ISOTOPE TRACING OF THE PARANÁ RIVER, ARGENTINA

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Abstract. The Río de la Plata estuary is the collector of a vast drainage basin of about $3.1 \cdot 10^6 km^2$. There are many tributaries to the estuary but the Paraná and Uruguay rivers discharge directly more than the 99% of the average 24000 m^3/s.

We study the stable isotope compositions since 1997. From 120 isotopic pairs, it could be established that ^{18}O and ^2H exhibit a cyclical pattern with maxima in November and minima in May. Values are in correspondence with the ITCZ position. When it is located near10º N, the rain over the basin is lower and hence the isotopic composition of both elements is less depleted. Conversely, when the ITCZ moves southwards, the pluviosity increases leading to ^{18}O and ^2H to more negative values. This signal is recordered with a delay of *ca* 4 month in the estuary. The derivate magnitude, deuterium excess, showed important variations, from 1 to 18 per mil, being related the higher values to positive ENSO (El Niño) and the lower to negative ENSO (La Niña).

1. INTRODUCTION

The Río de la Plata estuary is the collector of a vast drainage basin of about $3.1 \cdot 10^6 km^2$ known as the “Cuenca del Plata” (Fig 1, Table 1). Its major tributaries are the Paraná and Uruguay rivers. The main course of the Paraná River starts at the "Planalto do Brasil", located at the central eastern Brazil. The Pilcomayo and Bermejo rivers contribute to Paraná with water from the high Andes range. Paraguay River releases into the Paraná water coming from the Mato Grosso forming the hugest wetland in the world named “El Pantanal” [1] which behaves as a buffer. The Uruguay River, directly and the Iguazú River through the Paraná, also contribute to the estuary. Less significant are other rivers like the Salado del Norte, Negro, etc., although during April-May, 2003. the Salado del Norte River produced the most cathastrophic flooding in Santa Fe City, Argentina, were water level reached more than 7 m over its normal level [2].

Table 1. Areas covered in South America by the Cuenca del Plata

Country	**Covered area x 10^3 km^2**	**% of total area**
Argentina	890	32
Bolivia	200	19
Brasil	1.410	17
Paraguay	410	95
Uruguay	150	80
Total area	3.209	100

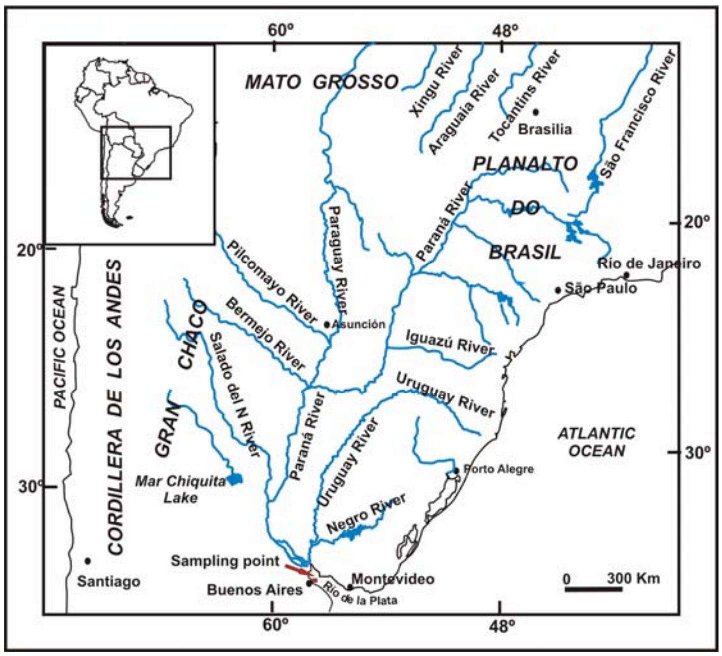

FIG. 1. . Map of the del Plata basin showing the main contributors

The Paraná River discharges an average of 17 300 m^3·s^{-1} with peak values up to 54 000 m^3·s^{-1} (1958) causing major floods in nearby cities. High river discharges and subsequent floods in its last 1000 km towards the Río de la Plata estuary were related to El Niño South Oscillation Phenomena (ENSO)[3][4]. Isotopic studies carried out with data of the Global Network for isotopes in precipitation (GNIP-IAEA-WMO) and our National Network account for the increase in the rainfall and the yearly enlargement of the zone of South America affected by the Intertropical Convergence Zone (ITCZ) [5][6]. As it was preliminary demonstrated in [7] it is possible to relate the stable isotope compositions of hydrogen and oxygen to the Intertropical Convergence Zone (ITCZ) winter-summer movement and to the ENSO. The deuterium excess is associated to variations in the kinetics factors during evaporation produced by El Niño South Oscillation (ENSO) related phenomena, and to the capture of recycled moisture from the Amazon rainforest during enhanced ITCZ shifts In addition the signals of ENSO and the ITCZ movements reach the estuary in *ca* 4 months, due to the mean transit time from the catching areas to the sampling point.

The Instituto de Geocronología y Geología Isotópica (INGEIS) started to measure the isotopic composition of the Río de la Plata Estuary in front of the coast of the Buenos Aires city in 1997 (Fig.1). Studies carried out on the zone and satellite images demonstrated that the Uruguay River has no influence on the Buenos Aires coast, therefore the isotopic values obtained until the present reflect only the composition of the Paraná River (Fig.2), allowing us to compare the river compositions at different localities, i.e. Corrientes and Santa Fe.

FIG. 2. Landsat image of the Rio de la Plata showing that the Uruguay river has no influence on the Buenos Aires coast

2. MATERIALS AND METHODS

A 2 liter sample is collected every 15 days in the sampling point, near the water works of Buenos Aires city in front of the Ciudad Universitaria. Since November, 2004 samples were taken daily. Composite 30 days grab samples and day by day samples were analyzed during the months November, 2004 and May, 2005 that in most cases represent the lowest and highest values respectively. Other aliquot was used for tritium analysis. In addition it is collected one month cumulative humidity samples during the year in the tank of the main engine of the central air compressed service of the INGEIS. Humidity in the air of the INGEIS building is considered to be in isotopic equilibrium with river water given its proximity (*ca.* 300m) to the river.

In order to check the reliability of grab samples, May and November samples were analyzed by deuterium and oxygen-18. Fig.3 shows the distribution of daily samples and the value of the grab sample taken in November, 15th (this is what had been taken as representative for the 30 days). In this case the δ^2H value is the same for the monthly averaged daily samples and the grab sample of November, 15th the but the composite, $\delta^{18}O$ is sligthly diffentet instead (Fig.3). As a check of the data quality, a sample obtained for the mixture of 30 subsamples of 1 mL was also analyzed being its isotopic values identical to that of the arithmetic media of the 30 individual analyses.

At the moment of this report not all the samples of May were measured (only deuterium is available), but it is probable that daily samples averaged in a monthly one represents more accurately the mean composition of the river for the period of a month. In addition individual samples are available for further studies to be carried out when it is possible for the labortory to measure such a lot of samples.

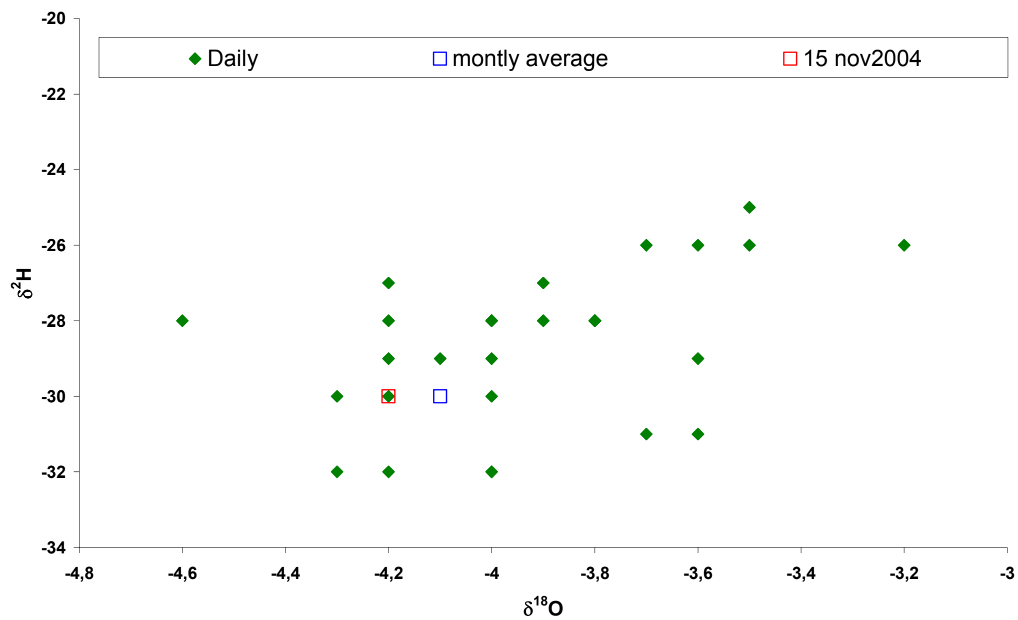

FIG. 3. Scatter plot showing the distribution of daily grab samples, the monthly average and the grab sample of the day 15th

Isotope analyses were done at INGEIS Laboratories. ^2H in water samples were prepared by standard procedures [8] and for ^{18}O was used the methodology described in [9]. Isotope ratios were measured with a multicollector McKinney type mass spectrometer, Finnigan MAT Delta S. Results are expressed, as δ (‰), defined as:

$$\delta = 1000 \frac{R_S - R_P}{R_P} ‰$$

where: δ: isotopic deviation in ‰; S: sample; P: international standard; R: isotope ratio ($^2H/^1H$, $^{18}O/^{16}O$). The standard is Vienna Standard Mean Ocean Water,V-SMOW [10]. The analytical uncertainities are ±0.1‰ and ±1.0‰ for $\delta^{18}O$ and δ^2H respectively.

Tritium samples were measured by liquid scintillation direct counting in the laboratory of the Atucha Nuclear site, Argentina. Results are expressed in TU (1 TU = $1^3H : 10^{18}$ H). The detection limit is < 5 TU. Samples below this value are considered as 0.

3. RESULTS AND DISCUSSION

3.1. Paraná River discharge

Fig.4 shows a comparative picture of discharge among years at Corrientes station, while, Fig. 5 and Fig.6 exhibit the daily discharge of Paraná River in Corrientes and Santa Fe gauge stations [11].

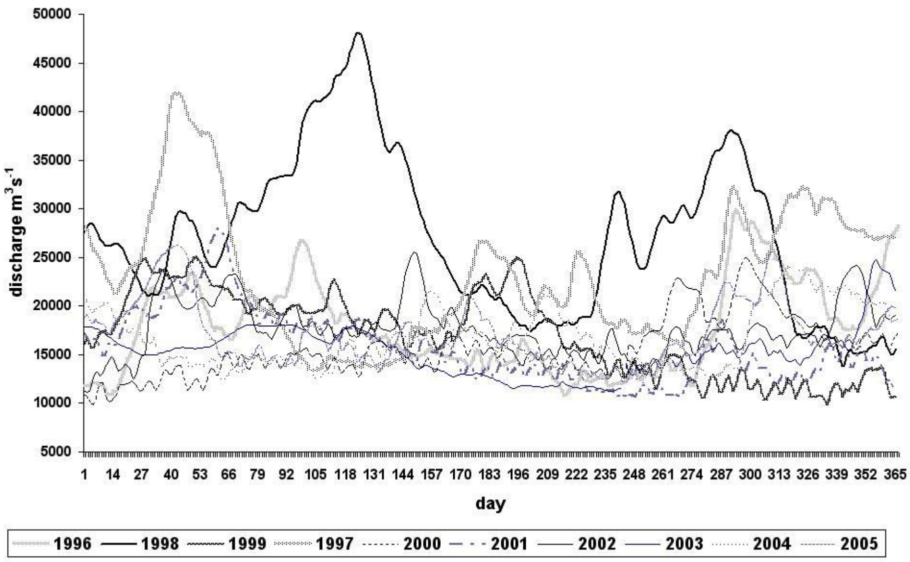

FIG. 4. Discharge of the Paraná River at Corrientes station. Note the increased volumes during the "El Niño" years. See fig. 13

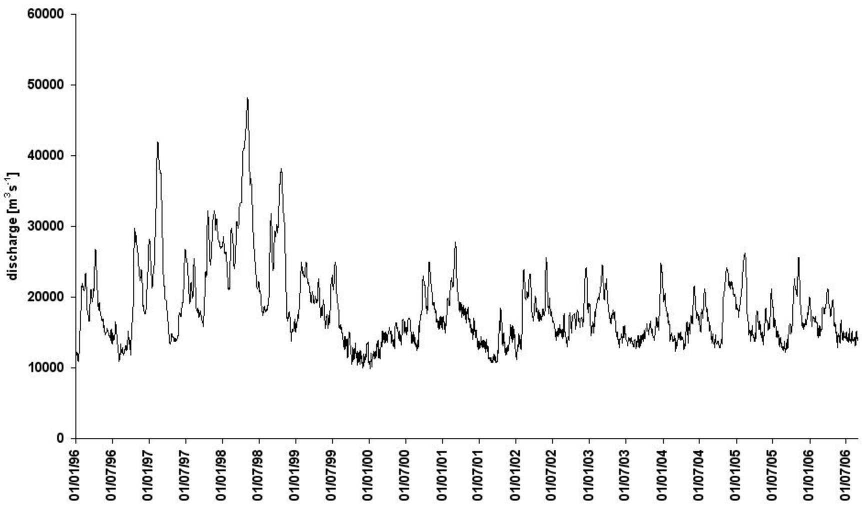

FIG. 5. Daily Discharge of the Paraná River at Corrientes station period 01/1996-08/2006. Source: [11]

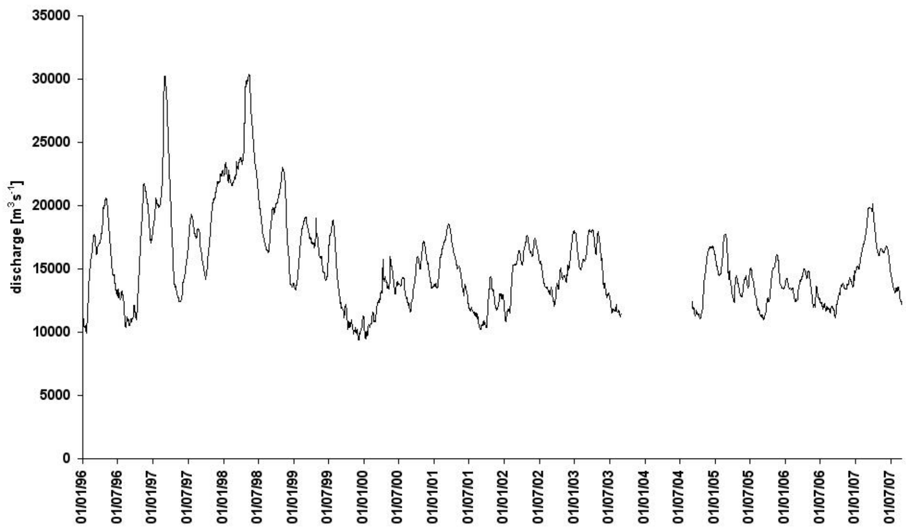

FIG. 6. Daily Discharge of the Paraná River at Santa Fe station period 01/1996-08/2007. Source: [11]

As it was previously mentioned, it was observed a delay of about 4-5 months between the time of the meteorological event and its signal in the estuary. It was assumed as the mean transit time from the catchments to the sampling point. An estimation of the feasibility of this number was made studying during 7 years the time employed by the Paraná river to cover the trajectory between Corrientes and Santa Fé stations (about 570 km). Calculations were made characterizing maximal and minimal peaks in Corrientes and their homologues in Santa Fe (Fig.7).

If we consider the time span between the occurrence of a peak (valley) in Corrientes and the same pick (valley) in Santa Fe and plot them *versus* the discharge in Corrientes, we obtain the graph of Fig. 7. A weak correlation is evidenced suggesting that the transit time increases whit discharge, ranging between 3 to 24 days, averaging a medium speed of 38 km/day. Taking into account the dimension of the basin, the signal from the catchments would be reflected in the sampling point delayed in about 3 months, an observed time of 4 months is considered reasonable taking into account the dams and natural flooding that hold back the flow in zones occurring along the river course. Figure 8 shows a transit time simulation between Corrientes and Santa Fe stations. It consists in shift the discharge corresponding to the Santa Fe station keeping that of Corrientes constant. The the best fit corresponds to τ = 17 days and is the average span time that best explain the correspondence betwenn peaks and valleys.

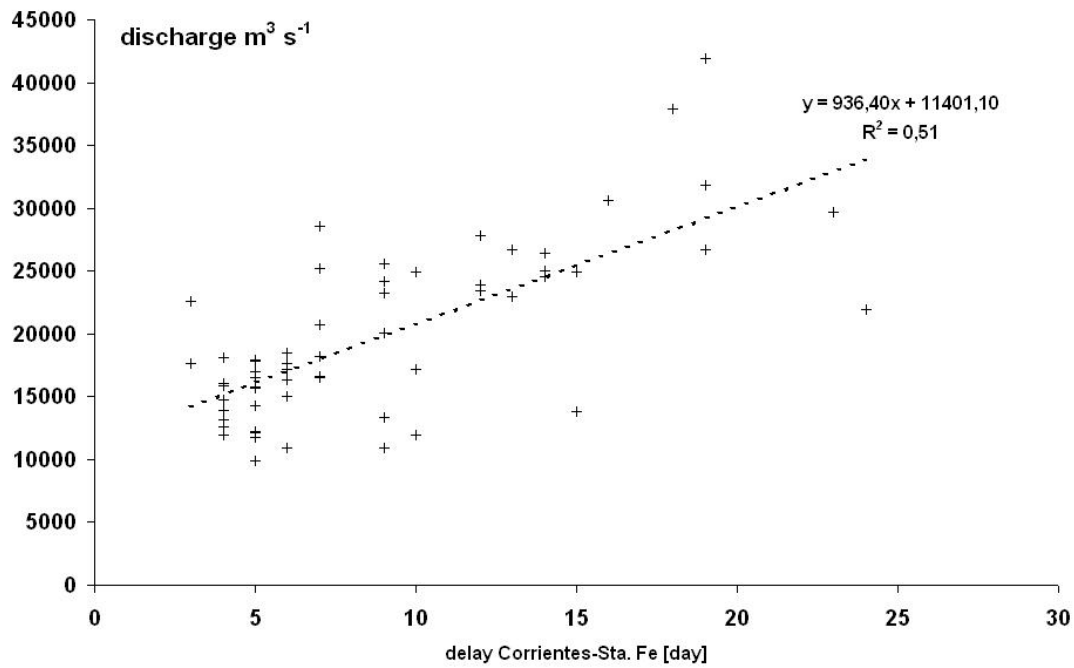

FIG. 7. Correlation between discharge at Corrientes and transit time Corrientes- Santa Fe (570 km).

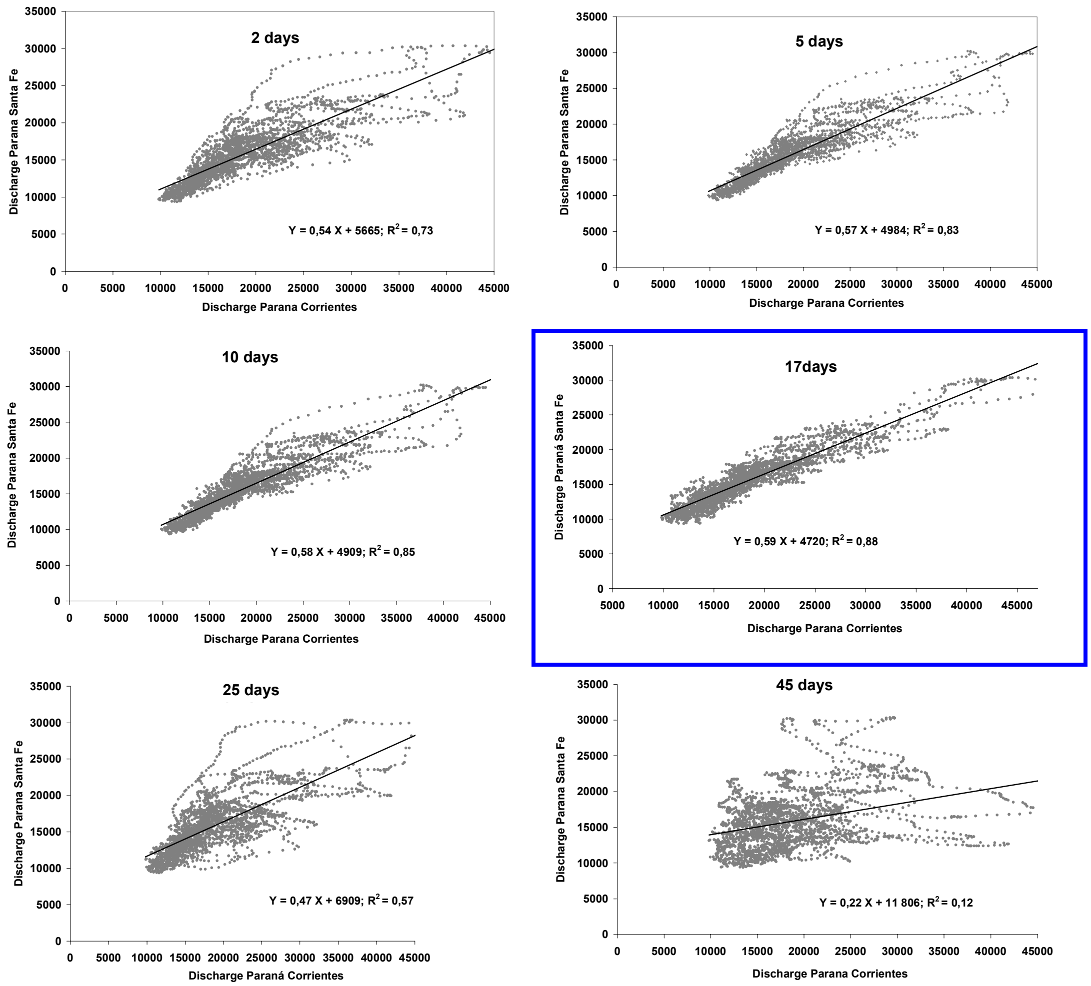

FIG. 8. Transit time simulation between Corrientes and Santa Fe stations. Note that the best fit corresponds to τ = 17 days

3.2. Stable Isotopes

Figures 8, 9 and 10 show the time series for $\delta^{18}O$, $\delta^{2}H$ and deuterium excess. In Fig.8, we can observe that the isotope concentration of ^{18}O follows a well defined cyclic pattern with time. $\delta^{2}H$ exhibit a similar scheme for the two first periods, but the third and fourth ones are clearly depleted in comparison to the other ones (Fig. 9). This fact can also be observed in the time series for the "d" parameter, produced by the deuterium depletion not accomplished by an ^{18}O decrease (Fig. 10).

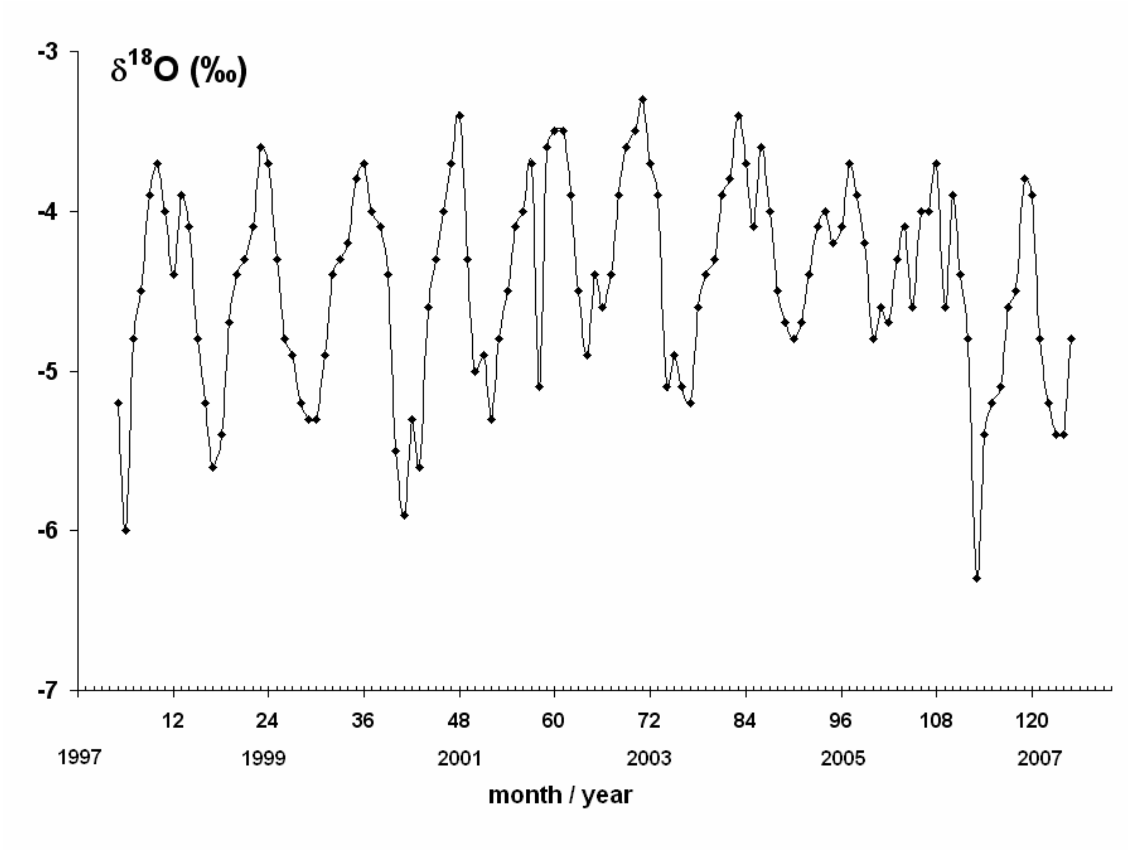

FIG. 9. . $\delta^{18}O$ time series for the period 1997-2007

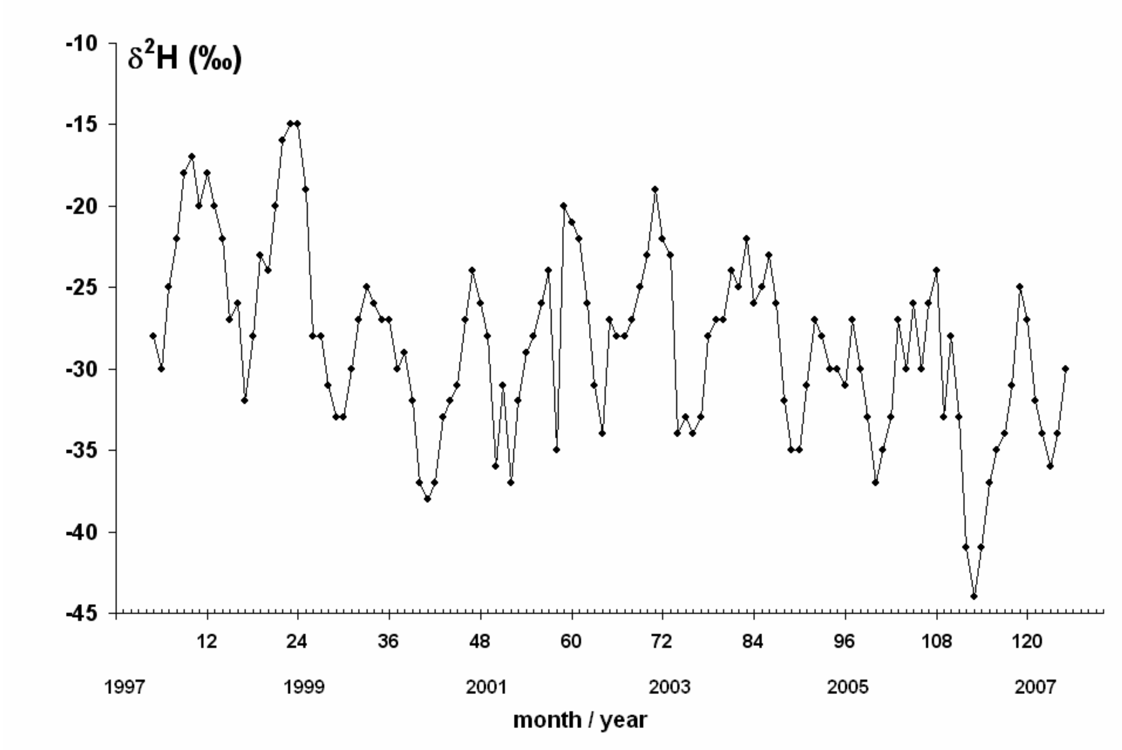

FIG. 10. . δ^2H time series for the period 1997-2007

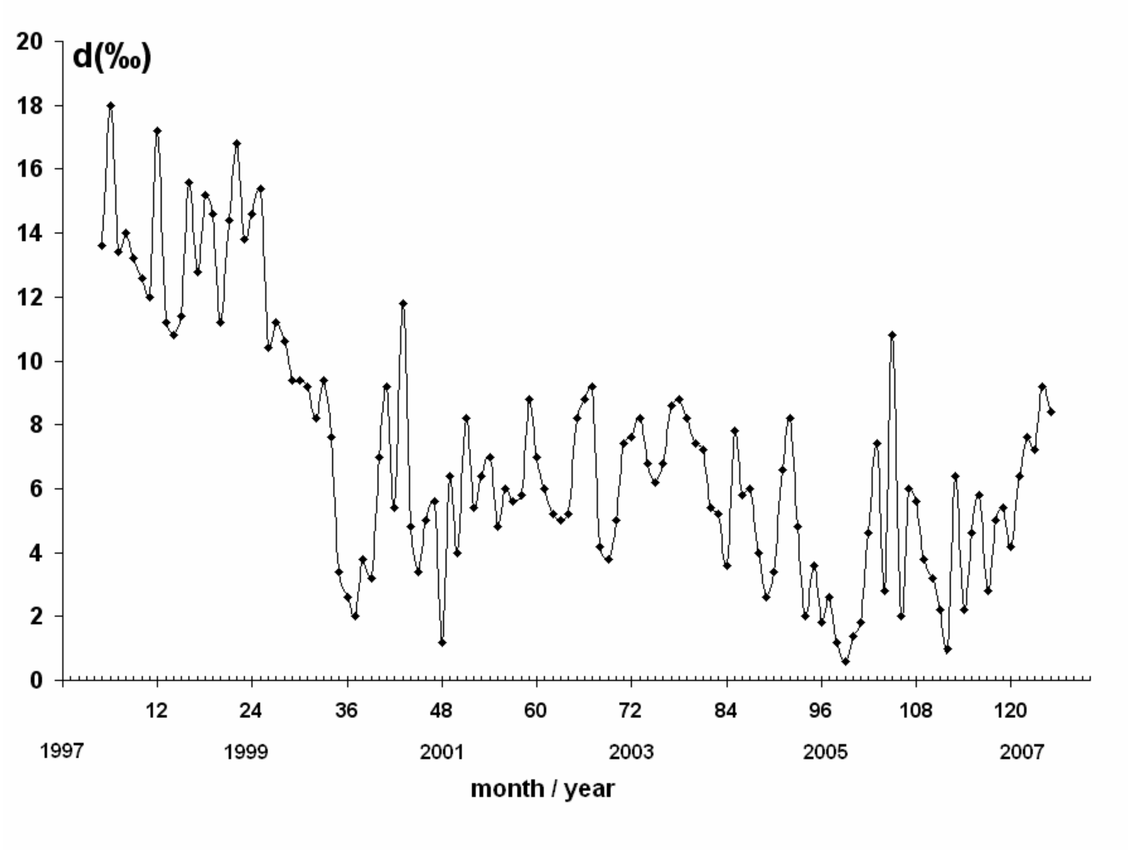

FIG. 11. Deuterium excess time series for the period 1997-2007

4. BACKGROUND

4.1. The amount effect

As was first noted by [12] and largely proved in later works, the socalled "amount effect" governs the stable isotopic composition in tropical zones, where the dependence on temperature is less significant than in middle and high latitudes. Albero and Panarello [13] observed the existence of this effect in Belem, Brazil, where temperature variations are negligible through the whole year. Figure 11 shows samples grouped in months with heavy rain around -5‰ ($\delta^{18}O$). Conversely the drier season exhibits enriched values similar of those of ocean. Also in Río de Janeiro, Brazil (Fig 12) a correlation between amount and isotope depletion was found corresponding both regression lines to more than one source of water vapor [14]

At present, the amount effect is considered as a consequence of a Rayleigh condensation of vapor and rainout. Thus, as the condensation progress, the composition of raindrops is a function of the remaining vapor fraction of the cloud

$$\delta / \delta_O - \varepsilon \ln f$$

Where f is the remaining fraction of vapor in the cloud W / W°. As the precipitation proceeds the isotopic composition of rain becomes lighter.

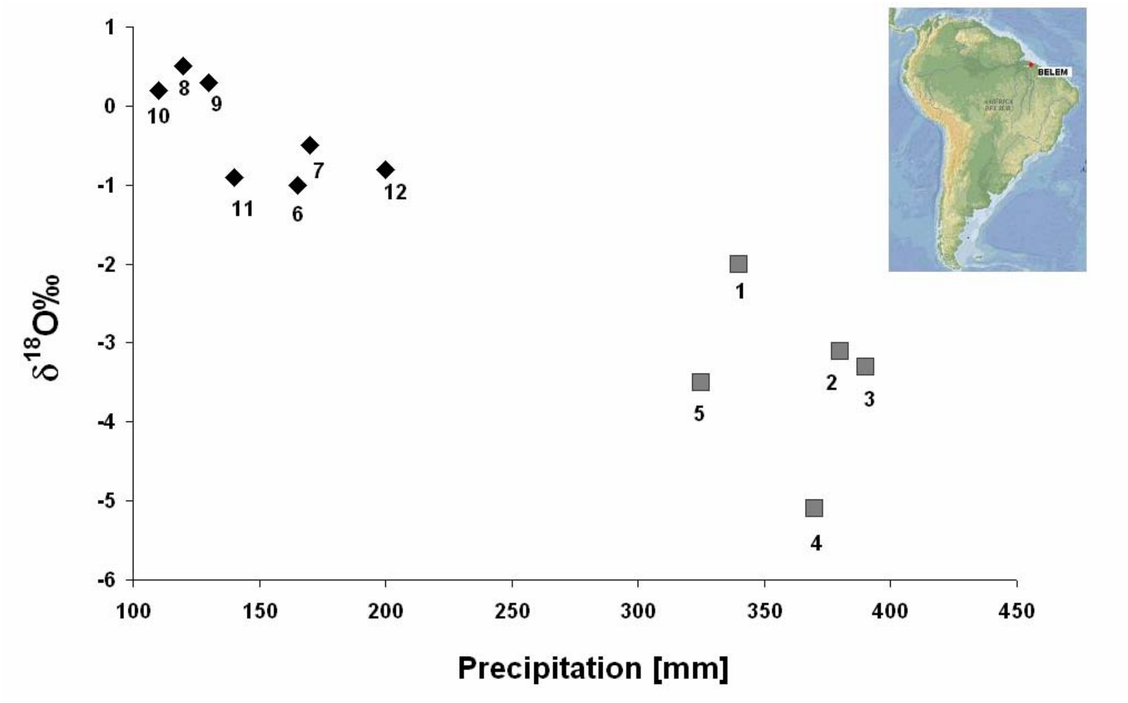

FIG. 12. Amount effect in Belem, after [13]

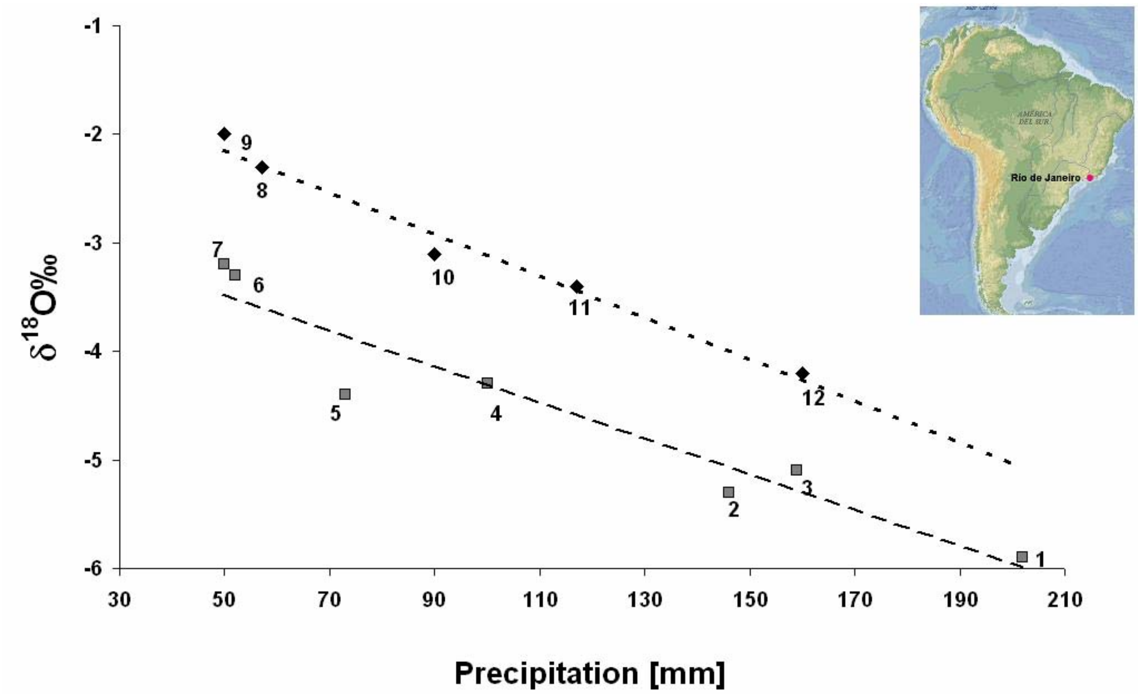

FIG. 13. Amount effect in Rio de Janeiro, after [13]

4.2. The Hadley cells and the ITCZ

At low latitudes the air column rises and moves poleward on either side of the Equator. At higher latitudes cooling air causes the column to descend. This results in the development of large convective wind cells, called Hadley Cells, with low pressure along the equator and high-pressure around 30^o latitude (Fig.13).

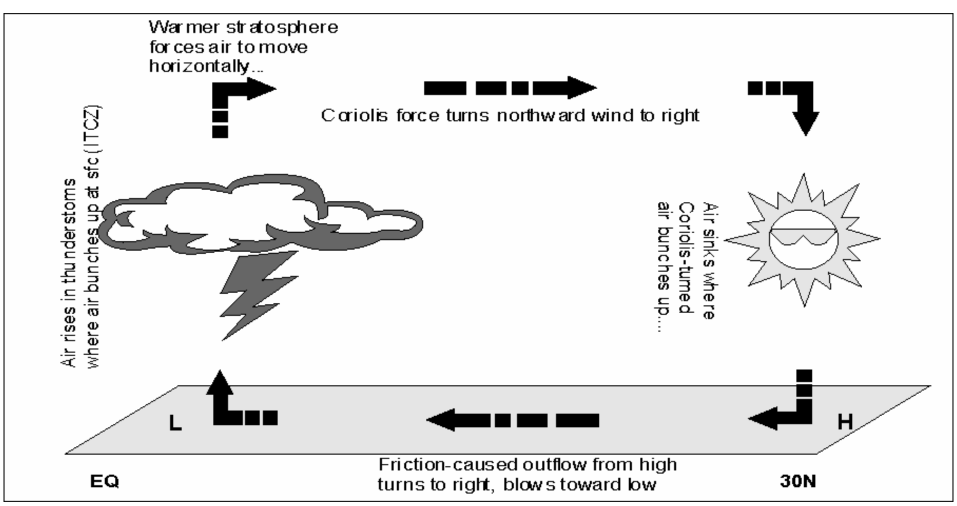

FIG. 14. Sketch of the Hadley Cells

The Earth's rotation causes the separation of the high-pressure belt into divergent spiraling anticyclone cells. The compensating back-flowing air produces the northeasterly and southeasterly trade winds, which converge in the equatorial area, and is therefore also known as the Intertropical Convergence Zone (ITCZ) [15]. As these winds converge, moist air is forced upward. This causes water vapor to condense, or be "squeezed" out, as the air cools and rises, resulting in a band of heavy precipitation around the globe. This band is not stationary and have a strong seasonal behavior, always being drawn toward the area of most intense solar heating, or warmest surface temperatures.

During the austral winter (July) it places lightly to the North (parallel to Equator) till 8ºN. During the Austral summer (January) the ITCZ shifts southwards making a strong inflexion over the continent reaching till 30º S, between 50ºW y 60ºW. (Fig.14) [5].

When it shifts southwards provides the synoptic conditions for a great increase in precipitation. These produce an amount effect that is recorded delayed in the stable isotopes of the Río de la Plata. Therefore, the maximal depletion in both values, $\delta^{18}O$ and $\delta^{2}H$, take place in the months of May to June, delayed *ca*. 4 months respect the souththern movement of the ITCZ due to average transit time of the river from the heads to the mouth.

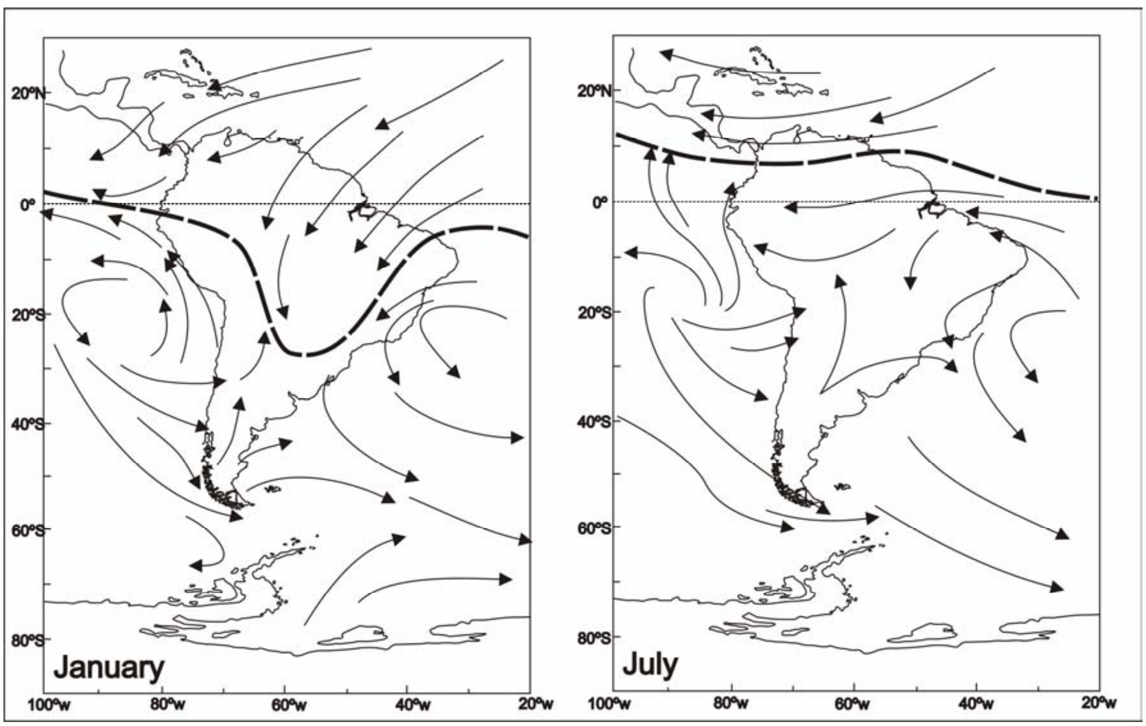

FIG. 15. Seasonal position of the Inter-tropical Convergence Zone , cited in [5]

A more datailed distribution of the amount of precipitation and the ITCZ position is given in Fig. 15[16]. These plots evidence dry periods for July-August (reflected in the values of November) and humids in December January, responsibles for the isotopic composition of May.

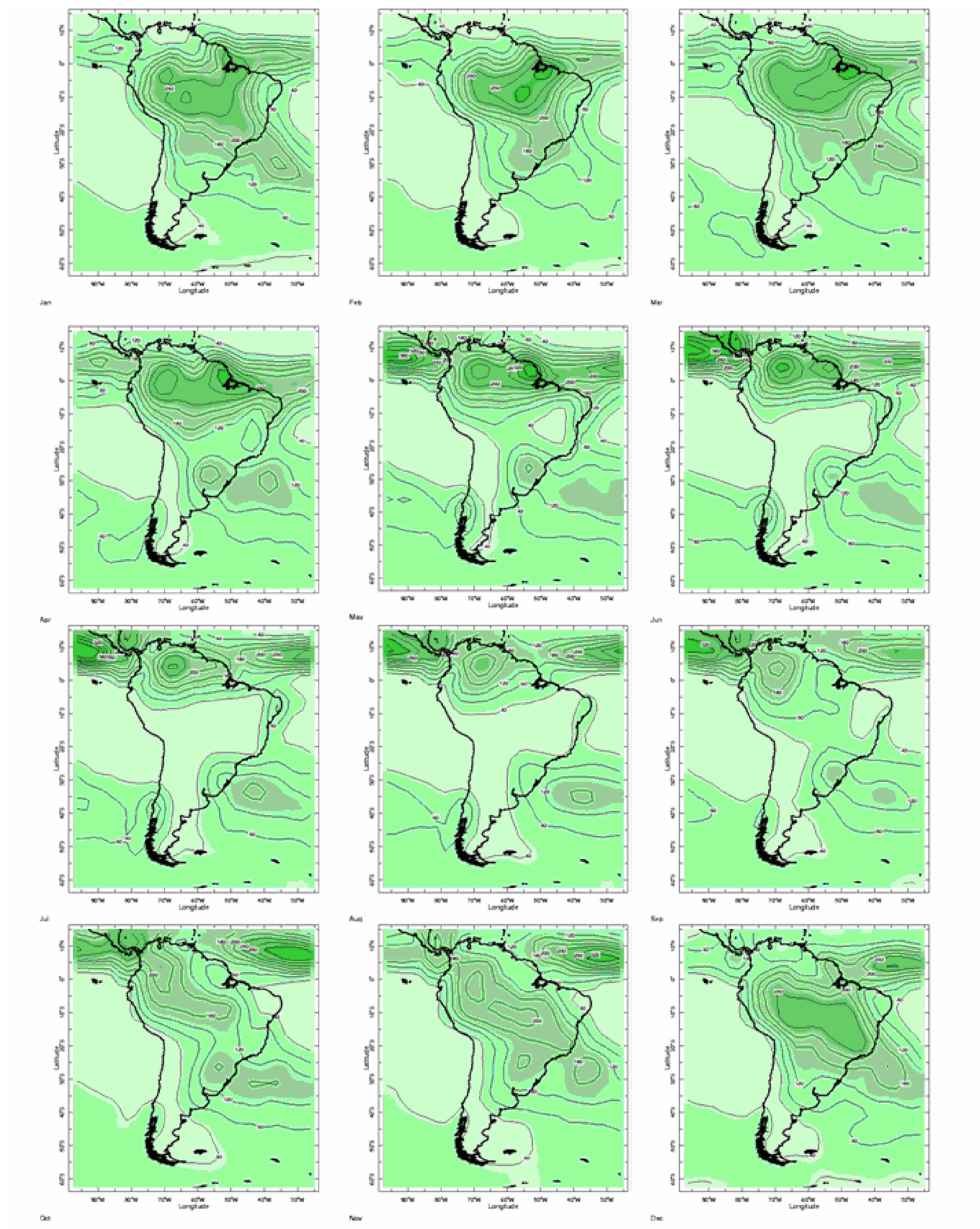

FIG. 16. .   ITCZ and rain distribution at the catching areas [16]

4.3. EL NIÑO SOUTH OSCILLATION (ENSO)

El Niño South Oscillation (ENSO) is a generic name for oceanic-atmospheric coupled cyclic phenomena, which changes significantly the meteorological conditions. When associated to an ocean temperature increase, we refer as "El Niño, conversely when ENSO is associated to an ocean temperature decrease, we refer as "La Niña". In addition, neutral (or normal) events are referred as "Non Niño-Non Niña" episodes. ENSO phenomena are defined for the Pacific Ocean at the 30ºS but they have induced consequences at global scales knowon as "teleconnections".

El Niño episode 1997-1998 was associated with a dramatic alteration of the global pattern of tropical rainfall and deep tropical convection, as indicated by above-normal rainfall across the eastern half of the tropical Pacific and by significantly below-normal convection across Indonesia and the western equatorial Pacific. The combined zonal extent of these rainfall anomalies covered a distance more than one-half the circumference of the earth.

Selected impacts associated with these warm episode conditions included:

1) Excessive rainfall across the eastern half of the tropical Pacific,

2) Significantly below-normal rainfall and drought across Indonesia and the western tropical Pacific,

3) Below-normal hurricane activity over the North Atlantic during August-October, with a simultaneously expanded region of conditions favorable for tropical cyclone formation over the eastern subtropical North Pacific

4) Excessive rainfall and flooding in equatorial eastern Africa during October-December

5) A dramatic eastward extension of the South Pacific jet stream to well east of the date line during June-December, which resulted in enhanced storminess across southeastern South America and central Chile.

6) Abnormally dry conditions across the Amazon Basin, Central America and the Caribbean Sea. Both phenomena are coupled with the atmospheric circulation producing anomalies in the trade winds.

When a warm ENSO (El Niño) take place, the southwards movement of the ITCZ is pronounced and reaches lower latitudes than in normal or cold episodes (enhanced ITCZ). Under these conditions, winds capture more recycled vapour from the Amazon. In the other hand, when a cold ENSO (La Niña) occur, the southwards movement of the ITCZ is limited or interrupted, leading to a decrease in the amount of precipitation, which can produce drought in many cases. The climate over large parts of South America is strongly influenced by the El Niño/Southern Oscillation. During warm episodes, drier-than-normal conditions are generally observed across northeastern South America during July-March, while enhanced precipitation tends to be observed throughout southeastern South America during November-February [17], and throughout central Chile during the austral winter [18]. Also, above-average temperatures are typically observed along the west coast of South America from May-April [17]. During the very strong 1997 warm episode, all of these conditions were prominent aspects of the South American climate.

In an early work [3] it has been found a good correlation between El Niño episodes and the increase of the Paraná River discharge. Flooding events produced by the Paraná River on May 1998 are in response to the greatest El Niño in the 20^{th} Century[4].

4.4. Deuterium excess and the ENSO

The deuterium excess is caused by the different diffusion rate of water species, $^{2}H^{1}H^{16}O$ (mass 19) and $^{1}H_2{}^{18}O$ (mass 20), during evaporation. The differential diffusion rate for the above molecular species produces kinetic fractionation. The kinetic factor for this process is related to the ocean temperature, moisture and wind strength, among other causes [19].

As can be observed in Fig. 16, there is correlation between the ENSO and deuterium excess. During El Niño episodes waters show high d values, that reached up to 18‰ in 1997-1998. Conversely, during La Niña lower d-values were observed reaching up to 1‰ in 2006.

The warmer ocean surface during El Niño increases the kinetic factor and thus evaporation occurs faraway the equilibrium conditions. In this case, the d-values are larger than those in which the process takes place under equilibrium conditions. The colder of ocean surface can lead to a decrease in the kinetic factor, evaporation occurs closely to equilibrium and thus the d-values approximate to zero. However, the changes in temperature are not enough to explain the entire variation of d-values; although changes in air moisture and wind velocity could also occur. For the mentionted above, when El Niño forces an enhanced-ITCZ, a large area of Amazon-moisture, which is already tagged with exceptionally high d-values is captured. In this way, the ENSO and the ITCZ synergise yielding very high values of deuterium excess.

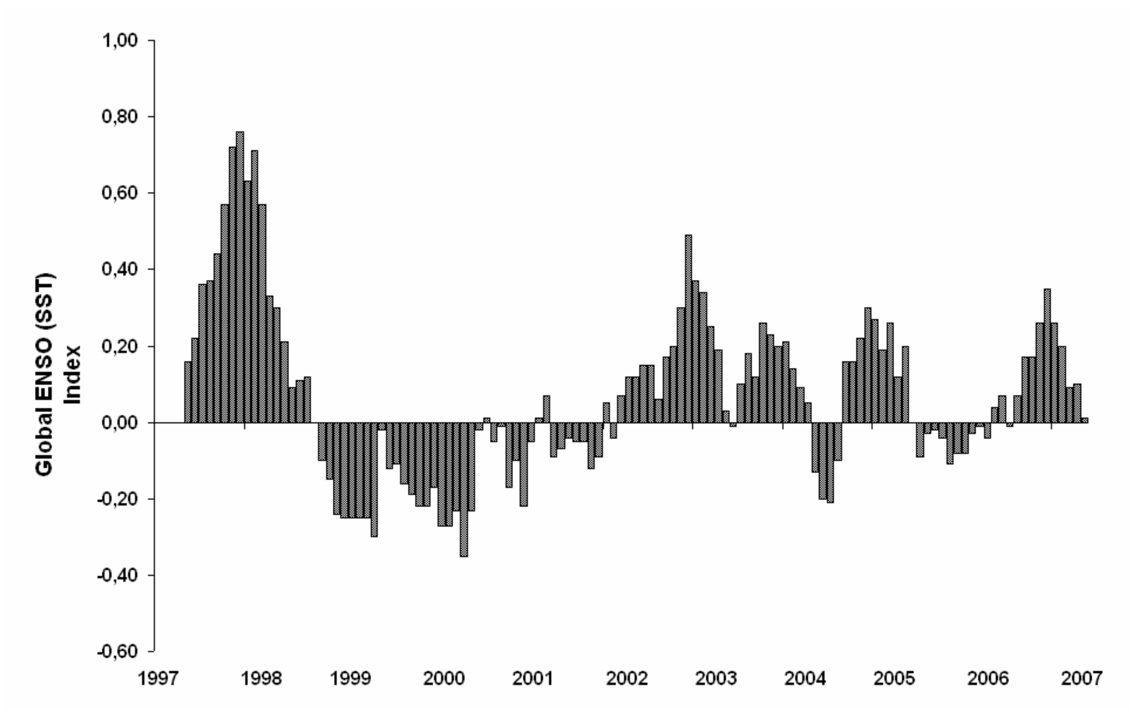

FIG. 17. ENSO index period 1996/2007[20]

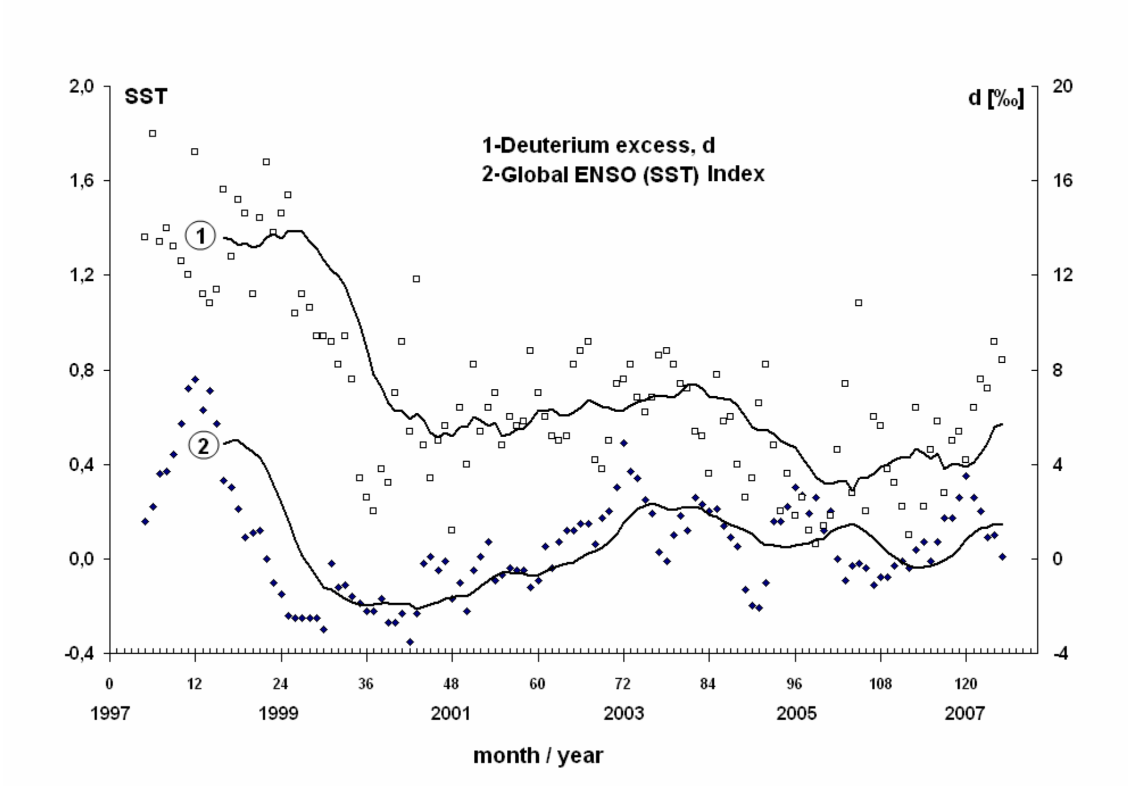

FIG. 18. 12 month mobile average for (1) the deuterium excess and (2) the ENSO Global Index (SST). Both signals show a similar general pattern shifted in about 4 months despite all the potential factors that could modify the isotopic composition along the river path (≈ 2800 km) Most differences are probably due to variations in transit time from the catchments to the mouth and also to the large number of tributaries whose contribution to the Paraná River change with time. See text for more details

5. TRITUM

In the informed period, it was measured tritium concentrations at the Río de la Plata and the Buenos Aires, Ciudad Universitaria rain collection station on samples collected in 2001 (Fig. 17) We considerer that the most probable source of tritium in the estuary is the discharge of water from the cooling system of the Atucha nuclear site. Tritium content of river waters is too high, with peaks of more than 1400 T.U. Rainwater has also tritium concentrations more elevated than those expected.

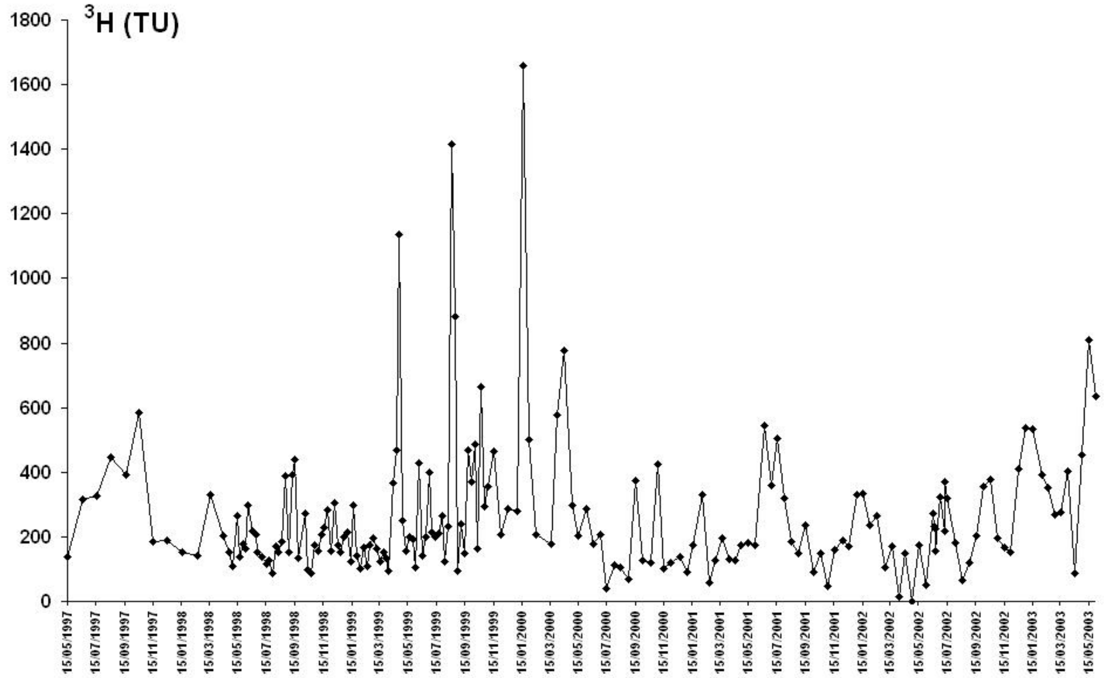

FIG. 19. Tritium values on Rio de la Plata in the Ciudad Universitaria Station during 1997-2003. Concentrations have been measured by direct counting, values below 5 TU, are considered as 0 TU

6. CONCLUSIONS

The amount of precipitation defines the rain isotope composition in tropical zones as central South America.

The ITCZ is the main factor controlling rain amount and thus the isotope composition of the Paraná River, whose catchment areas are located in the mentioned zones.

The ENSO phenomena influences the southwards shift of the ITCZ enhancing it (El Niño) or preventing it (La Niña).

The ENSO-enhanced ITCZ captures Amazon deuterium-rich moisture thogether with marine vapour also deuterium-rich lead to deuterium excess values up to 18‰ during El Niño 1997-1998.

This pattern reverts during La Niña onset *i.e.* a more reduce zone from where capture Amazon deuterium-rich moisture and less significant kinetic fractionation during evaporation under cooling conditions. This fact is shown in the dramatic drop after the warm episode of 1997-1998. During 2006 under La Niña condition the d-value reached to 1‰ .

Despite all the interactions with groundwater and physical processes suffered along *ca.* 2,800 km, the Paraná River still reflects at its mouth all these climatic phenomena that modified the ^{2}H and ^{18}O contents at its catchment areas

ACKNOWLEDGEMENTS

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