

Acidez en la lluvia de los Andes venezolanos en la Hechicera, Venezuela

Acid wet deposition flux in a Venezuelan Andes urban site at la Hechicera, Venezuela

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Resumen

En este estudio se determinó la acidez de muestras de lluvia recolectadas diariamente en La Hechicera, Venezuela (N08 37.728; W71 09.005; 1880 msnm), lugar urbano con clima tropical húmedo al norte de la Cordillera de Los Andes; con la finalidad de conocer la influencia de la deposición húmeda sobre la calidad de los suelos y otras esferas ambientales. Se tomaron muestras en dos campañas trimestrales durante los años 2007-2008 y 2011, siguiendo todos los protocolos sugeridos por el Programa de Observación de la Atmósfera Global y la Química de la Precipitación de la Organización Meteorológica Mundial. La mediana y la desviación absoluta de la mediana (DAM) para la concentración de iones hidrógeno fueron respectivamente $8.78 \pm 2.83 \mu\text{mol L}^{-1}$ ($n=34$) y $8.15 \pm 3.59 \mu\text{mol L}^{-1}$ ($n=43$) para valores de pH de 5.06 y 5.09. La conductividad eléctrica en 2011 mostró una mediana y DMA de $5.10 \pm 2.58 \mu\text{S cm}^{-1}$ ($n=43$) variando entre $3.79 \mu\text{S cm}^{-1}$ y $11.14 \mu\text{S cm}^{-1}$. Se observó el efecto de dilución debido a una correlación negativa ($\alpha=0.05$) entre la concentración de iones hidrógeno y la tasa de precipitación diaria. Los flujos de deposición húmeda ácida fueron de $138.34 \pm 126.28 \text{ mol ha}^{-1} \text{ año}^{-1}$ y $106.40 \pm 99.23 \text{ mol ha}^{-1} \text{ año}^{-1}$ para concentraciones ponderadas por volumen de $(11.15 \pm 0.48) \mu\text{mol L}^{-1}$ y $(8.57 \pm 1.68) \mu\text{mol L}^{-1}$. Aunque las muestras de lluvia mostraron niveles de acidez y conductividad muy similares a los observados en otras regiones remotas de elevada altitud en zonas tropicales o en ciudades agrícolas con poca población e industrialización, es necesario continuar el monitoreo de la deposición húmeda debido a la fuerte susceptibilidad de los suelos a la lluvia ácida, y a la importancia de su productividad agrícola en la economía de la región.

Palabras clave: Lluvia ácida; deposición húmeda; neutralización de acidez libre; conductividad calculada; concentración ponderada por volumen.

Abstract

We reported here the acid deposition flux for a urban site at high altitude in La Hechicera, Venezuela (N08 37.728;W71 09.005; 1880 masl) using 24-h rainwater samples collected on a wet-only monitor and following protocols by the Global Atmospheric Watch Precipitation Chemistry Programme (GAW-PC) of the World Meteorological Organization. We conducted 120-d sampling campaigns on 2007-2008 and 2011 to assess the inter-annual variation. Median and absolute median deviation for the hydrogen ion concentrations were $(8.78 \pm 2.83) \mu\text{mol L}^{-1}$ ($n=34$) and $(8.15 \pm 3.59) \mu\text{mol L}^{-1}$ ($n=43$) for pH values of 5.06 and 5.09, respectively. Rain sample conductivity at 2011 showed a median and median absolute deviation of $5.10 \pm 2.58 \mu\text{S cm}^{-1}$ ($n=43$), meanwhile the 25% and 75% percentiles were $3.79 \mu\text{S cm}^{-1}$ and $11.14 \mu\text{S cm}^{-1}$. We found negative significant Pearson correlation factors ($\alpha=0.05$) between the hydrogen ion concentration and conductivity and daily precipitation rates. This is usually considered as a dilution effect. We did not find signals of long transport of polluted air masses from industrialized areas of surrounding states. The volume weighted average (VWA) concentrations for hydrogen ions were $(11.15 \pm 0.48) \mu\text{mol L}^{-1}$ and $(8.57 \pm 1.68) \mu\text{mol L}^{-1}$ and deposition fluxes were $138.34 \pm 126.28 \text{ mol ha}^{-1} \text{ year}^{-1}$ and $106.40 \pm 99.23 \text{ mol ha}^{-1} \text{ year}^{-1}$. Although rainwater samples showed acidity and conductivity levels similar to those observed in pristine areas of high altitude in tropical regions, and could be considered as typical for a small urban city

without industries and an agricultural background; the susceptibility of soils to acid rain and the importance of agriculture in the regional economy, are important reasons to do continuous monitoring of the deposition fluxes and rain chemistry.

Key words: Acid rain; conductivity calculation; Latin American; volume weighted average concentration.

1 Introducción

Acid rain is in the modern culture a synonym of air pollution, no doubt due to its relation to NO_x and SO_2 emissions from combustion processes. Its negative effects go from water acidification (lakes, rivers, etc.), changes in plant communities and forest growth to reduction in crops and fishery productivities and soil depletion (Charles, 1990);(Kuylenstierna, *et al.*, 2001);(Reynolds, *et al.*, 2000) when there is not enough buffer capacity in the environmental compartments where it is deposited. The whole natural equilibrium is altered. Plants and animals are damaged by exposure to toxic metals released during lixiviation of soil minerals (F. Menz, 2004);(Johnson, *et al.*, 1981). Not less important is the damage to art pieces, buildings and other structures exposed to acid rain.

Acid rain is one of the most studied atmospheric problems around the world, but not in Venezuela. This South American country lacks of atmospheric deposition and meteorological networks. There are sparse meteorological and small atmospheric chemistry stations, mainly around the most industrialized areas. However their information is not collected or analyzed for any institution, and if there are some results about this topic, they are not public or are available. In the absence of detailed emission inventories, the study of the atmospheric chemistry and the air quality is hard work. There is no way to know how the emissions coming from Venezuelan petrochemical and crude oil processing plants, the biggest ones in Latin America, are affecting the public health and natural systems. In 1989, rain samples collected by event in La Esperanza and Catatumbo, agricultural and uncultivated land areas downwind of the El Tablazo and Cardon-Amuay Oil and Petrochemical Complexes (Zulia State, Venezuela) and Aruba-Curacao refineries, showed volume weighted average pH values between 4.23 and 4.64 and individual values as low as pH 3.0, with an excess of 96% for non-sea salt sulfate, and a 93% of the acidity made up to inorganic acids, mainly sulfuric acid. The high levels of sulfate, nitrate and ammonium in all samples suggested a strong anthropogenic influence over rain chemistry (Morales *et al.*, 1998)

Our research pretends to highlight the need of a national/regional monitoring program for the atmospheric deposition flux around the country, especially for those areas where the crops and fishery productivities can be affected due to soils or lakes susceptible to the rain chemistry. Acid wet deposition fluxes between 0.01 and $0.05 \text{ kg ha}^{-1} \text{ month}^{-1}$ (equivalent to 0.12 and $0.60 \text{ kg ha}^{-1} \text{ year}^{-1}$) measured by Morales *et al.* (1998) were identified as problematic for ag-

riculture in the western Lake Maracaibo basin due to soils with high Fe and Al contents, low exchange capacities and acid pH values (4.0-6.0). The same situation can be expected for Mérida, a bordering state of Zulia, one of the most industrialized Venezuelan states where petrochemical, crude refining, and cement industries are the dominant ones. Half of the soils in Mérida state are acidic with low exchangeable base contents and therefore susceptible to acid rain deposition (Morales *et al.*, 1998);(López de Rojas, 1992) These soils have been classified as Level 2 in a system of classes of relative sensitivity of terrestrial ecosystems to acidic deposition developed by Kuylenstierna and col. (2001) based on base saturation (BS) and cation exchange capacity (CEC) average values from a reference soil database. Soils at this class have three different BS/CEC levels: BS between 0-20 % and CEC from $>25 \mu\text{eq } 100\text{g}^{-1}$, BS between 20-40 % and CEC from $10-25 \mu\text{eq } 100\text{g}^{-1}$, or BS between 40-60 % and CEC below $10 \mu\text{eq } 100\text{g}^{-1}$ (Kuylenstierna, *et al.*, 2001) The high precipitation rates in Mérida State guarantees an important role for the rain in the base cation pools of soils.

Mérida city is the capital of the state with the same name. It is at the end of Andes Mountain range in the top of South America. At 2012 Mérida State has an estimated population of 675,318 inhabitants, 53% of this total concentrated in the Libertador and Campo Elías municipalities (INE, 2012). Both municipalities have grown so fast during the last ten years that there are no longer borders between them, and currently both can be considered as the Mérida metropolitan area. Although there are not inventories for emissions, anthropogenic emissions have increased with a noticeable reduction in the city air quality, especially during the traffic peak hours There is, however, no way to measure or predict how the current growth of human activities is going to deteriorate the health of its natural systems and its population. Currently Mérida is considered as the one of the best touristic destination due to the life quality, spectacular mountain environments and the world longest cable car system that takes people close to Pico Bolívar (4,978 masl).

Mérida city is in a valley between two mountain ranges, and thermal inversion episodes are possible, therefore we need atmospheric research stations focused on the regular monitoring of the air quality before its decay to irreversible values.

In this study we measured acidity in rainwater samples collected in La Hechicera, one of the campuses of Universidad de Los Andes in Mérida city in Venezuela. We collected samples in two 120-day sampling campaigns at 2007-

2008 and 2011 in order to assess the inter-annual variability of the rain acidity. It is our best interest to provide information for policy-makers in order to avoid reaching critical loads with irreversible changes in natural systems and air quality.

2 Methodology

2.1 Sampling Monitoring Site

The sampling campaign was conducted at a urban site at high altitude in La Hechicera, Mérida, Venezuela (N08 37.728; W71 09.005; 1,880 masl). This site is at a temperate humid tropical climatic area. The monitoring site is ~3.6 km in straight line from Mérida downtown (Fig. 1). Mérida city is located on a plateau at 1,630 masl, in the small valley formed by the Chama and Albarregas rivers between the two mountain chains of Sierra Nevada and Sierra de La Culata, both in the Venezuelan Andes.

We used a wet-only rain sampler designed, tested and donated to our research group by the Stockholm University. The rain sampler was placed at the roof of the Engineering Building at La Hechicera Campus of Universidad de Los Andes (~25 m above street level). The sampler was placed 2 m above the floor. We avoid all possible interferences with buildings, other structures and vegetation. This site was selected due to its proximity to our laboratory for fast sample analysis after collection, its accessibility during all times of the year and its low risk of vandalism. The site is surrounded by the Pure Sciences and Architecture buildings that comprise La Hechicera campus. The campus is surrounded by green areas with low traffic density. The building complex is between mountains and shows apparently higher precipitation rates compared to the city. We were unable to find meteorological data during our sampling. However in order to assess the meteorological effects over rain chemistry, we used old data available from La Hechicera Station (2000 and 2002-2004). This station was placed at the roof of the Pure Sciences Building at La Hechicera Campus, very close to our sampling site. Average values from hourly data are shown at Table 1 for typical meteorological parameters. The local climate is characterized for low temperature, high humidity and rain, and calm winds mainly blowing from La Culata mountain (~ pristine areas). The rose wind (fig. 2) shows a wind resultant vector blowing from 313 degrees at 0.9 m s^{-1} . The distance and location of our sampling site from this met station can be seen at figure 3 in relation to the rose wind.

We must say that our site does not satisfy all requirements to be a regional station in accordance with WMO/GAW (World Meteorological Organization, 2004), because it is not entirely free of local pollution sources (~downtown city is 3.6 km away in straight line, 250 m below the station altitude) and it is not close enough to an active meteorological station with surface and rawinsonde

observations. We think, however that our sampling could help to estimate deposition fluxes representative of the surrounding few hundreds of kilometers. The position of our station relative to Mérida's downtown and other topographic details can be seen in three dimensional view on figure 1 (Grupo GPS_YV de Venezuela, 2011)

2.2 Sampling Campaign

In order to assess the inter-annual variability for the acid wet deposition flux, a first sampling campaign was carried out between December 12th, 2007 and April 14th, 2008. The precipitation coverage length (PCL) was 60% and the total precipitation (TP) was 94.1% for a total of 68 rain samples, 30 of which had not enough volume for pH measurements and 4 were contaminated. A second campaign was conducted between March 1st, 2011 and June 16th, 2011. The PCL and TP values were 82.4% and 73.2% respectively, for a total of 73 rain samples with 15 low-volume samples and 16 contaminated samples (mainly contaminated with insects). Both sampling periods satisfy the completeness criterion for measurement of precipitation depth and its related chemical analyses for quarter periods established by the OMM-GAW-PC program (World Meteorological Organization, 2004)



Fig. 1 Tridimensional view of the monitoring site relative to Mérida Downtown (Grupo GPS_YV de Venezuela, 2012)

2.3 Precipitation rates, Sampling Collection, preparation and Analysis

The wet-only rain collector was equipped with an electronic device to count the number of times the collector opens and the time during which the equipment remains opened. Those variables were recorded to estimate the number and length of precipitation events during the 24-h sampling period. We did not count with a rain gauge, and therefore daily precipitation rates and hourly precipitation rates were estimated from samples by weighting, the collection surface area and the time during which the collector was opened.

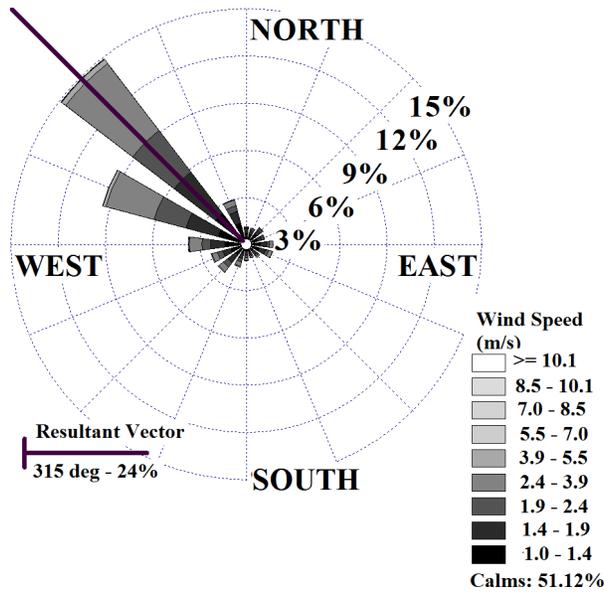


Fig. 2. Rose Wind for La Hechicera meteorological station (2000, 2002-2004) (Lakes Environmental Software, 2011 ; Red de Estaciones Bioclimáticas, 2007)

Table 1. Average values at La Hechicera meteorological station (2000, 2002-2004) (Red de Estaciones Bioclimáticas, 2007) (n: hourly data points)

Year	Air Temperature (deg C)	Relative Humidity (%)	Rain (mm)	Wind Speed (m s ⁻¹)	Pressure (bar)
2000 n=3814	16,8±3,7	87,6±14	0,1±1	0,9±0,9	978±320
2002 n=7497	17,5±3,9	94,7±11,1	0,2±1,3	1,1±1	995±424
2003 n=6272	17,2±3,8	88,8±15,1	0,1±1,1	1,1±1,1	996±427
2004 n=1376	16,2±3,9	87,1±14,9	0±0,3	0,1±0,4	997±411

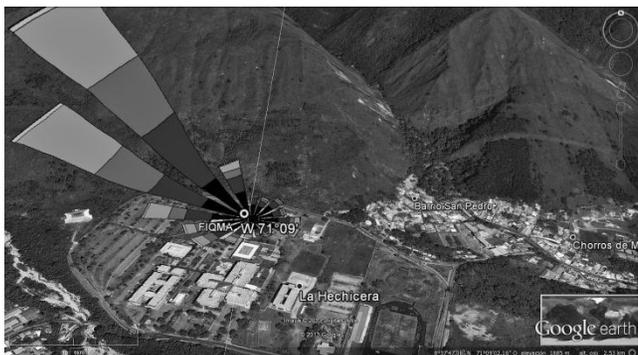


Fig. 3. Rose Wind for La Hechicera meteorological station (2000, 2002-2004) relative to the sampling site (Lakes Environmental Software WRPlot View, 2013; Google Earth, 2012; Red de Estaciones Bioclimáticas, 2007)

Clean high density polyethylene (HDPE) bottles were set every day at the wet-only rain sampler at 9 am, local

time, and collected 24 hours later. Samples were taken immediately to the lab for thermal equilibration and analysis. After that, sample volumes were measured by weighting and using a water density of 1 g cm⁻³ as a conversion factor. Sample weights were measured using an electronic scale with 0.01 g of tolerance and 3,100 g of capacity (PA3102 Pioneer, Ohaus, USA).

Samples were not filtered or treated with any biocide. The collector surface at the rain sampler was rinsed with deionized (DI) water every day before collecting a new sample. Pure ethanol (Riedel de Haën, Germany) was used to clean any carbonaceous deposits at the collector before rinsing if necessary.

Samples were analyzed for duplicate or triplicate when possible. All sampling and analytical procedures were done as possible in accordance with WMO/GAW criteria and standards (World Meteorological Organization, 2004). pH measurements were done with a digital pH-meter with 0.001 resolution (Orion-3 star, Thermo Fisher Scientific, USA). Calibration was done every day using pH 4 and 7 buffer solutions (Orion, buffer solutions from Thermo Electron Corporation, USA).

A different set of buffer solutions (biphthalate and phosphate solutions from J.T. Baker USA) were used to check that pH was ± 0.05 pH unit of the expected value (World Meteorological Organization, 2004). Sample conductivities were measured only at the second campaign using a digital conductivity meter with a range from 0.001 to 3000000 mS cm⁻¹ (Orion-3 star, Thermo Fisher Scientific, USA). A one-point calibration was conducted every day using a standard solution of 84.0 µS cm⁻¹ at 25 °C (Orion, buffer solutions from Thermo Electron Corporation, USA). Calibration was checked using a different standard solution with the same conductivity (KCl solution, Oakton, USA). All samples were handled with HDPE tools or contained in HDPE vessels. All materials were cleaned and rinsed with DI water (~1.0 µS cm⁻¹). The use of fresh DI water was impossible due to the lack of an ultrapure water production system at our lab. DI water was donated by other labs. However DI water conductivity was checked every day and water was not used when its conductivity was over 1.0 µS cm⁻¹. Contamination levels were tested using lab and field blanks prepared with DI water from rinses of laboratory materials, containers and the rainwater collector surface. Blanks were analyzed every 5 or 7 days and processed identical to the samples. Samples were frozen without adding any preservative for posterior atomic absorption analysis.

2.3 Statistical Analyzes and Calculations

pH and conductivities values from samples replicates were compared and averaged to find random errors associated with procedures. Samples with pH and conductivity values out of the range of three times the interquartile range were neglected from deposition calculations. Media values

for the pH and daily precipitation values from both campaigns were compared through t-test and F-test analyses. The normality of the data was verified through probability plots.

Deposition fluxes ($D \pm \sigma_D$) were calculated using volume weighted average concentrations and the mean precipitation depth (\bar{P}) using equations 1 and 2. Volume-weighted average concentrations ($VWA \pm \sigma_{VWA}$) for hydrogen ions using Eqs. 3 and 4. V_i and C_i represent volume and hydrogen ion concentrations for the i^{th} sample, n represents the total number of valid samples. σ_m represents the scale tolerance or error associated to sample weight, σ_c is the error associated to sample concentration, which is equal to standard deviation from sample replicates, or from the pH meter tolerance in case of samples without replicates.

$$D = VWA \times \bar{p} \quad (1)$$

$$\left(\frac{\sigma_D}{D}\right)^2 = \left(\frac{\sigma_{VWA}}{VWA}\right)^2 + \left(\frac{\sigma_p}{\bar{p}}\right)^2 \quad (2)$$

$$VWA = \frac{\sum_{i=1}^n (C_i \times V_i)}{\sum_{i=1}^n V_i} \quad (3)$$

$$\left(\frac{\sigma_{VWA}}{VWA}\right)^2 = \frac{\sum_{i=1}^n (C_i \times V_i)^2 \times \left[\frac{(\sigma_{C_i})^2}{(C_i)^2} + \frac{(\sigma_{m_i})^2}{(m_i)^2} \right]}{\left(\sum_{i=1}^n (C_i \times V_i) \right)^2} + \frac{n \times (\sigma_m)^2}{\left[\sum_{i=1}^n m_i \right]^2} \quad (4)$$

3 Results

3.1 Descriptive Statistics

Average daily precipitation rates for both campaigns per Julian day are shown in Figure 4. In the absence of meteorological data for our monitoring site, we also show average values for the same variable from the available data at the closest meteorological stations: La Hechicera (~200 m in straight line from our monitoring site) with data from 2000-2004 and Santa Rosa (~600 meters in straight line) with data from 1974-2001 (Grupo GPS_YV de Venezuela, 2011). There are more similarities between average daily precipitation rates at La Hechicera station and our sampling site. This will be considered later for annual precipitation depth calculations. Both stations were inactive during our sampling periods.

The annual variation of daily precipitation rates clearly show two peaks, one between April and May, and one from October to November, this behavior has been observed be-

fore and reported in the literature (Ferrer and López, 2004). Our sampling campaigns covered the first peak, but could not be extended during the whole year due to limitations in the deionized water supplies.

The hydrogen ion concentrations and pH of rainwater samples per Julian day are shown in Figure 5. There was a significant negative correlation factor of -0.349 ($p < 0.05$) between pH and Julian day for the first campaign, not observed in the second one. In this case, the hydrogen ion concentration correlates negatively with the Julian day ($r = -0.313$; $p < 0.05$), showing the opposite tendency at 2011. This agrees with the behavior observed for conductivity and Julian day for the same year. There was a significant negative correlation factor of -0.505 ($p < 0.05$) between conductivity and Julian day for the 2011 campaign. This could not be explained with our data and needs more future research.

Figure 6 shows the data distribution for daily and hourly precipitation rates, pH and conductivity for rainwater samples. Daily precipitation rates were higher at the second campaign, the distribution is right-tailed showing more frequent rain events in the range of 20 and 60 mm day^{-1} . As a matter of fact, the 75% percentile was 10 mm hr^{-1} higher for the second campaign in relation with the first one. t-comparison analyses between means at 95% confidence level confirmed this. The mean and mean absolute deviation values for both campaigns were respectively $4.03 \pm 2.35 \text{ mm day}^{-1}$ and $11.50 \pm 7.22 \text{ mm day}^{-1}$. Hourly precipitation rates behaves in the same way, the mean and mean absolute deviation values for both campaigns were respectively $5.27 \pm 3.29 \text{ mm hr}^{-1}$ and $8.19 \pm 4.61 \text{ mm day}^{-1}$.

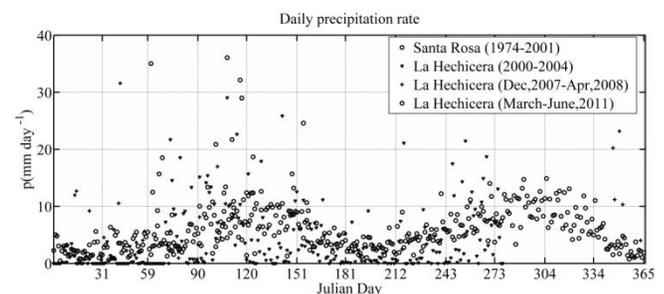


Fig. 4 Daily precipitation rates of the monitoring sites in relation with data from the closest meteorological stations

On the contrary, the mean pH values of rainwater samples for both campaigns are not significantly different from each other at 95% confidence level. The 75% percentiles are around 5.23 units showing a limit in the alkaline region for rainwater pH. This value is related with "clean atmospheres" where natural emitted carbon dioxide is the main acidic source (J. H. Seinfeld, 1997). However, lower pH values were observed at the second campaign, the 25% pH-percentiles were 4.82 and 4.94, respectively. This suggests an increase in the acidic sources, mainly because more intense precipitation events were registered and dilution was not observed. Conductivity values for the second campaign were at low level (e.g. compared to tap water) and similar to

those observed in the pristine regions (Beiderwieden E. , 2005);(Honório, *et al.*, 2010);(Sanhueza, *et al.*, 1999). The median and median absolute deviation was $5.10 \pm 2.58 \mu\text{S cm}^{-1}$, the 25% and 75% percentiles were $3.79 \mu\text{S cm}^{-1}$ and $11.14 \mu\text{S cm}^{-1}$. This could indicate an effective neutralization process between cations and anions in rainwater samples, as well as an absence of free hydrogen ions from strong acids such as nitric and sulfuric acid, produced under anthropogenic influence. This will be explored later.

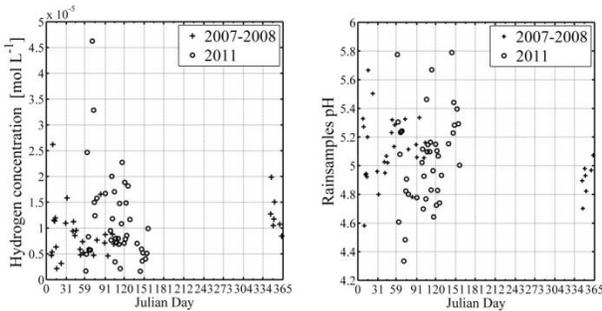


Fig. 5. Hydrogen ion concentration and pH in rainwater samples from La Hechicera, Venezuela

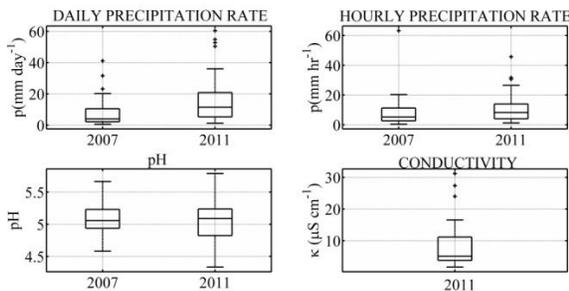


Fig. 6 Descriptive statistics for daily and hourly precipitation rates, pH and conductivity values per sampling campaigns (MAD: median absolute deviation)

It is difficult to compare our results with others, because there are not many. The most recent were published in 1990's and 2000's and performed at the Canaima National Park, the sixth largest in the world with 30000 km², tropical humid moonsonic climate (Rubel, 2010) pristine characteristics and average annual precipitation rates of 1500 mm (Sanhueza, *et al.*, 2003). Results from places in Venezuela and Latin America with similar geographic and meteorological characteristics are shown in Table 2. Pristine areas in La Gran Sabana (Venezuela), Parintins (Brazil) and Podocarpus National Park (Andes mountain chain, Ecuador) showed very similar acidity and conductivity levels in rainwater samples. Although it is necessary to perform a complete chemical characterization to our samples, it is evident that there is not a strong influence of anthropogenic sources. Our rain acidity levels reflect natural sources possibly represented by organic compounds, normally present in natural atmosphere coming from vegetation and acid compounds scavenged from soil suspended particles. This agrees with

the fact that prevailing winds at the sampling site come from a pristine area at the Culata mountain chain. Lower pH-values at specific days could be related with winds blowing from downtown city carrying acids from vehicle emissions or from Santa Rosa where agriculture and livestock emissions can carry other ions to rainwater and modify its composition. Studies on chemical composition of rainwater samples in La Gran Sabana, Venezuela (cited in Table 2) found that 64% of the rain acidity in rural areas could be explained by the formaldehyde, the formic and acetic acids, also produced by oxidation of natural emitted hydrocarbons (Sanhueza, *et al.*, 2005). The low conductivity in our samples could be explained by the low dissociation of these organic acids. Earlier studies done in the savannah climatic region of Venezuela found that 50 % of the anion content in rainwater was due to the dissociation of formic and acetic acids (Sanhueza, *et al.*, 1992) .

Table 2 pH and conductivity average values for different sampling sites around the world

Sampling Site	Climate and other characteristics	AAPR (mm)	T (°C)	A (mosl)	VWA - pH	VWA-κ
La Hechicera, Venezuela (2007-2008) *This study	Urban, temperate humid tropical (Cfb) ¹ or Gmi ²	684, [423-1342]*	16, [13-20]*	1880	4.95 (n=34)	-
La Hechicera, Venezuela (2011) *This study	Urban, humid subtropical ¹	684, [423-1342]*	16, [13-20]*	1880	5.07 (n=43)	5.13 (n=43)
Parupa, Gran Sabana, Venezuela (Sanhueza, <i>et al.</i> , 2005)	Tropical humid moonsonic (Ami) ²	1611	[17-24]	1226	5.09 (n=207)	7.49 (n=194)
Yuruaní, Gran Sabana, Venezuela (Sanhueza, <i>et al.</i> , 2005)	Tropical humid moonsonic, (Ami) ²	2548	[17-24]	878	5.49 (n=12)	4.17 (n=12)
Kanavayen, Gran Sabana, Venezuela (Sanhueza, <i>et al.</i> , 2005)	Tropical humid moonsonic, (Ami) ²	2552	[17-24]	1200	5.18 (n=51)	4.51 (n=51)
Podocarpus National Park, Ecuador (Beiderwieden E. , 2005)	Humid tropical (Cfb) ¹	1500	10	2825	5.26 (n=11)	6 (n=11)
Parintins, Brazil (Honório, <i>et al.</i> , 2010)	Amazon, urban agricultural region, Tropical monsoon climate (Am) ¹	2452	[24-31]	28	5.0 (n=82)	6.4 (n=82)
Maracaibo, Venezuela (Sánchez, <i>et al.</i> , 2009)	Tropical Savannah (Aw) ³ affected by anthropogenic emissions	517.4			4.8 (n=91)	-

AAPR: Average Annual precipitation (mm)
T: Average Daily Temperature and Range (oC)

A: Altitude (masl)

VWA -pH: Volume Weighted Average pH

VWA-κ: VWA-Conductivity (μS cm-1)

1 (Rubel, 2010) 2 (Foghin-Pillin, 2002) 3 (Sanhueza, *et al.*, 1987)

On the contrary, Camburito (Sanhueza, *et al.*, 1992);(Sanhueza, *et al.*, 1987) and Maracaibo (Sánchez, *et al.*, 2009) have shown acid rain episodes with average pH values under 4.8. These monitoring sites are affected by polluted emissions coming from the most industrialized areas in Venezuela; one city is close to the Maracay-Valencia-Caracas group, Venezuelan largest industrial area; and the other is close to the largest oil refineries and petrochemical complexes in Latin America.

In order to assess the role of hydrogen ions in the conductivity levels of our 2011 samples, we used the pH, the molar conductivity at infinite dilution for the hydrogen ions and calculate the possible carbonate ion concentrations in accordance with WMO/GAW methods to predict conductivity samples (World Meteorological Organization, 2004). Measured and calculated conductivities, as well as discrepancies between both can be seen in Figure 7. The Pearson correlation factor between variables was 0.802 ($p < 0.05$, $n=42$) indicating the strong influence of hydrogen ions in the electrical conductivity of aqueous solutions. With few exceptions, all samples were between the acceptable discrepancies or under their lower limit as expected when the rain chemical composition is incomplete. This is an important result because over predictions could be a signal of contaminated samples.

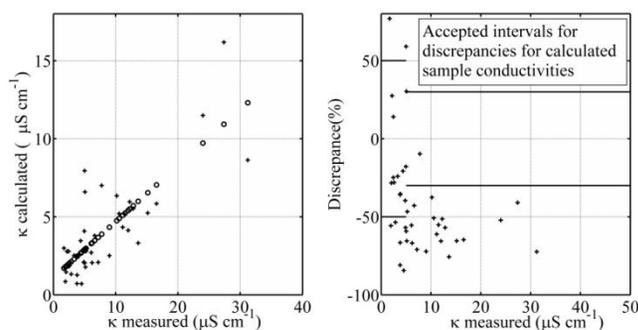


Fig. 7 Calculated and measured conductivity for rainwater samples 2011 campaign from La Hechicera, Venezuela

4.2 Pearson Correlation Coefficients

Table 3 shows the Pearson correlations coefficients and their p-values in order to explore possible linear relations between precipitation rates and pH or conductivity values for our rainwater samples. Strong linear correlations (0.833 and 0.828, $p < 0.05$) were seen in both campaigns between daily and hourly precipitation rates, this could suggest that the precipitation events were so long that the rain collector was opened during all the sampling period. There were not more significant correlation factors for the first campaign. For the second campaign there were significant negative correlation factors ($p < 0.05$) between daily and hourly precipitation rates and hydrogen concentrations and conductivity. Those correlations represent a dilution effect,

if acid sources were local and fixed in magnitude, more intense precipitation events should produce diluted samples. It is necessary to highlight that there are not governmental emissions inventories for Mérida. By observation we know that our monitoring site is mainly affected by emissions from vegetation and vegetation burning, agricultural activities with use of poultry litter as fertilizer, livestock, laboratory hoods at the university and vehicles. Traffic is low, the road is ~50 m in straight line from our monitoring site, traffic rates are below 800 vehicles per day with average speeds under 15 miles per hour.

Table 3 Pearson correlation factors for each sampling campaign dataset
Lower triangular matrix: 2007-2008 ($n=34$) Upper triangular matrix:
2011($n=43$)

r^2	dp	hp	[H ⁺]	pH	κ	log10(dp)
dp	1	0,823	-0,338	0,393	-0,459	0,874
hp	0,833	1	-0,285*	0,311	-0,430	0,746
[H ⁺]	nss	nss	1	-0,889	0,801	-0,304
pH	-0,325*	-0,296*	-0,937	1	-0,699	0,317
log10(dp)	0,863	0,665	nss	-0,297*	-0,502	1

Variables: dp: daily precipitation rate, hp: hourly precipitation rate, κ : conductivity, [H⁺]: hydrogen ion molar concentration
nss: not statistically significant at $\alpha=0.1$ or at $\alpha=0.05$
* Significant at $\alpha=0.1$

4.3 pH vs. Precipitation

Figure 8 shows how the hydrogen ion concentration, pH and conductivity change with the daily precipitation rate for our rainwater samples. The dilution effect was confirmed; the higher the precipitation rates, the lower the hydrogen ion concentration, the higher the pH sample value and the lower the sample conductivity. The same behavior is observed for both campaigns. As it was mentioned before, this suggests that local sources could be responsible for the rain acidity observed at La Hechicera. There are not points out of the data general tendency, which suggests that there is not long-range transport of polluted air masses from industrial regions of the surrounding states.

4.4 Volume Average Weighted concentrations and Wet deposition fluxes

Volume-weighted average values for the hydrogen concentration, pH and conductivity of rainwater samples are reported in Table 4. Due to the lack of meteorological data for our sampling periods, the annual precipitation depth used for deposition calculations was the 2000-2004 average annual precipitation depth of 864 mm (see Table 1) measured at La Hechicera Meteorological Station. Due to its proximity to our monitoring site, this station was preferred before Santa Rosa Station, although its 40-year data base (1974-2001).

We must remember that pH mean values for both campaigns were not significant different from each other at 95% confidence level, meanwhile the mean values for daily precipitation rates were higher at the second campaign. This explains the higher value for the volume-weighted average pH in 2011 compared to 2007-2008, as well as the lower deposition flux for the 2011 campaign.

At La Hechicera, Venezuela, the wet acid deposition flux varied from 0.11 to 0.14 kg ha⁻¹ year⁻¹. Similar deposition fluxes (~0.1 kg ha⁻¹ year⁻¹) were estimated at the central west part of the United States of America for 2007-2010 (National Atmospheric Deposition Program (USA), 2010) Venezuela does not have a national atmospheric deposition program, and therefore there is not data to compare with, just few studies done independently by researchers from national universities.

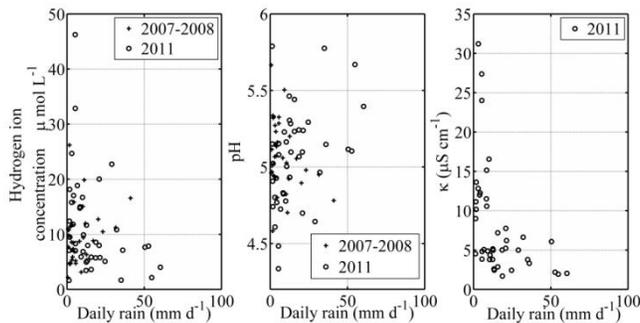


Fig. 8 Variation of hydrogen concentration, pH and conductivity of rainwater samples as a function of daily precipitation rates at La Hechicera, Mérida, Venezuela

The 1982-1984 average bulk acid deposition flux was 0.03 kg ha⁻¹ year⁻¹ (Montes and San Jose, 1989) and the VWA-pH was 5.8 units (Montes, *et al.*, 1985) at a Trachypogon savanna in Calabozo, Venezuela (8 o 56' N; 67 o 25'W). Although this is also a pristine area, soils from this region are also acidic with low CEC, as soils around our monitoring site, and the annual precipitation rate is 1228 mm, comparable to the maximum annual precipitation depth for our site; strong differences exist for acid sources (mainly vegetation burning), type of vegetation, soil use and soil geomorphology and composition.

A more recent study reports a 1989-2001 average wet acid deposition flux of 0.075 kg ha⁻¹ year⁻¹ for Maracaibo city (Zulia state, Venezuela). The average annual precipitation rate was 517.4 mm and the volume weighted average hydrogen concentration was 14.4 μeq L⁻¹ for a pH of 4.8 units. Our deposition flux looks much larger than this, giving us the false sense of a more polluted atmosphere. However we must consider that our volume weighted average hydrogen concentration for 2011 was 8.56 μeq L⁻¹, almost half of Maracaibo's value. The big difference is caused by the annual precipitation rate that in our case can be as high as 1342 mm. Besides, the authors found abundant ammoni-

um, calcium and magnesium that neutralized sulfate, nitrate and chloride ions, leaving just 5 % of free acidity in rain (Sánchez, *et al.*, 2009). Maracaibo is the second largest city in Venezuela with an estimated population of around 2 million people; it has very well developed industries of crude oil extraction, cement and fertilizer manufacture, etc., besides it receives marine emissions from the Maracaibo Lake. These important differences make us impossible to compare our results with those for this city.

Table 4. Volume Weighted Average hydrogen ion concentrations and acid we deposition fluxes at La Hechicera, Venezuela

Sampling Campaign	Dec. 2007- Apr. 2008 (n=34**)	March-June, 2011 (n=42)
VWA-κ: (μS cm ⁻¹) ± σ (μS cm ⁻¹)	-	5.134 ± 0.122
Volume Weighted Average Concentration (mol L ⁻¹) ± σ (mol L ⁻¹)	1.115*10 ⁻⁵ ± 4.842*10 ⁻⁷	8.574*10 ⁻⁶ ± 1.682*10 ⁻⁶
VWA -pH	4.94	5.07
Deposition Flux* (g ha ⁻¹ year ⁻¹) ± σ (g ha ⁻¹ year ⁻¹)	138.34 ± 126.28	106.40 ± 99.23

* Using the median and median absolute deviation as equivalent values for precipitation depth and its error

** Samples minus those samples with values out of the 3*IQR range for pH

Conclusions

Rainwater samples from La Hechicera, Venezuela showed acidity and conductivity levels similar to those observed in pristine areas of high altitude in tropical regions, even though the monitoring site was close to a city downtown with an estimated population for 2012 of 248,433 inhabitants and could be exposed to local pollutant sources from traffic and long-range transport of air masses.

The agriculture and fishing are the most important economical activities in Mérida, and although the estimated wet acid deposition flux was low (~0.1 kg ha⁻¹ year⁻¹) it is necessary to continue the atmospheric deposition monitoring due to the susceptibility of soils to acid deposition. Venezuelan soils, especially those in Merida State, are mainly acidic, susceptible to acid precipitation due to their low cation exchange capacities (CEC) and high exchangeable aluminum contents (Sanhueza, *et al.*, 1988). Soils around our monitoring site, in the Santa Rosa Area (8°38' 21'' N; 71° 08' 48''W; 1900 masl) are classified as inceptisols (Humic Dystrudepts, NRCS-USDA) with metamorphic and igneous rocks with few signals of mechanical erosion. pH values are from 5.9 to 5.3, CEC values from 16 to 4, base saturation values from 58.8 to 9.7 %, and aluminum contents from 0 to 1.4 cmol kg⁻¹ from 0 to 1 m of depth (Ferrer and López, 2004). Those characteristics indicate susceptibility to acid deposition (Kuylenstierna, *et al.*, 2001);(Sanhueza, *et al.*, 1988). However from the data obtained in this study, it is impossible to predict how crop productivity could decrease with an increase in atmospheric

deposition fluxes.

Additional research contributions are related to the generation of data for deposition fluxes and chemical composition of rainwater for a region where this type of data is scarce and usually not accessible to researchers around the world. We also established the laboratory procedures and equipment to continue the monitoring of chemical rainwater composition in accordance with international standards.

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References

- Beiderwieden E TW and Klemm O, 2005, Chemical characterization of fog and rain water collected at the eastern Andes cordillera, *Hydrol. Earth Sys. Sci. Discuss.*, Vol. 2, No. pp. 863-885.
- Charles DF, 1990, Effects of acidic deposition on North America lakes: palaeolimnological evidence from diatoms and chrysophytes, *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, Vol. 4, No. pp. 403-412.
- Ferrer G and López R, 2004, Topsoil loss compost addition and crop yield in an inceptisol of the venezuelan Andes, *Revista Geográfica Venezolana*, Vol. 45, No. 2, pp. 153-164.
- Foghin-Pillin S, 2002, *Tiempo y Clima en Venezuela: Aproximación a una geografía climática del territorio venezolano*. 1st ed. Vicerrectorado de investigación y postgrado de la Universidad Pedagógica Experimental Libertador. Caracas. p. 159. pp.159.
- Grupo Gps_Yv De Venezuela. Mapa digital de Venezuela. Accessed on Se encuentra en: www.gpsv.net. Fecha de consulta: Marzo, 2012
- Honório BaD, Horbe AMC and Seyler P, 2010, Chemical composition of rainwater in western Amazonia -- Brazil, *Atmospheric Research*, Vol. 98, No. 2-4, pp. 416-425.
- Inc. G, 2012, Google Earth (Versión 7.0.2.8415) [Software] Se encuentra en: <http://www.google.com/earth/download/ge/agree.html>
- INE. Censos de población y vivienda. Censo 2001. Instituto Nacional de Estadística República Bolivariana de Venezuela. Se encuentra en: http://www.ine.gov.ve/index.php?option=com_content&view=category&id=95&Itemid=26. Fecha de consulta: Enero, 2012
- Johnson NM, Driscoll CT, Eaton JS, Likens GE and McDowell WH, 1981, Acid rain, dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire, *Geochimica et Cosmochimica Acta*, Vol. 45, No. 9, pp. 1421-1437.
- Kuylenstierna JCI, Rodhe H, Cinderby S and Hicks K, 2001, Acidification in Developing Countries: Ecosystem Sensitivity and the Critical Load Approach on a Global Scale, *Ambio*, Vol. 30, No. 1, pp. 20-28.
- Lakes Environmental Software L (2011) WRPLOT VIEW (Versión 7.0.0) [Software] Se encuentra en: <http://www.weblakes.com/products/wrplot/index.html>
- López De Rojas I, Gilabet De Brito, J., García, E. , 1992, Características de Acidez de los suelos Venezolanos, vista a través los resúmenes de análisis rutinarios, FONAIAP DIVULGA, Vol. 2007, No. Enero-Marzo, pp. 1-2.
- Menz HS, 2004, Acid rain in Europe and the United States: an update, *Environmental Science & Policy*, Vol. 7, No. pp. 253-265.
- Montes R and San Jose JJ, 1989, Chemical Composition and Nutrient Loading by Precipitation in the Trachypogon Savannas of the Orinoco llanos, Venezuela, *Biogeochemistry*, Vol. 7, No. 3, pp. 241-256.
- Montes R, San Jose JJ and García-Miragaya J, 1985, pH of bulk precipitation during 3 consecutive annual courses in the Trachypogon savannas of the Orinoco Llanos, Venezuela, *Tellus*, Vol. 37B, No. pp. 304-307.
- Morales JA, Bifano C and A Escalona, 1998, Atmospheric Deposition of SO₄-S and (NH₄+NO₃)-N at two rural sites in the Western Maracaibo Lake Basin, Venezuela, *Atmospheric Environment*, Vol. 32, No. 17, pp. 3051-3058
- National Atmospheric Deposition Program (USA) N-. Annual MDN Maps for 2007-2010. Se encuentra en: <http://nadp.sws.uiuc.edu/mdn/annualmdnmaps.aspx>. Fecha de consulta: Marzo, 2012
- Red De Estaciones Bioclimáticas ULA (2007) Datos Meteorológicos para la Estación La Hechicera Mérida. (Lagula) LDGDLUDLA Data from Se encuentra en <http://www.cecalc.ula.ve/redbc>
- Reynolds B, Wood MJ, Truscott AM, Brittain SA and Williams DL, 2000, Cycling of nutrient base cations in a twelve year old Sitka spruce plantation in upland mid-Wales, *Hydrology and Earth System Sciences*, Vol. 4, No. 2, pp. 311-321.
- Rubel F and Kottek M, 2010, Observed and projected climate shifts 1901-2100 depicted by world maps of the Köppen-Geiger climate classification, *Meteorologische Zeitschrift*, Vol. 19, No. pp. 135-141.
- Sánchez L, Morales J, Velázquez H, Portillo D, Cano Y, Montilla B, Iriarte Nand Mesa J, 2009, Composición Iónica y niveles de acidez de las lluvias en Maracaibo, Venezuela, entre 1989-2001, *Rev. Int. Contam. Ambient.*, Vol. 25, No. 3, pp. 169-179.
- Sánchez JO and Ochoa J, 1998, Suelos de la Cuenca del Santo Domingo, Secto El Baho (Caracterización Físico-Química) Mérida- Venezuela, *Revista Forestal Venezolana*,

Vol. 42, No. 1, pp. 71-77.

Sanhueza E, Alfonzo Y and Santana M, 2003, Compuestos orgánicos volátiles en la atmósfera de la Gran Sabana. II: HCHO, HCOOH y CH₃COOH en lluvias, *Interciencia*, Vol. 28, No. 1, pp. 29-35.

Sanhueza E, Arias M, Donoso L, Graterol N, Hermoso M, Martí I, Romero J, Rondón A and Santana M, 1992, Chemical composition of acid rains in the Venezuelan savannah region, *Tellus*, Vol. 44B, No. pp. 54-62.

Sanhueza E, Cuenca G, Gómez MJ, Herrera R, Ishizaki C, Martí I and Paolini J. Characterization of the Venezuelan Environment and its potential for acidification. On Acidification in tropical countries. John Wiley & Sons Ltd. 197-255.

Sanhueza E, Donoso L, Santana M, Fernández E and Romero J, 1999, Atmospheric Chemistry over the Auyantepuy, *Interciencia*, Vol. 24, No. 6, pp. 372-380.

Sanhueza E, Graterol N and Rondón A, 1987, Rainfall pH in the Venezuelan savannah, *Tellus*, Vol. 39B, No. pp. 329-332.

Sanhueza E, Santana M, Donoso Land Pacheco M, 2005, Química atmosférica en la Gran Sabana III: Composición iónica y características ácido-básicas de las lluvias, *Interciencia*, Vol. 30, No. 10

Seinfeld JH and Pandis PS (1997) *Atmospheric Chemistry and Physics : Air Pollution to Climate*. ed. Wiley, John & Sons, Incorporated. New York, USA.

World Meteorological Organization GaW, 2004, Manual for the GAW Precipitation Chemistry Programme, GAW Precipitation Chemistry Science Advisory Group WMO Vol. 160, No. 1251.

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