

Cationes base en la lluvia de Los Andes Venezolanos en la Hechicera, Venezuela

Base cations in rainwater from a Venezuelan Andes urban site at la Hechicera, Venezuela

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Resumen

Son escasos los estudios sobre química atmosférica para Sur América, especialmente para Venezuela. Aquí se muestra el análisis de la composición química de muestras de lluvia recolectadas diariamente en La Hechicera (Mérida, Venezuela) bajo la modalidad sólo lluvia. El muestreo (Marzo-Junio 2011) cumplió con los criterios internacionales para la cobertura de precipitación (82.4 %) y completitud de la composición química para Ca^{+2} y Mg^{+2} (77.2 %, $n=73$), Na^+ (60.4 %, $n=34$) y K^+ (63.3%, $n=38$). En todas las muestras, las concentraciones de Ca^{+2} y Mg^{+2} estuvieron por debajo de los límites de detección ($\text{Ca}^{+2} < 1.8 \mu\text{eq L}^{-1}$; $\text{Mg}^{+2} < 0.4 \mu\text{eq L}^{-1}$). Las concentraciones ponderadas por volumen para K^+ y Na^+ fueron respectivamente $0.04 \pm 0.01 \text{ ppm}$ ($1.0 \mu\text{eq L}^{-1}$) y $0.14 \pm 0.04 \text{ ppm}$ ($6.2 \mu\text{eq L}^{-1}$); para flujos de deposición húmeda equivalentes a $49 \pm 46 \text{ mg m}^{-2} \text{ año}^{-1}$ ($130 \mu\text{g m}^{-2} \text{ año}^{-1}$) y $177 \pm 168 \text{ mg m}^{-2} \text{ año}^{-1}$ ($480 \mu\text{g m}^{-2} \text{ día}^{-1}$). Los valores de pH y conductividad fueron usados para estimar la fracción desconocida de la composición química, y la fracción ácida, estimándose valores promedios de $31.7\% \pm 22.9\%$ para la fracción ácida; y $2.9 \text{ ppm} \pm 2.6 \text{ ppm}$ para la concentración iónica. Esto indicó que un $92.0\% \pm 15.3\%$ de la composición química es desconocida. Los bajos valores para la concentración de cationes base, sodio y conductividad de las muestras sugieren una atmósfera limpia con emisiones naturales. La correlación positiva entre los iones K^+ y H^+ , y Na^+ y H^+ sugieren a la quema de biomasa (madera, vegetación) como principal fuente. Los bajos valores para los flujos de deposición húmeda para los cationes base representan un problema a futuro, pues si la deposición atmosférica no compensa los iones lixiviados, los suelos merideños pudieran perder sus nutrientes y la capacidad para ser cosechados.

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

Abstract

Atmospheric chemistry studies are scarce for South-American, especially for Venezuela. We studied the rainwater chemistry of La Hechicera (Mérida, Venezuela) using 24-h samples collected using a wet-only rain collector from March, 2011 to June, 2011. Samples were analyzed using atomic absorption spectroscopy for base cations (K^+ , Ca^{+2} and Mg^{+2}) and sodium (Na^+), pH and conductivity using the international suggested standards methods. We reached a precipitation coverage of 82.4 % and a total precipitation of 77.2 % for calcium and magnesium; 60.4% for sodium and 63.3% for potassium. Calcium and magnesium concentrations were under detection limits ($n=73$; $< 1.8 \mu\text{eq L}^{-1}$ and $< 0.4 \mu\text{eq L}^{-1}$ for calcium and magnesium respectively). For potassium and sodium we found volume-weighted average concentrations of $0.04 \pm 0.01 \text{ ppm}$ ($1.0 \mu\text{eq L}^{-1}$) and $0.14 \pm 0.04 \text{ ppm}$ ($6.2 \mu\text{eq L}^{-1}$), and wet depositions fluxes of $49 \pm 46 \text{ mg m}^{-2} \text{ year}^{-1}$ ($130 \mu\text{g m}^{-2} \text{ day}^{-1}$) and $177 \pm 168 \text{ mg m}^{-2} \text{ year}^{-1}$ ($480 \mu\text{g m}^{-2} \text{ day}^{-1}$), respectively. We used pH and conductivity values to estimate the ionic mass concentrations and the acid fraction of samples. Average values were $31.7\% \pm 22.9\%$ for the acid fraction and $2.9 \text{ ppm} \pm 2.6 \text{ ppm}$ for the ionic mass concentration. This suggested that $92.0\% \pm 15.3\%$ of the rain composition was unknown. Even though the low levels for base cation concentrations and conductivity, and the low acid fractions and the low ionic mass

concentrations in our samples indicated a clean atmosphere, mainly affected by natural emissions. Positive correlation factors between K^+ and H^+ and Na^+ and H^+ suggested the biomass burning as a possible source for these ions. The low levels of base cations in rain represent a future problem because if atmospheric deposition cannot compensate the cation losses, Mérida's soils can become deficient in nutrients.

Key words: Acid rain; wet deposition, free acidity, conductivity calculation; volume weighted average concentration.

1 Introducción

Atmospheric deposition is fundamental for the equilibrium of biogeochemical cycles. The weathering of soil parent rock material releases minerals from soils, leaving them free to be transported to the atmosphere as airborne particles (soil dust). When soil dust is scavenged by water droplets, minerals in their ionic form can be deposited over terrestrial and aquatic surfaces by rain, mist, fog, snow or ice, or simply by mechanical processes such as sedimentation or interception. Both pathways are identified as wet and dry deposition respectively (J. H. Seinfeld, 1997). Wet deposition has been widely studied in the last decades, mainly due to its negative role (acid rain, eutrophication, nuclear rain, etc.) However its positive side effects can be seen when nutrients, such as potassium and calcium, are deposited over poor soils (Montes and San Jose, 1989) or aminoacids over lakes where fishery occurs (Méndez, 2009)

This study pretended to know more about the wet deposition flux at La Hechicera, Mérida, Venezuela. It was focused on potassium, magnesium, calcium and sodium rainwater concentrations. The first three ions are grouped and identified as base cations, because they help to regulate the soil pH, buffer the acid inputs from precipitation and plant decomposition, and provide the plant macronutrients (Green, et al., 2004). Atmospheric deposition and weathering are the major inputs to the soil base cation pool, meanwhile harvesting and leaching are the sinks. Weathering is a very slow process, therefore if deposition cannot compensate the cation losses, soils can become deficient in nutrients (Akselsson, et al., 2007), especially if rains and soils are acidic. Hydrogen ions can break the electrostatic attractions that keep bonded the base cations to the clay particles and organic matter, leaving them free to be leached from the soil matrix (Green, et al., 2004)

Base cations also play an important role regulating the pH of rainwater and together with ammonium and hydrogen ions are the most important contributors to the positive ionic charge and electrical conductivity of rainwater (Hedin and Likens, 1996). Nitric and sulphuric acids, formed in the presence of water and nitrogen and sulphur oxides from the combustion emissions of biofuels (wood, vegetation, etc.) or fossil fuels, can be neutralized by base cations in raindrops. As an example of this process, Tirupati, an industrialized city of India, showed alkaline rains with pH ranging from 6.13 to 7.74 not due to lack of acidity but rather due to an excess of basic cations, especially calcium, com-

ing from alkaline soil dust (Chandra Mouli, et al., 2005). Another example can be seen in rains from Maracaibo city, Venezuela; where ammonium (industrial and natural emissions), calcium and magnesium (from marine and crustal sources) neutralize sulfate, nitrate and chloride ions (from industrial emissions), leaving just 5 % of free acidity in rain (Sánchez, et al., 2009).

Base cations are essential nutrients for plant development and growth. Their ionic forms allow the root development and chlorophyll production (Navarro and Navarro, 2003). In soils, together with sodium, they define the soil resistance to acidification, its ionic exchange capacity and its base saturation (Akselsson, et al., 2007). Studies on Central Amazonian forests showed that fine root growth is restricted by both soil pH and low Ca. Higher fine root production was observed after addition of $CaCl_2$ and $CaCO_3$ using ingrowth bags (Luizão et al., 2007)

If base cations are present in rainwater with specific ratios and correlations between them, it is possible to identify the emission sources affecting a monitoring place. For example, marine sources can be identified if ions such as sodium, chloride, magnesium and potassium, are present with ratios between them of 1.8 for Cl^-/Na^+ , 0.04 for K^+/Na^+ and Mg^{+2}/Na^+ , 0.12 for Ca^{+2}/Na^+ (Chandra Mouli, et al., 2005); and also if they show good correlations with chloride concentrations ($r^2 > 0.60$ at 95% confidence level) (Tiwari, et al., 2007) If crustal emissions are present there must be good correlations between one another for Ca^{+2} , Na^+ , Mg^{+2} and K^+ (Tiwari, et al., 2007). Crustal emissions are an important source when a factor analysis reveals good correlations between concentrations of K^+ , Al^{+3} , Cr^{+2} , Mg^{+2} , Ca^{+2} , Ni^{+2} , Sr^{+2} , Ti^+ , NO_3^- and SO_4^{-2} . This has been observed in rainwater samples collected close to unpaved roads (Türküm, et al., 2008; Artiñano, et al., 2009). Good correlations with Na^+ , Ca^{+2} , Mg^{+2} , NH_4^+ , Cl^- , and SO_4^{-2} concentrations are expected for marine sources (Jacobson, 2002). A good correlation between Ca^{+2} and Mg^{+2} suggests crustal sources such as unpaved roads, wind blown dust from bare soils and ploughing (Zunckel, et al., 2003). Sources for each ion can be numerous, and each one has specific ratios for ionic concentrations in atmospheric samples. In the case of sodium, its non-marine sources can be ethanol and wood burning with a Cl^-/Na^+ ratio of 0.26 and cement particles from construction areas (Dos Santos, et al., 2007). In the case of potassium, its crustal sources can be potassium feldspar ($KAlSi_3O_8$) from granite rocks and potassium oxide K_2O (Jacobson; Adams, 1995), fertilizers (Muriate of Potash

KCl, Sulfate of Potash K_2SO_4 ; Potassium Magnesium Sulfate $K_2SO_4 \cdot 2MgSO_4$; Nitrate of Potash KNO_3 ; potassium phosphate KH_2PO_4 ; potassium carbonate K_2CO_3 ; potassium hydroxide KOH; potassium thiosulfate $K_2S_2O_3$, marine spray and wood burning. Potassium is also a tracer of wood burning emissions (J. H. Seinfeld, 1997), also has been detected together with calcium ions after episodes of vegetation burning (Sanhueza, et al., 1992) Potassium can be scavenged from coarse particles from soil weathering and from fine particles in wood combustion gases (Zunckel, et al., 2003). In general, sources of the same nature can be expected for calcium and magnesium. Minerals in soil dust containing calcium and magnesium can be calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4 \cdot 2H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$) (Jacobson, 2002). Other calcium sources can be biomass and vegetation burning, but in this case calcium concentrations in rainwater are well correlated to the other basic cations and also to organic acids such as formic acid (Sanhueza, et al., 2003), and NO_3^- and SO_4^{2-} concentrations (Jacobson, 2002).

Although the available literature offers thousands of papers about the chemical composition of rainwater for North America, Asia and Europe, there are very few studies about rain chemistry in Venezuela. Those available are focused on highly industrialized cities or pristine or rural places in preserved areas such as national parks. In general, almost nothing is known about the atmospheric chemistry for the rest of the country. We studied the chemical composition of rainwater samples collected at La Hechicera, Venezuela in order to continue a previous study on acid wet deposition, the first one for our city. Our inter-annual comparison study at this monitoring site showed acidity and conductivity levels similar to those observed in pristine areas of high altitude in tropical regions. Weighted average pH values were 4.97 ($n=34$, 2007-2008) and 5.07 ($n=42$, 2011), while the weighted average conductivity was $5.13 \pm 0.12 \mu S cm^{-1}$ ($n=42$, 2011). The average acid wet deposition flux was $122 \pm 114 g ha^{-1} year^{-1}$, reflecting the highly variable annual precipitation rates during years.

Our study gained an initial understanding of rainwater chemistry in order to know more about the influence of anthropogenic activities over the atmosphere and soils, especially about the processes affecting the base cation pool of soils. This is particularly important because Mérida's economy is mainly based on agriculture, and their soils are acidic with low cation exchange capacities and base saturation values, showing a remarkable susceptibility to acid rain and base cation deposition, especially due to the high annual precipitation rates.

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). The monitoring site is inside La Hechicera Campus of Universidad de Los Andes, ~3.6 km in straight line from Mérida downtown (Figure 1). The site is surrounded by green areas (with pine forests), it has paved and unpaved roads with low traffic rates. Although there are not emission inventories for Mérida State, our site could be affected by combustion emissions from vehicles and vegetation burning, chemicals from laboratory hoods, fertilizers and other substances coming from agricultural activities and dairy cattle at Santa Rosa (< 1 Km in straight line from the site). The campus is practically enclosed by mountains from La Culata mountain chain. As winds blow typically from there, natural emissions from vegetation and soil weathering are likely. These mountains belong to the La Culata National Park. There are evidences of a particular microclimate for this area, especially because shows higher precipitation rates compared to the city. (Red de Estaciones Bioclimáticas, 2007). The relation between pH and precipitation rates from our previous study did not show signals of long-range transport of air masses from more polluted areas. More details about Mérida State can be found elsewhere (Calderón, et al., 2013).



Fig. 1. Rose Wind for La Hechicera meteorological station (2000, 2002-2004) relative to the sampling site, labeled as LAB FIQMA (WRPlot View Lakes Environmental Software, 2011; Google Earth, 2012; Red de Estaciones Bioclimáticas, 2007)

We used a wet-only rain sampler designed, tested and donated to our research group by the Stockholm University. The rain sampler was positioned and operated following the recommendations presented by the Global Atmospheric Watch- Precipitation Programme from the World Meteorological Organization (WMO/GAW-PC) (World Meteorological Organization, 2004).

2.2 Sampling Campaign, Sampling Collection, preparation and Analysis

24-hour samples were collected from March 1st, 2011 and June 16th, 2011. The completeness criterions (WMO/GAW-PC) for precipitation monitoring were over passed for a quarter period with values of 82.4% (World Meteorological Organization, 2004). We collected a total of

73 rain samples, 15 of them were contaminated (mainly with insects), leaving a total of 58 valid samples, from which just 43 samples had enough volume for pH and conductivity measurements. The Total Precipitation (TP), variable that represents the completeness of precipitation depth associated with valid chemical analysis and valid sample collection (World Meteorological Organization 2004) was 77.2 % for calcium and magnesium; 60.4% for sodium and 63.3% for potassium. TP values were lower for sodium and potassium because some samples could not be analyzed immediately after defrosting and were lost. In all cases TP values were over 60% as required for a quarter period (World Meteorological Organization, 2004)

Daily precipitation rates were estimated using the collection surface area, sample weights and monitoring time. Hourly precipitation rates were estimated using the time during which the collector was opened. There were not active meteorological stations around our lab during our sampling period.

Immediately after collection and thermal equilibration, samples were weighted and frozen in high density polyethylene (HDPE) bottles without filtration or biocide addition. Sample weights were measured using an electronic scale with 0.01 g of tolerance and 3,100 g of capacity (PA3102 Pioneer, Ohaus, USA). 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 rain collector before rinsing with DI if necessary.

All materials were washed with distilled water and rinsed with DI water ($\sim 1.0 \mu\text{S cm}^{-1}$). The use of fresh DI water was impossible; however the conductivity was checked every day and water was not used when it overpasses the limit of $1.0 \mu\text{S cm}^{-1}$. Contamination levels were tested using lab and field blanks prepared with DI water from rinses of laboratory materials, containers and the rain-water collector surface. Lab and field blanks were analyzed every 5 or 7 days and processed identically to the samples.

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. The protocols followed for conductivity and pH measurements can be found elsewhere (Calderón, et al., 2013). Basic cations were measured by atomic absorption (AAS) and atomic emission spectrometry (AES) using a Spectrophotometer (VARIAN, SpectrAA55B, EE.UU). Individual calibration curves with five points were prepared by sequential dilution from 1000 ppm certified standard solutions (UltraScientific, USA) by weighting using a micro-analytical scale (Tolerance 0.0001 g, Denver Instrument Company AA-160). Three standard check solutions per ion were prepared from 1000 ppm certified standard solutions from a different supplier (MERCK, Germany). Standard check solutions (0.25 ppm and 0.5 ppm for sodium and potassium, 0.1 and 0.25 ppm for calcium and magnesium) were always $\pm 20\%$ around the expected values. In order to

avoid interferences, a solution of Cesium-Lanthanum (1 ppm CsCl₂ and 0.5 ppm La₂O₃ from) was added to all calibration and check solutions, samples and blanks as suggested by WMO/GAW-PC (World Meteorological Organization, 2004). All solutions were prepared using fresh deionized water. Calcium and Magnesium were measured by AAS using an acetylene/nitrous oxide flame with individual hollow cathode lamps (VARIAN, EE.UU) at 422.7 nm and 285.2 nm, respectively. Sodium and potassium were measured by AES at 589 nm and 766.5 nm using an air/acetylene flame. Correlation coefficients for all calibration curves were higher than 0.999. Detection limits were estimated using the IUPAC method (Harris, 2001) and their values were 0.035 ppm, 0.005 ppm, 0.009 ppm and 0.0024 ppm for calcium, magnesium, potassium and sodium, respectively.

2.3 Statistical Analyzes and Calculations

Results from sample replicates were compared and averaged to find random errors associated with procedures. In the case of sodium and potassium, blank concentrations were subtracted from sample concentrations in order to isolate the atmospheric sources. This procedure was not necessary for calcium and magnesium. The normality of the data was verified using probability plots. Correlation coefficients and comparison analyses were calculated with a 95 % confidence level.

Deposition fluxes ($D \pm \sigma D$) were calculated using volume weighted average concentrations and the mean precipitation depth (\bar{P}) with their errors using equations presented everywhere (Calderón, et al., 2013).

3 Results

3.1 Descriptive Statistics

During 108 days of monitoring we collected 73 rain-water samples. The average daily precipitation rate was $16.4 \pm 15.6 \text{ mm d}^{-1}$. Quartiles for this variable were [5.4, 11.5, 20.9] mm d^{-1} with a median absolute deviation of 7.2 mm d^{-1} . The sampling site has a rainy weather during the whole year with two peaks; one between April and May and one between October to November (Ferrer and López, 2004). We chose to monitor the first peak especially because there are frequent vegetation burning episodes or forest fires at this time of the year. Quartiles for sample pH and conductivity were [5.24, 5.09, 4.82] and [3.79, 5.10, 11.14] $\mu\text{S cm}^{-1}$ with an absolute median deviation of 2.58 $\mu\text{S cm}^{-1}$ and a maximum value of 31.29 $\mu\text{S cm}^{-1}$. Levels for acidity and conductivity were similar to those measured in remote areas (affected just by natural emission sources and/or few antropogenic sources) as explained in previous studies (Calderón, et al., 2013)

Sodium, potassium and hydrogen ions concentrations

are shown in Figure 2, together with the conductivity of the rainwater samples and the daily precipitation rate for every Julian day. There were not visible correlations between concentrations, as it is expected when there are common sources for ions. For example when fertilizers (e.g. potassium-magnesium sulfate) are used around sampling sites, raindrops could contain them from scavenging of airborne particles; and we should find that the higher the concentration of potassium the higher the concentration for magnesium is in the rain samples.

All rainwater samples ($n=73$), even those contaminated with insects or particles, and lab and field blanks, had concentrations of Ca^{+2} and Mg^{+2} under the detection limit (<0.035 ppm equivalent to $1.75 \mu\text{eq L}^{-1}$ for Ca^{+2} and <0.005 ppm equivalent to $0.41 \mu\text{eq L}^{-1}$ for Mg^{+2}). In order to confirm this, a couple of samples were sent to a different laboratory for atomic absorption analyzes. Concentrations were under 0.101 ± 0.003 ppm for calcium and $0.0028 \text{ ppm} \pm 0.0001$ ppm for magnesium. This confirmed our laboratory results.

It is hard to explain the low levels of calcium and magnesium in our samples. We were expecting to find calcium in our samples because it is known that calcium is a major component in mineral soils in tropical mountain ecosystems such as those at the Andean ecosystems. Due to the higher precipitation rates and annual rainfall, Ca^{+2} should be present in rain droplets after particle scavenging during the erosion-leaching-dissolution-precipitation cycle (González and Aristizábal, 2012). Calcium volume-weighted mean average concentrations ranging from $14.6 \mu\text{eq L}^{-1}$ to $17.3 \mu\text{eq L}^{-1}$ were measured in rain from a bulk sampler at three sites in the Colombian Andes close to Manizales city (Colombia). Authors indicated that volcano ashes could be a source for calcium due to the proximity of Nevado del Ruiz volcano (González and Aristizábal, 2012). If we consider that the cloud formation is taking place in a mountain region where glacier rocks are highly resistance to weathering, there will not be enough minerals for rain scavenging. After comparisons between this study and ours, we could suggest that rain itself does not contain much Ca^{+2} and Mg^{+2} and the main source is dust and dry deposition.

34 samples were analyzed for sodium, ten of them showed concentrations under the detection limit (<0.0024 ppm). Three samples showed concentrations out of the interval of three times the interquartile range (IQR). This could suggest long-range transport of air masses from sodium sources (e.g. Maracaibo's Lake); however there is no way to know more without air trajectories or concentrations for anions, such as chloride ions. We determined a median and median absolute deviation equal to 0.040 ± 0.027 ppm. 25th and 75th percentiles were 0.023 ppm and 0.090 ppm, with minimum and maximum values of 0.0103 ppm and 0.440 ppm. Sodium concentrations are low as expected for continental areas due to the long distance between the sea and our sampling site.

38 samples were analyzed for potassium, six of them were under the detection limit (<0.009 ppm) and just one was out of the $3 \times \text{IQR}$ interval. The median and absolute deviation was 0.090 ± 0.055 ppm. 25th and 75th percentiles were 0.049 ppm and 0.360 ppm, with minimum and maximum values of 0.0103 ppm and 1.375 ppm.

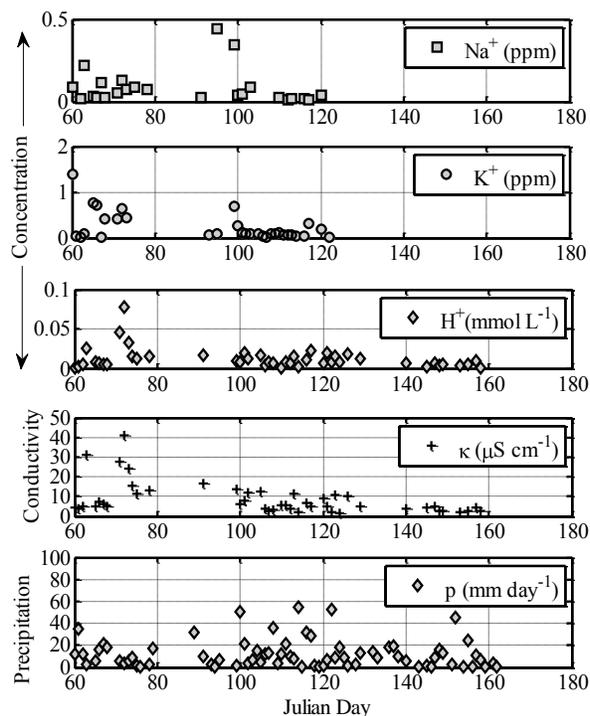


Fig. 2 Variation of cation concentration, conductivity and daily precipitation during the sampling period (March to June, 2011)

These results were very similar to those found at El Tiro (Ecuador), a meteorological station (2825 mosl, 1500 mm) in the Podocarpus National Park at the eastern Andes Cordillera at 100 Km from the coast; where the median, minimum and maximum values were 0.09 ppm, <0.09 ppm and 1.17 ppm for K^{+} ; and 0.10 ppm, 0.10 ppm and 0.40 ppm for Na^{+} . After a detailed chemical characterization of fogwater and rainwater samples in conjunction with a study of air trajectories, they found signature ions from anthropogenic emissions just in fogwater (hydrogen, ammonium, nitrate and sulfate ions). Rainwater was less loaded with compounds from ground-based emissions because raindrops were formed at very higher altitude compared to fog droplets (Beiderwieden E., 2005)

Figure 3 shows the box plots for each ion concentration as well as for pH and conductivity. Concentrations and conductivity values show right-tailed log-normal distributions.

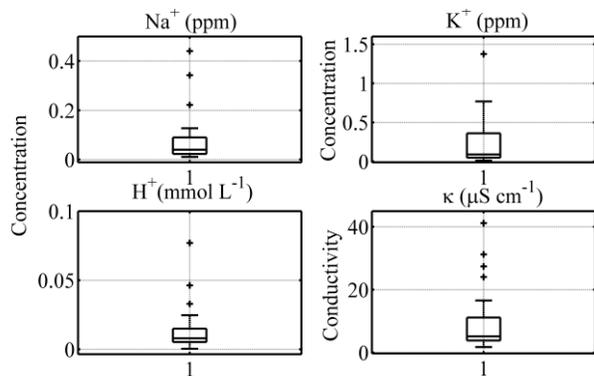


Fig. 3 Distribution of cation concentrations and conductivity of rainwater samples from La Hechicera, Venezuela

3.2 Completeness of the rain chemical composition

The rain chemistry from our study lacks of data for other important ions such as ammonium, phosphate, nitrate and sulfate. They are signature ions for emissions coming from agriculture and cattle activities, and for NO_x and SO_2 from combustions emissions, respectively. All of these sources were possibly affecting our sampling site, but without more information are impossible to distinguish.

We used two different approaches in order to assess the completeness of the rain chemical composition of our samples, as well as the weight of the unknown species over the total concentration. A first method is based on the behavior of ions in diluted solutions (e.g. 10^{-3}M) such as rainwater samples. In this case each ion in solution contributes to the total conductivity in a proportion equal to its concentration and its limiting ionic molar conductivity or ionic molar conductivity at infinite dilution according to equation 1. Using the ionic molar conductivity at infinite dilution at 25°C for the typical ions found in rainwater, we can predict the sample conductivities and compare it with measured values. The completeness of the rain chemical composition is assessed through the difference between measured and calculated conductivities. Acceptable differences (\sim complete rain chemical composition) are $\pm 50\%$ for measured conductivities under $5\ \mu\text{S cm}^{-1}$ and $\pm 30\%$ for measured conductivities higher than $5\ \mu\text{S cm}^{-1}$ but lower than $30\ \mu\text{S cm}^{-1}$ (World Meteorological Organization, 2004). In our study we predicted samples conductivities using the sample pH, the molar conductivity at infinite dilution and measured concentrations for hydrogen, sodium and potassium ions. We also used the sample pH to estimate carbonate ion concentrations in accordance with WMO/GAW methods (World Meteorological Organization, 2004). There was a strong and positive correlation factor ($r^2=0.885$, $p<0.05$) between measured and calculated values (Fig. 4). 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.

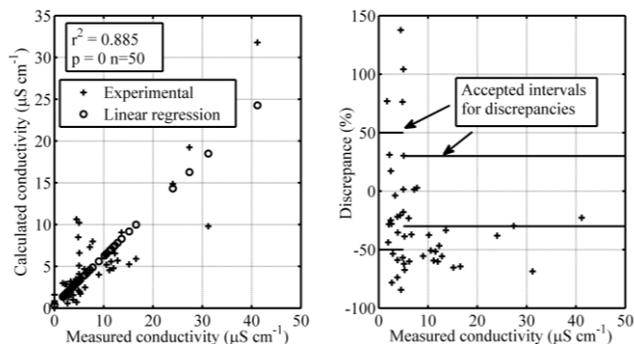


Fig. 4 Measured and calculated conductivities of rainwater samples from La Hechicera, Venezuela

Our second assessment of the rain chemistry completeness was based in the method proposed by Kramer et al. (1996) to estimate the sample ionic concentration and the sample acid fraction using just the sample pH and conductivity. This method uses the same principle of proportionality between the sample conductivity, the limiting ionic molar conductivity and concentrations of ions. As explained in Kramer et al. (1996), if we eliminate the hydrogen ion contribution to the total conductivity, the residual must be proportional to an equivalent solute concentration and a weighted mean equivalent conductivity of all ions in solution, except hydrogen ions. The authors found that the ionic molar fractions were acceptable weighting factors. This was also true for weighted mean equivalent conductivities of cations and anions individually. Using the experimental ionic concentrations in rainwater samples from several studies, they found similar weighted mean equivalent conductivities for sampling sites with similar geographic and atmospheric conditions. They actually suggested that the mean equivalent conductivity do not change significantly with changing ionic composition (Krämer, *et al.*, 1996)

In order to prove if the Kramer's estimation method was consistent and applicable to Venezuelan sampling sites; we used results for the chemical composition of rainwater samples collected at sites with similar geography, clima and meteorological conditions. In our case those sites were at pristine areas in La Gran Sabana (Bolívar State, Venezuela) Parupa, Kanavayen and La Paragua (Sanhueza, *et al.*, 2005) We calculated average weighted mean equivalent conductivities equal to $0.0685\ \mu\text{Scm}^{-1}\mu\text{eq}^{-1}\text{L}$, $0.0598\ \mu\text{Scm}^{-1}\mu\text{eq}^{-1}\text{L}$ and $0.0698\ \mu\text{Scm}^{-1}\mu\text{eq}^{-1}\text{L}$ for solution, cations and anions, respectively. Our values were comparable to those found by Kramer et al. (1996) for mountain regions with rural background. We actually confirmed that small changes in rain composition produce very small changes in the weighted mean equivalent conductivities (solution, anionic and cationic)(Krämer, *et al.*, 1996).

$$[on]_{eq} \left(\frac{\mu eq}{L} \right) = \frac{\kappa - [H^+] \Lambda_{eq} H^+}{\Lambda_{eq}} + [H^+] \quad (1)$$

$$[on]_{mass} \left(ppm \right) = \frac{\kappa - [H^+] \Lambda_{eq} H^+}{\Lambda_{mass}} \quad (2)$$

$$AF = \frac{[H^+] \Lambda_{eq} Cat + \Lambda_{eq} An}{[H^+] \Lambda_{eq} H^+ + \Lambda_{eq} Cat} \quad (3)$$

The acid fraction represents the free acidity, including the hydrogen ions coming from atmospheric CO₂ absorption, therefore the sample ionic concentration (eq.1) includes the carbonate species (HCO₃⁻ and CO₃⁻²). An acid fraction of 20% indicates that 20% of the dissolved species are free acids (Krämer, *et al.*, 1996)

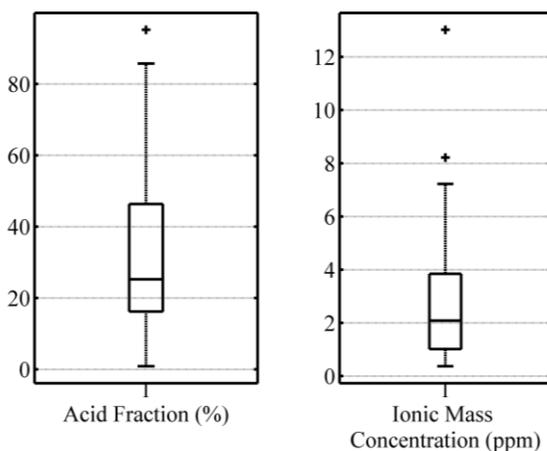


Fig. 5 Predicted values for acid fraction and ionic composition for rainwater samples from La Hechicera, Venezuela

Figure 5 shows distributions for the ionic mass concentration and acid fraction of our rainwater samples. Mean values for both variables (n=40) were 31.7% ± 22.9 % and 2.9 ppm ± 2.6 ppm respectively. Quartiles for the acid fraction were 16.2%, 25.3% and 46.4 %. Those values were similar to those found by Kramer *et al* (1996) for mountain sites with low anthropogenic influences. Quartiles for the ionic mass concentration were 1.01 ppm, 2.09 ppm and 3.85 ppm; and corresponded to equivalent ionic concentrations of 31.0 μeq L⁻¹, 58.4 μeq L⁻¹ and 110.4 μeq L⁻¹. Low acid fractions and low ionic mass concentrations in our samples suggested a clean atmosphere, mainly affected by natural emissions (e.g. organic acids). This is the expected behavior if prevailing winds blow from La Culata national park, a pristine place. A similar set of results was found at El Tiro

(Ecuador) where the total median ion equivalent concentration of rainwater samples was 34.4-34.8 μeq L⁻¹, pH ranged from 4.54 to 5.61 and the electrical conductivity from 3 μS cm⁻¹ to 11 μS cm⁻¹ (Beiderwieden E., 2005)

The main goal of this approach was to know more about the completeness of our chemical analyses for rainwater samples. In that sense, we estimated for each sample the unknown fraction of the chemical composition using the difference between the sum of all base cations and the estimated ionic mass concentration. The average value for this residual was 92.0 % ± 15.3 %, which indicated the need for more analyses. Only six samples showed overestimation of their compositions (negative residuals) suggesting good sample handling.

We did not measure ammonium ion, which is most likely main neutralizing cation. Future studies must be focused in this ion in order to have more information about the acid fraction.

3.3 Effect of the precipitation rate and possible ion source

Figure 6 shows how the precipitation rate affected the base cation concentration, pH and conductivity for our rainwater samples. All variables show the typical behavior of sites affected by sources with constant emission rates, where higher precipitation rates produce a dilution effect on the rain composition. The higher the precipitation rate the lower the potassium, sodium and hydrogen concentration and the conductivity are. The potassium ions show unexpected peaks for low precipitation rates, maybe associated with potassium emissions in winds blowing from Santa Rosa, where fertilizers are commonly used in agriculture. The dilution effect for acidity was proved for our samples in a previous study. The correlation factor between the hydrogen ion concentration and the daily precipitation rate was -0.338 (p<0.05, n=43) (Calderón, *et al.*, 2013). This number was different from those reported in Tables 1 and 2 for the same pair of variables. Because we could not determine potassium and sodium concentrations in all our rainwater samples, tables 1 and 2 show Pearson correlation factors for sampling days where potassium and sodium concentrations, and pH and conductivity could be measured simultaneously in our rainwater samples. This reduced our total number of points, and therefore our ability to observe the right behavior of variables. For example, in the case of hydrogen ions and daily precipitation rates from potassium data, there was a negative and significant correlation factor of -0.349 (p<0.05, n=27) but at 93 % confidence level instead of 95%. This was not the case for conductivity, its negative and significant correlation with the daily precipitation rate reproduced our last results with a r² of -0.515 (p<0.05)(Calderón, *et al.*, 2013).

Log-normal concentrations of potassium ions were negatively correlated to daily precipitation rates with a r² of -0.385 (p<0.05), and to log-normal precipitation rates with a r² of -0.441 (p<0.05). These significant and negative corre-

lations were not seen for hourly precipitation rates; however they confirmed the dilution effect mentioned before.

The opposite applied to sodium ions, their log-normal concentrations were negative and significant correlated ($r^2 = -0.486$, $p < 0.05$, $n = 20$) to hourly precipitation rates but not to daily precipitation rates. This was difficult to explain especially due to the small number of points. However we could think that sodium is not entirely coming from a local source, and therefore its concentration depends strongly on wind speed and direction and on the time at which the collector was opened.

Rather weak relation between precipitation rate and cation concentrations show that the main source is not through rain itself, but through dry deposition, which is then washed by rain from surfaces.

Log-normal concentrations of potassium and sodium ions were positively correlated to conductivity with Pearson correlation factors of 0.45 ($p < 0.05$, $n = 27$) and 0.51 ($p < 0.05$, $n = 20$), respectively. This was expected because the higher the ionic concentration in solution the higher its ability to conduct electricity is. Because all ions do not transfer electricity at the same rate, the Pearson correlation factors for potassium and sodium ions were half the value of those observed for hydrogen ions ($r^2 = 0.89$ and $r^2 = 0.94$; $p < 0.05$). Hydrogen ions are better conductors.

An interesting correlation was observed between H^+ and K^+ ions, and H^+ and Na^+ ions. Even when K^+ and Na^+ concentrations did not show a linear correlation between them (not even their log-normal values), maybe due to the small number of points analyzed ($n = 17$, $p > 0.05$); each one of the ions showed individually, a positive correlation factor with H^+ ions, $r^2 = 0.40$ ($n = 27$, $p < 0.05$) for potassium and $r^2 = 0.47$ ($n = 20$, $p < 0.05$) for sodium. Without more information about which anions were present in our rainwater samples, it was difficult to precise explanations for this behavior. However it is known that potassium phosphate (KH_2PO_4) is used as a fertilizer, and its dissolution would produce hydrogen and potassium ions. Also cropping and grassland preparation can produce high levels of K^+ in rain (Zunckel, et al., 2003) In the case of Na^+ it is more difficult to find acidic sources. Biomass burning is an important source of organic acids and particles that maybe after rain scavenging releases K^+ and Na^+ originally present in vegetation (Zunckel, et al., 2003)

Table 1. Pearson Correlation Factors ($p < 0.05$) for potassium concentrations

Variables	r^2 (n = 27)
dp vs. hp	0.846
κ vs. dp	-0.515
dp vs $\log_{10}(K^+)$	-0.385
$\log_{10}(dp)$ vs K^+	-0.403
$\log_{10}(dp)$ vs $\log_{10}(K^+)$	-0.441
κ vs. hp	-0.427
H^+ vs κ	0.890

H^+ vs K^+	0.430
H^+ vs $\log_{10}(dp)$	-0.392
H^+ vs $\log_{10}(hp)$	-0.488
H^+ vs $\log_{10}(K^+)$	-0.385
pH vs κ	-0.694
pH vs $\log_{10}(dp)$	0.382
pH vs $\log_{10}(hp)$	0.396

Table 2. Pearson Correlation Factors ($p < 0.05$) for sodium concentrations

Variables	r^2 (n = 20)
dp vs. hp	0.755
κ vs. dp	-0.413
hp vs Na^+	-0.435*
hp vs $\log_{10}(Na^+)$	-0.486
$\log_{10}(dp)$ vs Na^+	-0.378*
$\log_{10}(dp)$ vs $\log_{10}(Na^+)$	-0.411*
$\log_{10}(hp)$ vs Na^+	-0.571
$\log_{10}(hp)$ vs $\log_{10}(Na^+)$	-0.594
H^+ vs $\log_{10}(Na^+)$	0.405*
κ vs. hp	-0.427
H^+ vs κ	0.940
H^+ vs Na^+	0.474
H^+ vs $\log_{10}(hp)$	-0.418*
H^+ vs $\log_{10}(K^+)$	-0.385
pH vs κ	-0.681
κ vs. $\log_{10}(dp)$	-0.453
κ vs. $\log_{10}(hp)$	-0.511
κ vs. $\log_{10}(Na^+)$	0.510

*Significant at $\alpha = 0.1$

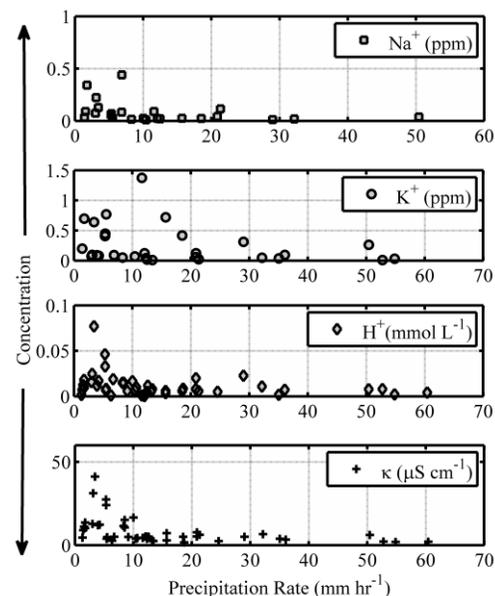


Fig. 6 Relations between cation concentrations and conductivity of rainwater samples and daily precipitation rates

3.4 Wet Deposition fluxes

Volume-weighted average concentrations were 0.039 ± 0.008 ppm ($1.0 \mu\text{eq L}^{-1}$) for potassium and 0.143 ± 0.037 ppm ($6.22 \mu\text{eq L}^{-1}$) for sodium. VWAC's at La Paragua, Guri and Parupa in La Gran Sabana (Bolívar State) were $1.08 \mu\text{eq L}^{-1}$, $0.23 \mu\text{eq L}^{-1}$ and $1.05 \mu\text{eq L}^{-1}$ for potassium and $3.5 \mu\text{eq L}^{-1}$, $1.34 \mu\text{eq L}^{-1}$ and $2.71 \mu\text{eq L}^{-1}$ for sodium. Authors associated these levels of ions in rain with little anthropogenic influence by comparison with the rain chemistry of remote continental sites at Europe and North America (Sanhueza, et al., 1992). These sites at the Venezuelan savannah region have similar altitude, geological characteristics and annual precipitation compared to our site. In the Koppen climatic classification, it is classified as tropical humid monsoonic (Sanhueza, et al., 1992), while our site is temperate humid tropical (Rubel, 2010), however our samples were comparable to those from these sites in terms of their acidity and conductivity levels too. There are not more Venezuelan studies to compare with.

Wet depositions fluxes were $49 \pm 46 \text{ mg m}^{-2} \text{ year}^{-1}$ ($130 \mu\text{g m}^{-2} \text{ day}^{-1}$) and $177 \pm 168 \text{ mg m}^{-2} \text{ year}^{-1}$ for potassium and sodium respectively ($480 \mu\text{g m}^{-2} \text{ day}^{-1}$). At the time of this study we could not find more wet deposition fluxes at similar site to compare with. Bulk deposition fluxes for these ions were measured between 1981 and 1983 at Calabozo, Venezuela. This region belongs to the Orinoco Llanos, and it has a different climate with mean annual rainfall of 1228 mm and mean annual temperature of 26 °C. Mean average values were $361.3 \text{ mg m}^{-2} \text{ year}^{-1}$ and $594.5 \text{ mg m}^{-2} \text{ year}^{-1}$ for potassium and sodium respectively (Montes and San Jose, 1989). These fluxes are higher than ours values. Authors indicated that biomass burning to obtain palatable and nutritional food-stuffs for cattle, was the most important source of K^+ and Na^+ . They found relatively higher concentrations of phosphate, sulfate, calcium, magnesium, potassium and sodium in the particulate matter collected (Montes and San Jose, 1989).

4 Conclusions

Results from base cations, pH and conductivity of rainwater samples suggested that La Hechicera is not particularly affected by antropogenic emissions from vehicles, agricultural or cattle activities from the surrounding areas. If rain is formed at high altitudes in La Culata mountain chain, where the atmosphere is not loaded with anthropogenic emissions from the ground, the in-cloud scavenging gives to the future rain droplets a natural chemical composition. If then rainclouds travel from this direction to our site, and very few pollutants are available from ground-based emissions, after the below-cloud scavenging, rain will contains just the natural compounds expected from a mountain site, and washed from surfaces containing the dry deposition. This is certainly a good finding however it is necessary to carry out a detailed chemical characterization of fog and

rainwater samples when "natural" conditions still prevail at the atmosphere in order to identify possible future impact of anthropogenic emissions.

The low rainwater concentrations of base cations, especially calcium and magnesium, represent a future problem. Without enough base cations to neutralize the free acidity in rain, an increment in the antropogenic emissions coming from growing residential areas, will affect not only the rain acidity but also the quality of soils. If we remember soil weathering is a very slow process, therefore if deposition cannot compensate the cation losses, soils can become deficient in nutrients.

Acknowledgments

This research has been sponsored by Consejo de Desarrollo Científico Humanístico, Tecnológico y de las Artes de la Universidad de Los Andes Project I-1067-07-08-A. The authors are grateful by the donations and advising giving by the University of Stockholm, Laboratorio de Fenómenos Interfaciales, Reología y Procesos (FIRP-ULA), the Laboratorio de Mezclado, Separación y Síntesis Industrial (LMSSI-ULA) and Laboratorio de Espectroscopía Molecular de la Universidad de Los Andes. They made possible this research.

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Recibido: 07 de mayo de 2012

Recibido: 20 de marzo de 2013

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