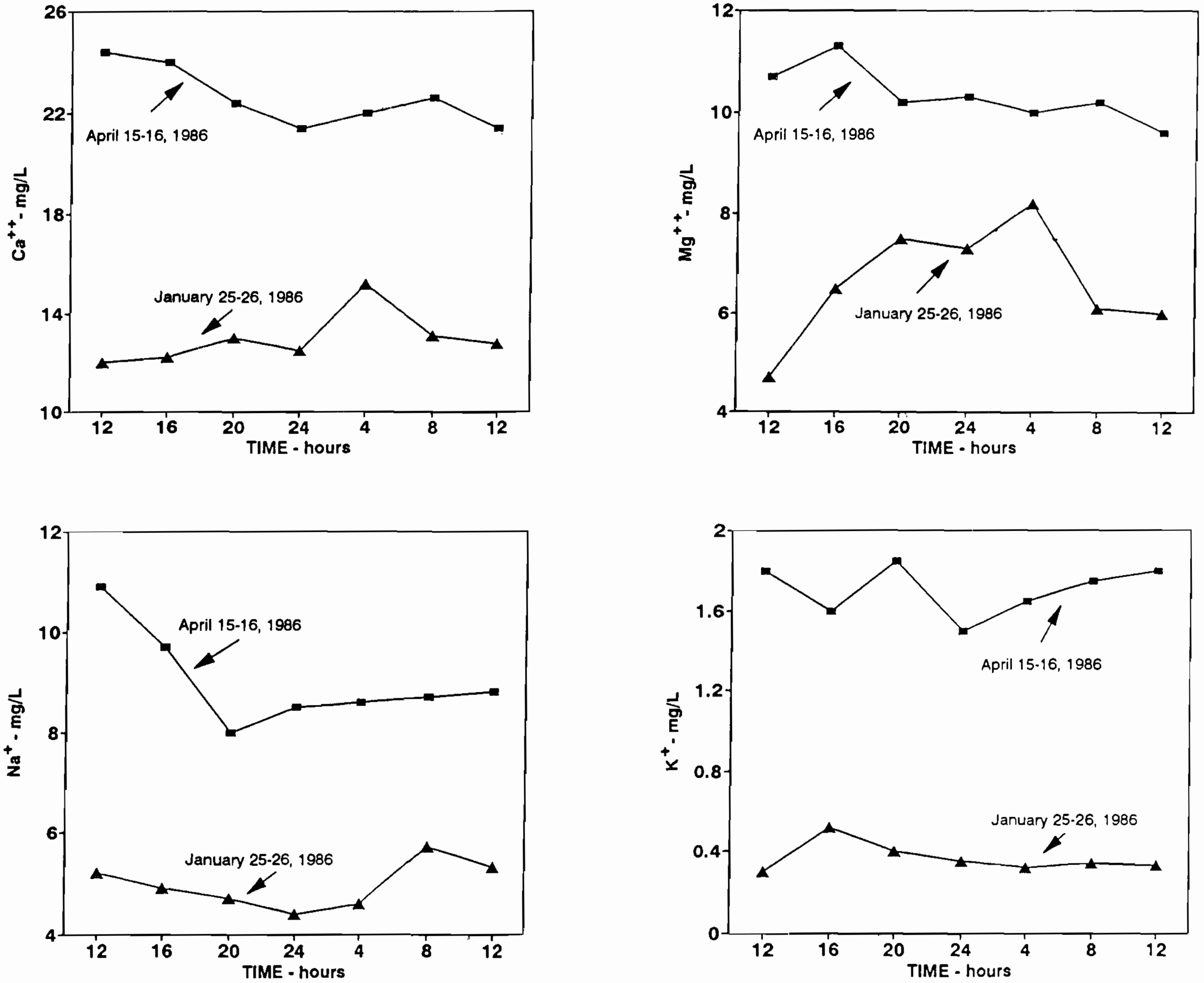

Figure 3. Diel fluctuations in calcium, magnesium, sodium and potassium in the Orituco River.

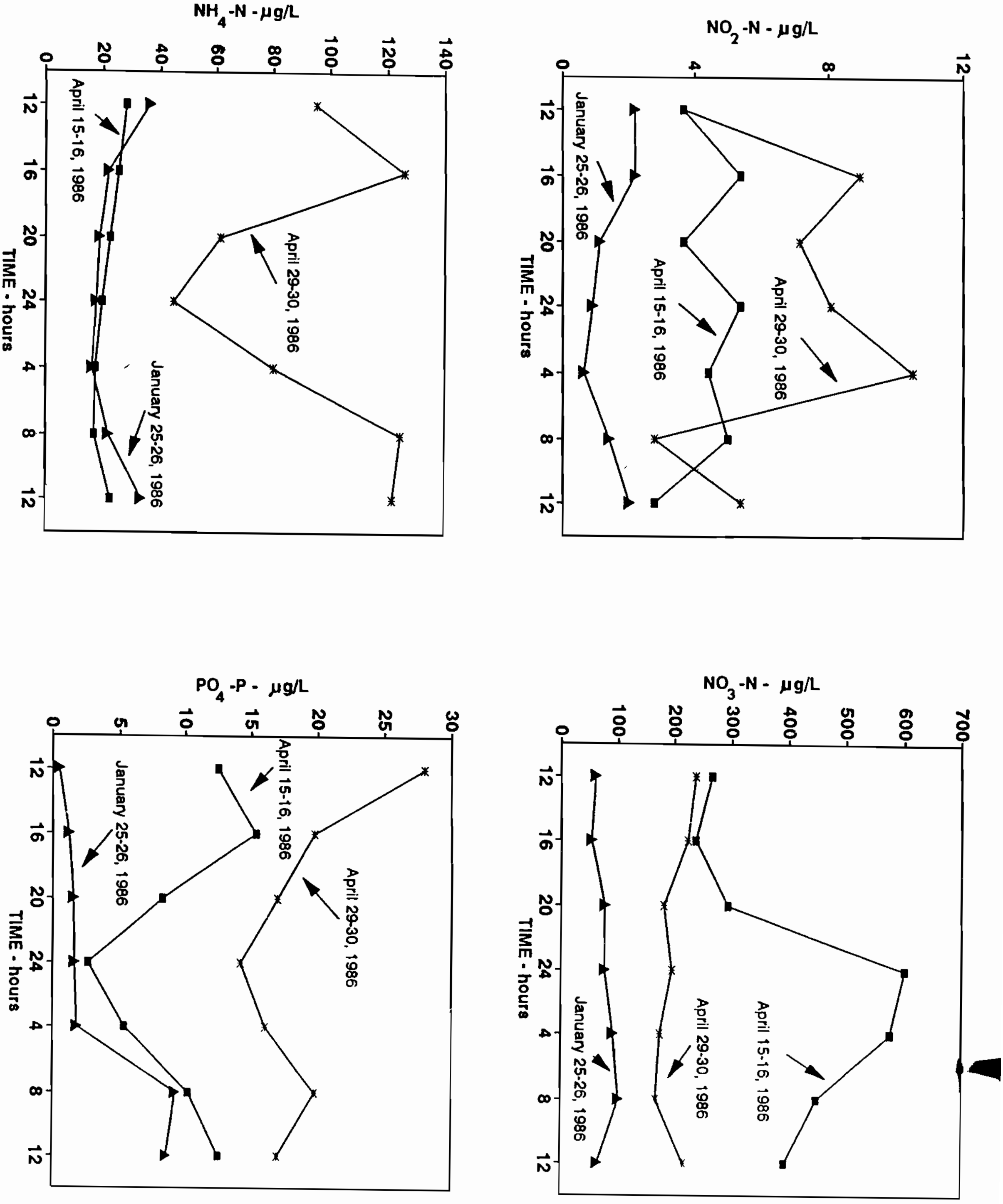

Figure 4. Diel changes in nitrite, nitrate, ammonium and soluble reactive phosphorus in the Orituco River.

significantly from the recorded seasonal variation observed during the years of study in the Orituco River (Cressa, in preparation). Therefore, it is possible to assume that the conditions prevalent on the river at the time of sampling are characteristic and thus the result obtained should reflect the diel changes on the river. However, since the changes were not constant among sampling dates a question arises to whether diel variations were of significant importance during a particular time of day. This is important in this case were the surrounding area is farming land subject to fertilization and where irrigation could significantly alter the chemical composition of the superficial runoff input to the stream.

In order to answer this question a Kolmogorov-Smirnov (Sokal & Rolf 1981) test was carried out in two steps. Firstly, to determine if a statistical difference does exist between sampling hours for a given date. Secondly, if a significant difference between hours do exist, a test must be conducted among sampling dates, for each one of the sampling hours to distinguish which hour is important for a particular variable.

The results of the analysis indicate that a significant difference does not exist in the diel fluctuations for any of the variables. Therefore, even though the data set is not large enough it can be concluded that, with the exception of dissolved oxygen, the irregularities observed do not follow a particular pattern.

Nevertheless, the statistical analysis of the data arise a troublesome question: How big the difference in concentration of a particular variable should be in order that a statistical significant difference be detected? As an example we should look at the diel variation of dissolved oxygen. From the biological point of view a difference does exist in dissolved oxygen during day and night even if the diel changes do not fall under a 100 % saturation and as in this case the diel fluctuations are small. Dissolved reactive phosphorus is another variable whose diel changes must be studied during a longer period of time in order to determine if the diel changes detected (Fig. 4) have any biological significance which in turn could increase our understanding of the dynamics of phosphorus in rivers. Furthermore, since we are dealing with a mass of water in movement, should be interesting to sample the river at two sites according to the velocity of the water (upstream site at time zero and downstream site at the time matching the corresponding velocity) in order to distinguish effects from non-point source from thus due to biological activities carried out inside the stream. This aspect is particularly important in this river where phosphorus concentration in daily-hour sampling was determined to be low (11.39 µg/L, Cressa in preparation) and thus we could have underestimate its concentration and recycling.

Aknowledgements

This work was supported in part by a CDCH grant (C03.20/83-85). I am greateful to Dr. Jorge Paolini and Mr. Saul Flores for the determination of cations at the IVIC. To Dr. Armando Ramírez and two anonymous reviewers whose comments on an early draft greatly increased this manuscript. I am indebted to all the personal at the Sub-Estación de Piscicultura-FONAIAP in Guanapito and particular to Licenciada Brunilda Heredia, for use of its facilities and to Mr. Pedro Hernández for access to his private land where the sampling station is located.

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