

# Atmospheric Pollution Research

[www.atmospolres.com](http://www.atmospolres.com)


## Chemical characteristics of rainwater at a southeastern site of Brazil

Marcos Rodrigues Facchini Cerqueira, Marcelo Fonseca Pinto, Ingrid Nunes Derossi, Wesley Tinoco Esteves, Mellina Damasceno Rachid Santos, Maria Auxiliadora Costa Matos, Denise Lowinsohn, Renato Camargo Matos

NUPIS (Núcleo de Pesquisa em Instrumentação e Separações Analíticas), Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora, 36036–330, Juiz de Fora, MG, Brazil

### ABSTRACT

A total of 50 rainwater samples were analyzed in order to investigate trace elements in wet precipitation of Juiz de Fora City, during February, 2010 and February, 2011. Samples were analyzed for major cations ( $\text{H}_3\text{O}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) and anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), some trace metals ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ), as well as some other physicochemical aspects like pH, conductivity and redox potential. Rainwater pH mean was of 5.77 ( $\pm 0.52$ ). Cations and anions mean values ranged from 7.12  $\mu\text{Eq L}^{-1}$  ( $\text{K}^+$ ) to 39.6  $\mu\text{Eq L}^{-1}$  ( $\text{Ca}^{2+}$ ). Principal Component Analysis (PCA) with Varimax normalized rotation was performed, grouping the major analyzed cations and anions into different factors.  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were assigned to soil contribution,  $\text{Na}^+$  and  $\text{Cl}^-$  to sea-salt contribution and  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  to anthropogenic sources. Hydrogen peroxide average concentration was of 19.2 $\pm$ 17.5  $\mu\text{mol L}^{-1}$  with higher values in summer and lower in spring and autumn, reverse case was observed for  $\text{H}_3\text{O}^+$  levels.  $\text{Zn}^{2+}$  (7.31 $\pm$ 2.74)  $\mu\text{g L}^{-1}$  and  $\text{Cu}^{2+}$  (4.07 $\pm$ 0.74)  $\mu\text{g L}^{-1}$  were within the range of other studied areas, while  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were below the detection limit.

**Keywords:** Rainwater, chemical composition, acidification process, marine contribution, source identification



**Corresponding Author:**

**Renato Camargo Matos**

☎ : +55-32-2102-3310

☎ : +55-32-2102-3309

✉ : [renato.matos@ufjf.edu.br](mailto:renato.matos@ufjf.edu.br)

**Article History:**

Received: 26 September 2013

Revised: 17 December 2013

Accepted: 01 January 2014

doi: 10.5094/APR.2014.031

### 1. Introduction

Rainwater is an important means of scavenging pollutants from the atmosphere, which can occur either in the gaseous or in the particulate phase. The composition of rainwater actually reflects the composition of the atmosphere through which it falls. Gromping et al. (1997) have reported that more than 90% of the total amount of pollutants present in the atmosphere is lixiviated by wet deposition, being the predominant cleansing mechanism to remove pollutants from the air. Thus, rainwater can be a way to reduce the atmospheric load of pollutants, as well as a source of contamination for soil, water and terrestrial vegetation (Flues et al., 2002).

A huge variety of substances can be found in the air being the anthropogenic sources responsible for issuing most of the potentially polluting substances. Those sources of pollution are mainly characterized by the combustion of fossil fuels, the usage and production of biocides and pesticides, mining activities and the inappropriate treatment of industrial effluents, which are directly responsible for the increasing levels of particulate matter suspended in the atmosphere (Seinfeld and Pandis, 2006). Those particulate materials, such as  $\text{SO}_2$  and  $\text{NO}_x$ , salts and trace metals, generally remain in the atmosphere until they are scavenged by precipitation, through dissolution, by falling rain droplets (Flues et al., 2002).

Rainwater composition is directly related to the level of local emissions, pollutant transport, climate conditions and drop size, which influences the rainout (in-cloud scavenging) and the

washout (below-cloud scavenging) of pollutants (Baron and Denning, 1993). Precipitation chemistry has already been studied in many different places, including rural and urban areas around Europe (Alastuey et al., 1999; Al-Momani, 2003; Hontoria et al., 2003), Brazil (Campos et al., 1998; de Mello, 2001; Lara et al., 2001; Flues et al., 2002; Migliavacca et al., 2004) and other places in the world (Tanner, 1999; Bravo et al., 2000; Halstead et al., 2000; Seto et al., 2000; Kulshrestha et al., 2003). Thus, systematic observations of the chemical composition of precipitation are needed to investigate the changes and other characteristics of atmospheric pollution in this region (Xu et al., 2011).

The objectives of the present work were to describe the chemical composition (such as major cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ , anions  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , hydrogen peroxide and trace metals  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ ) of the rainwater in Juiz de Fora, Brazil and to identify their possible sources.

### 2. Material and Methods

#### 2.1. Study area

Juiz de Fora City (JFC) is located in the southeast of Minas Gerais State (Brazil), in a region called Zona da Mata Mineira, at 21.8°S and 43.3°W and 180 km away from the littoral (see the Supporting Material, SM, Figure S1). The city has a total area of 1 429 875 km<sup>2</sup>, with 446 551 km<sup>2</sup> of urban area and 983 324 km<sup>2</sup> of rural area.

The regional climate of JFC can be classified as a high-altitude tropical, with two distinct periods, one hotter and rainy and other

colder and drier. Air dislocations are mainly characterized by winds from the north quadrant. This aspect, allied with the presence of a wide depression along a regional river depth (Paraibuna River), forms a preferential way for air dislocation directing to the city centre, located to the south of the industrial district.

JFC has around 520 000 habitants with a total of 152 509 vehicles, and is the third biggest city of Minas Gerais state. It is located over an important Brazilian industrial area distributed along two federal highways (BR-040 and BR-116). The local industry includes many medium and large industries, mainly the beverage, food, textile, metallurgy and steel sectors. In the past few years, the industrialization progress of JFC has rapidly increased, where, in 2010, its growth reached 20.5%, against 10% for total Brazilian growth.

Regional pollutant dispersion is favorable through September and April (the hot and rainy summer) due to meteorological conditions. Those periods are characterized by high climate instability in the southeast of Minas Gerais due to continental frontal systems, Amazon region humidity, and the sea breeze.

A micro scale study over Juiz de Fora city was made in order to encompass some critical areas of the city. Juiz de Fora Federal University (UFJF) campus and Cidade do Sol, Aeroporto, Cascatinha and Democrata districts were chosen as they represents areas with high vehicular traffic, construction and industrial activities. The precipitation events in JFC during the sampling campaign totaled 1 505 mm (INMET, 2013). In the months of June, July and August, no representative precipitation events occurred.

## 2.2. Solutions and reagents

All reagents were of analytical grade and the solutions were prepared with deionized water obtained from a Milli-Q water purification system (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}^{-1}$ ). Ultra-pure nitric acid (Vetec, Rio de Janeiro, RJ, Brazil) was used for pH corrections and decontamination processes. EDTA (Vetec, Rio de Janeiro, RJ, Brazil),  $\text{NH}_4\text{Cl}$  (Impex, Sao Paulo, SP, Brazil),  $\text{NH}_4\text{OH}$  (Vetec, Rio de Janeiro, RJ, Brazil) and the Eriochrome Black-T indicator (Grupo Quimica, Rio de Janeiro, RJ, Brazil) were used for hardness determinations.

For major cation analyses, performed by capillary electrophoresis, 85% lactic acid (m/m), 99% imidazole (m/m) and 18-crown-6-ether, all obtained from Sigma (St. Louis, MO, USA) were used for electrolyte preparation. A  $1.00 \text{ mol L}^{-1}$  acetic acid (Merck, Darmstadt, Germany) stock solution was used for electrolyte pH adjustments. Stock solutions of a mixture of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  were prepared by diluting standards acquired from Vetec (Rio de Janeiro, RJ, Brazil). A  $0.10 \text{ mol L}^{-1}$  NaOH (Vetec, Rio de Janeiro, RJ, Brazil) solution and ultrapure water were used for capillary cleaning and conditioning.

Major anion analyses were also performed by capillary electrophoresis. The electrolyte was composed by a chromophore group,  $5.00 \text{ mmol L}^{-1}$   $\text{CrO}_4^{2-}$  (Vetec, Rio de Janeiro, RJ, Brazil), which absorbs in the UV range, and  $0.25 \text{ mmol L}^{-1}$  CTAB (hexadecyltrimethyl-ammonium bromide) (Sigma, St. Louis, MO, USA). A 2-hydroxy-isobutylic acid (Sigma, St. Louis, MO, USA) solution was used for pH adjustment to 8.5. Stock solutions of a mixture of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were prepared by diluting standards acquired from Vetec (Rio de Janeiro, RJ, Brazil). A  $3.00 \text{ mg L}^{-1}$   $\text{ClO}_3^-$  (Vetec, Rio de Janeiro, RJ, Brazil) was used as the internal standard.

Hydrogen peroxide, mono- and di-hydrogen phosphates were obtained from Merck (Darmstadt, Germany). Phenol with greater than 99.5% purity and 4-aminoantipyrine were obtained from Sigma (St. Louis, MO, USA). Commercial peroxidase (EC 1.11.1.7–115  $\text{U mg}^{-1}$ ) was obtained from Sigma (St. Louis, MO, USA).

$\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ga}^{2+}$  and  $\text{Cu}^{2+}$  reference solutions, used for trace metal analysis, were prepared from standard solutions obtained from Vetec (Rio de Janeiro, RJ, Brazil) and SpecSol (Jacarei, SP, Brazil). Ultra-pure hydrochloric acid, obtained from Vetec (Rio de Janeiro, RJ, Brazil), was used for the preparation of standards and as an electrolyte.

## 2.3. Sample collection and analysis

Prior to rainwater sample collection, and to avoid contamination through the sampler recipient, a decontamination process was followed, as described by Campos et al. (2002).

Sampling was conducted by manually locating polyethylene trays at the cited locations, on open-air areas (in order to avoid contamination). The collecting was made just after the beginning of precipitation events and until it stopped. A total of 50 rainwater samples were collected between February, 2010 and February, 2011.

After collection, samples were sent to the laboratory for chemical evaluation with no more than 12 hours after sampling, being submitted to refrigeration ( $4^\circ\text{C}$ ) during this period. All samples were filtered through a  $0.45 \mu\text{m}$  filter, prior to storage, in order to determine only the dissolved chemical elements in atmospheric precipitation. Once at the laboratory, they were stored in a freezer at  $-5^\circ\text{C}$  as two different aliquots. One of them was simply stored at the freezer, without any prior treatment, while the other was acidified to  $\text{pH} < 2.0$  with ultra-pure nitric acid for trace metal determination.

Sample pH and hardness were determined with a potentiometer (Digimed DM 20) using a glass electrode (Methrom) combined with an  $\text{Ag}/\text{AgCl}_{(\text{sat})}$  reference electrode. Sample hardness was measured by titration with EDTA, in  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$  buffer pH 10.0, using Eriochrome Black-T as the indicator. A radiometer (Digimed DM 31) conductivity meter and a platinum electrode were used for conductivity measurements. All those cited analysis were made prior than freezing, as soon as the samples arrived at the laboratory.

$\text{HCO}_3^-$  was theoretically estimated following the Equation 1:

$$[\text{HCO}_3^-] = \{K(S + [\text{Me}^{2+}])\} / (10^{-\text{pH}} + K) \quad (1)$$

where,  $K = 4.2 \times 10^{-7}$  is the first ionization constant of  $\text{H}_2\text{CO}_3$ ,  $S = 3.05 \times 10^{-2} \text{ mol L}^{-1}$  is the solubility of  $\text{CO}_2$  in water at  $25^\circ\text{C}$  and 1 atm,  $[\text{Me}^{2+}] = ([\text{Ca}^{2+}] + [\text{Mg}^{2+}]) \text{ mol L}^{-1}$ . For samples with  $\text{pH} \leq 5.6$  the concentration of  $[\text{HCO}_3^-]$  was considered negligible.

Major ions were determined by a capillary electrophoresis system with an automatic sampler and a spectrophotometric detector (CE Hewlett-Packard), equipped with a DAD UV-Vis detector. Indirect detection was performed for cations at 214 nm and at 375 nm for anions (Fung and Lau, 1998). In order to determine the quality of sample analyses by capillary electrophoresis, a rainwater standard reference material (CRM 409 – Commission of the European Communities) was also analyzed. The reproducibility of the data obtained in six replicates was satisfactory and showed a coefficient of variation of 2%. The detection and quantification limits of each analyte were of  $1.80 \mu\text{Eq L}^{-1}$  and  $6.00 \mu\text{Eq L}^{-1}$  for  $\text{K}^+$ ,  $1.50 \mu\text{Eq L}^{-1}$  and  $5.00 \mu\text{Eq L}^{-1}$  for  $\text{NH}_4^+$ ,  $1.30 \mu\text{Eq L}^{-1}$  and  $4.33 \mu\text{Eq L}^{-1}$  for  $\text{Na}^+$ ,  $0.60 \mu\text{Eq L}^{-1}$  and  $2.00 \mu\text{Eq L}^{-1}$  for  $\text{Mg}^{2+}$ ,  $0.45 \mu\text{Eq L}^{-1}$  and  $1.50 \mu\text{Eq L}^{-1}$  for  $\text{Ca}^{2+}$ ,  $0.70 \mu\text{Eq L}^{-1}$  and  $2.30 \mu\text{Eq L}^{-1}$  for  $\text{Cl}^-$ ,  $0.25 \mu\text{Eq L}^{-1}$  and  $0.85 \mu\text{Eq L}^{-1}$  for  $\text{SO}_4^{2-}$  and  $0.60 \mu\text{Eq L}^{-1}$  and  $2.00 \mu\text{Eq L}^{-1}$  for  $\text{NO}_3^-$ , respectively.

A colorimetric assay was used to measure the concentration of hydrogen peroxide using peroxidase chemically immobilized in amberlite IRA-743 resin (Matos et al., 2006). The detection and quantification limits found for  $\text{H}_2\text{O}_2$  were of  $0.70 \mu\text{mol L}^{-1}$  and

2.30  $\mu\text{mol L}^{-1}$ , respectively.  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ , were analyzed by potentiometric stripping analysis (PSA), using a glassy carbon electrode (2.0 mm diameter) modified with a thin mercury film as working electrode, with a  $\mu$ -AUTOLAB Type III potentiometer (Metrohm Autolab, The Netherlands), coupled with a Faraday cage (Metrohm Autolab, The Netherlands). The detection and quantification limits found for each metal were of 0.96  $\mu\text{g L}^{-1}$  and 3.20  $\mu\text{g L}^{-1}$  for  $\text{Cu}^{2+}$ , 0.41  $\mu\text{g L}^{-1}$  and 1.36  $\mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$ , 0.38  $\mu\text{g L}^{-1}$  and 1.26  $\mu\text{g L}^{-1}$  for  $\text{Cd}^{2+}$  and 1.26  $\mu\text{g L}^{-1}$  and 3.83  $\mu\text{g L}^{-1}$  for  $\text{Zn}^{2+}$ . Trace metals were also analyzed by graphite furnace atomic absorption spectrometry (GFAAS) with a GF 95 spectrometer (Thermo Scientific, China) using single element hollow cathodic lamps (Photron Lamps, Australia) for comparative analysis.

#### 2.4. Data quality

The data quality for the collected samples was verified by comparison of the measured and calculated conductivity and by ionic balance evaluation. The sum of cations and anions ( $\Sigma\text{cations}=92.87\pm 68.72$  and  $\Sigma\text{anions}=51.59\pm 39.21$ ) indicates that other inorganic anions, like  $\text{F}^-$  and  $\text{PO}_4^{3-}$ , and organic anions, like formate ( $\text{HCOO}^-$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ), were probably present in the rainwater samples, but they were not measured. The cations and anions sum also showed an acceptable correlation ( $r=0.84$  significant at  $p<0.01$ ), as seen in Figure 1a. Furthermore, the mean percent contribution of individual cations and anions in precipitation are shown in Figure 1b, where it can be seen that almost 82% of the samples ionic composition was explained.

The average conductivity for the rainwater samples of JFC was 11.3 ( $\pm 7.65$ )  $\mu\text{S cm}^{-1}$ . The correlation between the calculated and measured conductivities was satisfactory ( $r=0.89$ , significant at  $p<0.01$ ), indicating that most of the major ions were analyzed, probably with the exception of those already described.

PCA was used in order to identify and associate the influence of anthropogenic and natural sources on wet atmospheric precipitation in the studied area. The software used for PCA analysis was SPSS 16.0 for Windows. The chemical variables used for applying PCA were selected from the Pearson correlation matrix for major ions, producing a new set of synthetic variables (principal components) based on the interrelations of the original data. All data used for PCA analysis were first auto-scaled, as they had the same importance for sample discrimination (Migliavacca et al., 2005).

### 3. Results and Discussion

#### 3.1. Rain water chemical composition

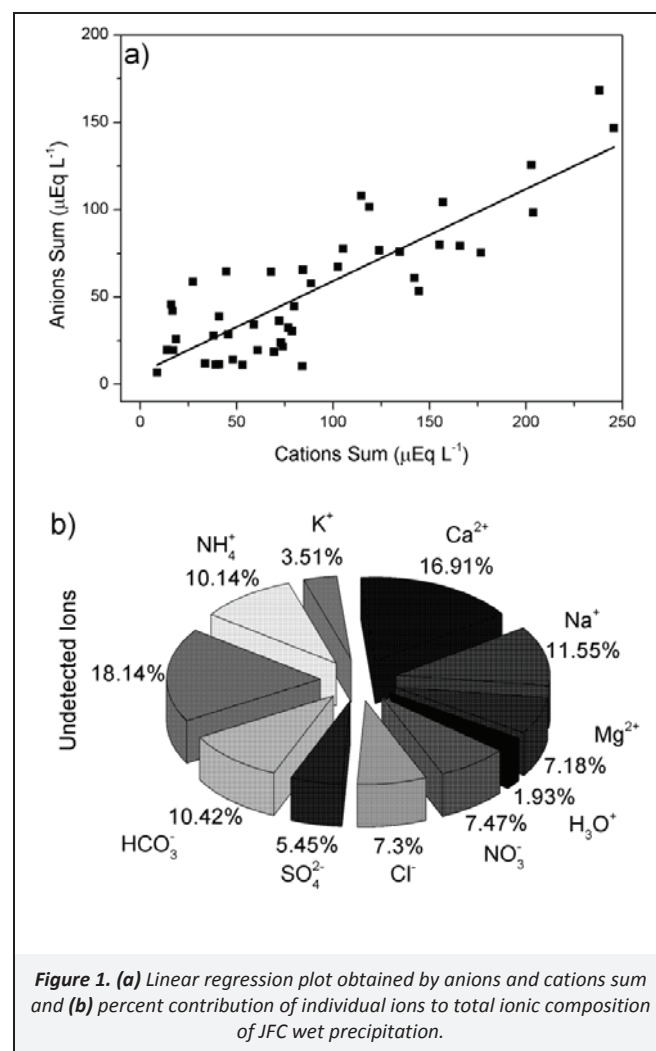
Table 1 shows the average and the range values for pH, conductivity, hardness, redox potential, hydrogen peroxide, trace metals and major ion concentrations of the 50 samples of atmospheric precipitation.

#### 3.2. pH, conductivity and major ions

JFC rainwater pH showed values ranging through 4.35 and 6.96, with an average value of 5.77. Thirty six percent of the analyzed samples had acidic characteristics, with pH between 4.0 and 5.6, and about 28% of the samples presented pH between 6.0 and 7.0. This slight acidity is acceptable if compared to the reference value of 5.6 for cloud water (Liljestrand, 1985). The sampling stations showed no significant variations in pH values.

Higher pH values were observed in spring (March, April and May) and autumn (September, October and November), and the lower values were obtained in summer (December, January and February). The same qualities were observed for sample conductivities. The evaluation of the data showed that sample

acidity and conductivity were slightly higher in less rainy periods. This can be explained by the fact that, in drought periods, the atmosphere is considerably more polluted, so the wet scavenging process carries a higher load of compounds which increases both measured parameters. The average and maximum values for conductivity were 11.3 and 35.2  $\mu\text{S cm}^{-1}$ , respectively. These values are relatively low, considering that the sampling stations were located in an urban area. The sample hardness showed an average value of 125  $\text{mg L}^{-1}$ , as the  $\text{CaCO}_3$  concentration, which indicates moderate hardness; however, during less rainy periods, especially in March and October, rainwater presented extremely hard characteristics with values that reached 579  $\text{mg L}^{-1}$ , as  $\text{CaCO}_3$ , probably due to intense concentration of atmospheric particulate matter in these months (Ahmed and Rahman, 2000).



**Figure 1.** (a) Linear regression plot obtained by anions and cations sum and (b) percent contribution of individual ions to total ionic composition of JFC wet precipitation.

Figures 2a–2c show the monthly average variation of major ions, trace metals and some physical chemical parameters evaluated at this study. In most cases, the ionic composition of rainwater followed the precipitation rate, where it can be seen that higher concentrations were found directly after drought periods.

#### 3.3. Hydrogen peroxide evaluation

The average  $\text{H}_2\text{O}_2$  concentration was 19.2  $\mu\text{mol L}^{-1}$ , with maximum and minimum values of 67.6  $\mu\text{mol L}^{-1}$  and 4.82  $\mu\text{mol L}^{-1}$ , respectively. These reported data indicate that  $\text{H}_2\text{O}_2$  levels in the studied area were comparable with those obtained by other investigators in different places (Matos et al., 2001; Pena et al., 2001).

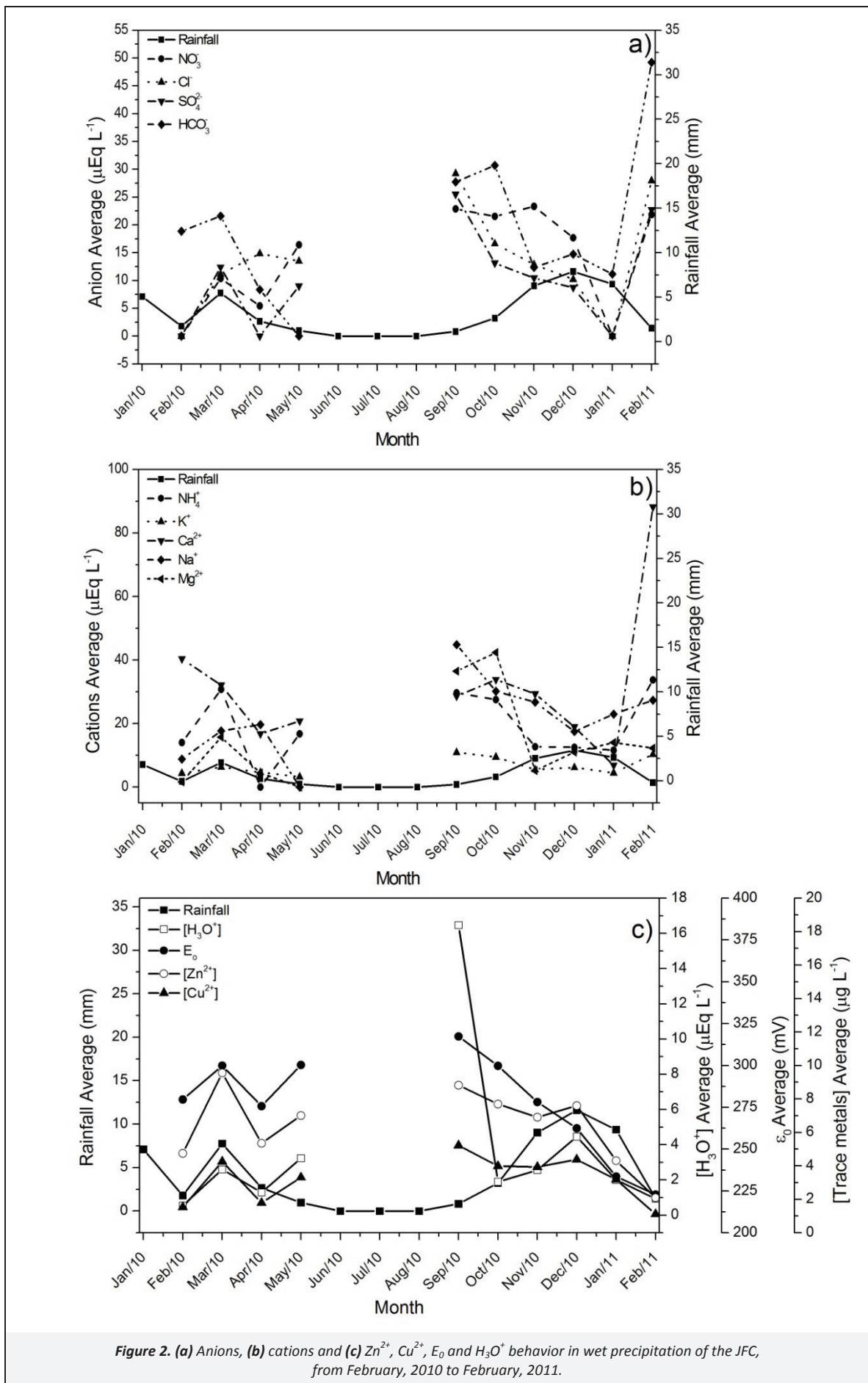


Figure 2. (a) Anions, (b) cations and (c) Zn<sup>2+</sup>, Cu<sup>2+</sup>, E<sub>0</sub> and H<sub>3</sub>O<sup>+</sup> behavior in wet precipitation of the JFC, from February, 2010 to February, 2011.

**Table 1.** Minimum, maximum and average values of the analysed parameters in JFC rainwater (n=50), through February/2010 and February/2011

	Minimum	Maximum	Average ( $\pm$ sd)
pH	4.35	6.96	5.77 (0.52)
Conductivity ( $\mu\text{S cm}^{-1}$ )	3.38	35.2	11.3 (7.65)
Hardness ( $\mu\text{g L}^{-1}$ , as $\text{CaCO}_3$ )	15.9	578	125 (105)
$\text{H}_2\text{O}_2$ ( $\mu\text{mol L}^{-1}$ )	4.82	67.6	19.2 (17.5)
Redox potential (mV)	335	218	278 (30.1)
$\text{Cl}^-$ ( $\mu\text{Eq L}^{-1}$ )	5.80	45.9	17.3 (10.4)
$\text{SO}_4^{2-}$ ( $\mu\text{Eq L}^{-1}$ )	4.27	39.8	14.2 (9.59)
$\text{NO}_3^-$ ( $\mu\text{Eq L}^{-1}$ )	3.35	72.7	16.2 (13.6)
$\text{HCO}_3^-$ ( $\mu\text{Eq L}^{-1}$ )	7.61	102	29.5 (24.2)
$\text{NH}_4^+$ ( $\mu\text{Eq L}^{-1}$ )	2.00	76.1	20.8 (16.7)
$\text{K}^+$ ( $\mu\text{Eq L}^{-1}$ )	0.33	20.1	7.12 (4.59)
$\text{Na}^+$ ( $\mu\text{Eq L}^{-1}$ )	5.30	70.4	25.0 (14.8)
$\text{Mg}^{2+}$ ( $\mu\text{Eq L}^{-1}$ )	1.56	153	24.1 (35.6)
$\text{Ca}^{2+}$ ( $\mu\text{Eq L}^{-1}$ )	3.54	239	39.6 (46.6)
$\text{Zn}^{2+}$ ( $\mu\text{g L}^{-1}$ )	3.93	13.8	7.31 (2.74)
$\text{Cd}^{2+}$ ( $\mu\text{g L}^{-1}$ )	<L.D. <sup>a</sup>	<L.D. <sup>a</sup>	<L.D. <sup>a</sup>
$\text{Pb}^{2+}$ ( $\mu\text{g L}^{-1}$ )	<L.D. <sup>a</sup>	<L.D. <sup>a</sup>	<L.D. <sup>a</sup>
$\text{Cu}^{2+}$ ( $\mu\text{g L}^{-1}$ )	3.18	5.96	4.07 (0.74)

<sup>a</sup> Below detection limit

In order to study rainwater pH effect over the  $\text{H}_2\text{O}_2$  concentration, Figures 3a, 3b and 3c shows the correlation between hydrogen peroxide and  $\text{H}_3\text{O}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . It has been observed that a higher concentration of  $\text{H}_2\text{O}_2$  corresponds to a lower  $\text{H}_3\text{O}^+$  concentration, as well as for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The highest  $\text{H}_2\text{O}_2$  values were found in summer, while the lowest were found in spring and autumn, the reverse of what was observed for  $\text{H}_3\text{O}^+$  concentration. This fact was expected, since  $\text{H}_2\text{O}_2$  is the principal oxidizing agent for  $\text{SO}_2$  in cloud and rain droplets at  $\text{pH}<5$ , and since  $\text{NO}_x$  competes with  $\text{H}_2\text{O}_2$  for the hydroperoxyl radical (which is one of the  $\text{H}_2\text{O}_2$  precursors) (Brandt and Vaneldik, 1995). Negative correlations between  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}_2$  ( $r=-0.18$ , non-significant at  $p<0.01$ , in this work) are usually found, whereas  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are the most significant ions that contribute to rainwater acidity.

The pH values for almost 94% of the collected samples were greater than 5.0; therefore, in these cases, the oxidation of  $\text{SO}_2$  by  $\text{O}_3$  is dominant. In the rest of the collected samples (6%), the pH was lower than 5; thus, oxidation by  $\text{H}_2\text{O}_2$  was the dominant pathway in these cases. If the non-sea salt sulfate found in the rainwater were solely derived from the interaction of  $\text{H}_2\text{O}_2$  with  $\text{SO}_2$ , a negative correlation between  $\text{H}_2\text{O}_2$  and  $\text{SO}_4^{2-}$  would exist. However, a weak inverse correlation ( $r=-0.21$ , non-significant at  $p<0.01$ ) was found indicating that  $\text{O}_3$  is the main precursor for the  $\text{SO}_2$  oxidation process. Also, a negative correlation ( $r=-0.09$ , non-significant at  $p<0.01$ ) between  $\text{NO}_3^-$  and  $\text{H}_2\text{O}_2$  showed that  $\text{NO}_3^-$  did not interfere significantly with the formation of  $\text{H}_2\text{O}_2$  (Matos et al., 2001).

### 3.4. Trace metal evaluation

The average, minimum and maximum values of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are shown in Table 1. Significant concentrations of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were not found in the analyzed samples.

Trace metals are only bioavailable if the metal is in its soluble form. The hydrolysis rates of trace metals present in rainwater depend on the anion and cation balance, the redox potential and the pH of these waters, as well as the size distribution and chemical nature of the depositing particles (Morselli et al., 2004).

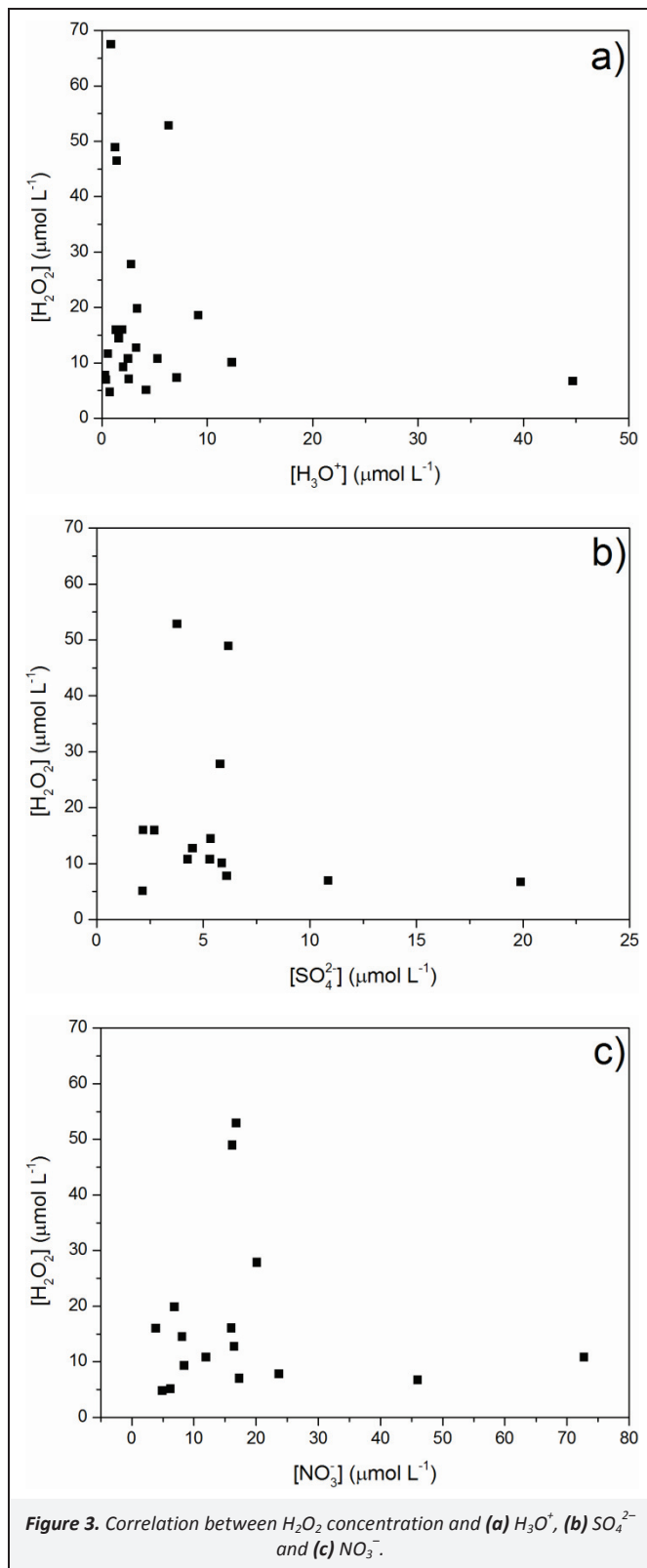
Through the comparison of trace metal concentrations with sample pH and redox potential (Table 1), it was possible to verify that the amount of dissolved metal in rainwater samples was directly related to these factors. The correlation between values allowed concluding that more acidic rain ( $r=-0.55$  and  $r=-0.22$ , for the correlation between pH and trace metals,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ , respectively) with a higher redox potential ( $r=0.85$  and  $r=0.23$ , for the correlation between  $\epsilon_h$  and trace metals,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ , respectively) has a higher concentration of dissolved metals.

Taking into account only the positive or negative influence of these factors through the analyzed trace metals, it can be concluded that trace metals solubility are higher as the pH decreases and the redox potential increases, observed at less rainy periods (Figure 2c). The values found for the analyzed trace metals were within the range for other studied urban areas (Migliavacca et al., 2005; Muezzinoglu and Cizmecioglu, 2006; Melidis et al., 2007; Al-Khashman, 2009; Koulousaris et al., 2009; Migliavacca et al., 2009; Ozsoy and Ornektekin, 2009; Sakata and Asakura, 2009; Sekabira et al., 2010).

### 3.5. Acidification and neutralization process

$\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and some organic acids are the main contributors to the wet precipitation acidification process (Migliavacca et al., 2005). Figure 4a shows the correlation between sample acidity and the sum of the variables related to the acidification process ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ). The linear regression found for these values ( $r=0.67$ , significant at  $p<0.01$ ) suggests that these species act as the main acidification agents.

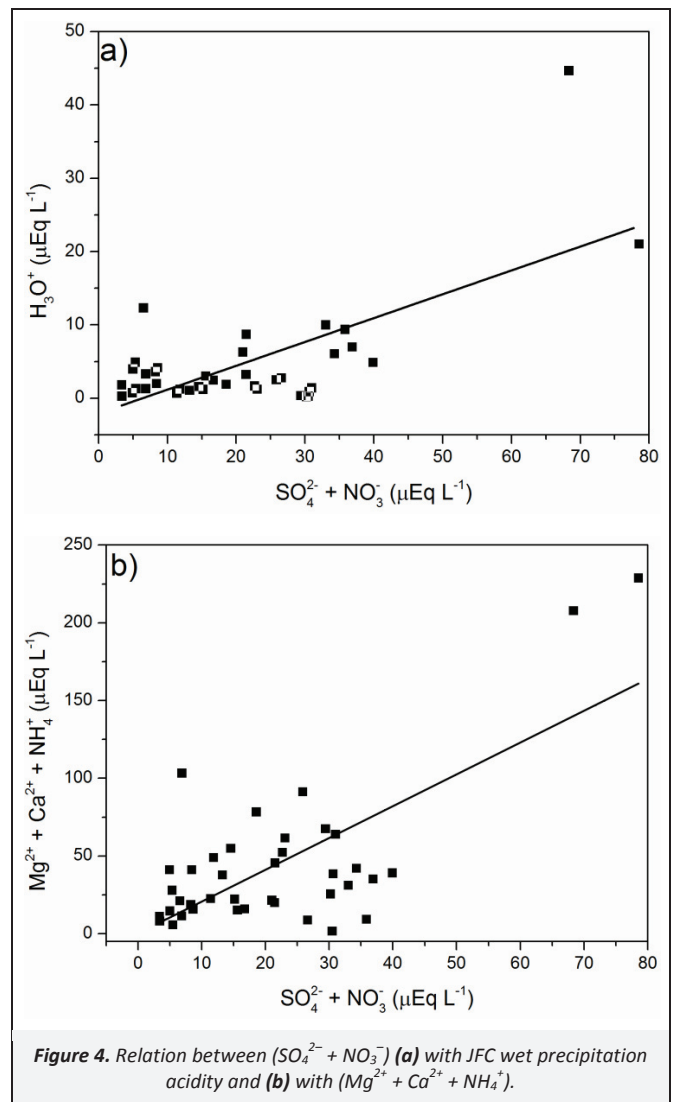
The neutralization of acidifying chemical species occurs due to the presence of basic substances, such as  $\text{MgCO}_3$ ,  $\text{CaCO}_3$  and  $\text{NH}_3$  (Migliavacca et al., 2005). Figure 4b shows the correlation between the sum of the variables related to acidification ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) and the neutralization process ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ ) for wet atmospheric precipitation in JFC. The linear regression between these values ( $r=0.70$ , significant at  $p<0.01$ ) suggests that these alkaline species act as the main neutralizing agents of rainwater acidity in the studied region.



The neutralization factors (NFs) for the alkaline species were calculated following Equation (2) (Panyakapo and Onchang, 2008):

$$NF_X = [X] / ([SO_4^{2-}] + [NO_3^-]) \quad (2)$$

where,  $X$  is the chemical species of interest, with all the ions expressed in  $\mu Eq L^{-1}$ . The values found for  $NF_{Ca}$ ,  $NF_{Mg}$  and  $NF_{NH_4}$  were 1.63, 0.86 and 1.03, respectively. This suggests that  $Ca^{2+}$  is the most important component participating in the neutralization of precipitation acidity in the study area.



$SO_4^{2-}/NO_3^-$  ratio may indicate the grade of anthropogenic sources in wet precipitation. The value obtained for JFC region was of 0.88, which was lower than the ratio found for most evaluations already made. This result implies that JFC rainwater free acidity is principally due to  $HNO_3$  either produced within the in cloud system or advected from sources outside of the system itself (Kumar et al., 2002).

The contribution of  $H_2SO_4$  to the acidity of atmospheric precipitation has decreased significantly compared to  $HNO_3$ . This is directly related to the control of emitting sources, as well as to the reduction of sulfur content of oil products, in contrast to the less restrictive control of  $NO_x$  emissions (Byron et al., 1991). As a result, since JFC is passing through a high vehicle and industrial growth in the past few years,  $NO_3^-$  values were commonly higher than  $SO_4^{2-}$  values. The same aspect was observed for a study described at suburban site of semiarid region in India (Kumar et al., 2002).

### 3.6. Marine and soil contribution

The chemical composition of atmospheric deposition can be controlled by local atmospheric dust/particulate, natural and anthropogenic emissions, and marine contribution. To assess the marine and soil aerosol contribution, the enrichment factors (EFs) are commonly used.

In order to evaluate the marine and soil contribution over JFC rainwater samples, the enrichment factors ( $EF_s$ ) for some ionic species were calculated using Equation (3):

$$EF_{X_i} = \frac{[X_i/X_r]_{\text{rainwater}}}{[X_i/X_r]_{\text{sea salt/soil}}} \quad (3)$$

where,  $X_i$  is the ion of interest and  $X_r$  is a reference ion, which is expected to have only a sea salt/soil origin. An  $EF$  approaching to unity suggests that the element is originated from sea salt/soil (not enriched elements). On the other hand, and  $EF$  greater than unity suggests that a significant fraction had an origin in a source different than sea salt/soil (enriched elements).  $\text{Cl}^-$  can be used as the reference ion for marine source (Ceron et al., 2008), while  $\text{Ca}^{2+}$  is a typical lithophilic element used as a reference ion for continental crust (Cao et al., 2009).

The results suggest the dominance of crustal/anthropogenic sources of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ .  $\text{Na}^+$  was found to be partially provided from sea salt aerosol and also from soil contribution, where both contributions were almost even.  $\text{SO}_4^{2-}$  also showed contributions from sea salt and soil, but those values corresponded to only 40% of the total. The other 60% was attributed to anthropogenic sources. As expected,  $\text{NO}_3^-$  showed no significant contribution from sea salt or soil, being exclusively provided from anthropogenic sources.

Positive correlations between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r=0.78$ , significant at  $p<0.01$ ) and between  $\text{Mg}^{2+}$  and  $\text{K}^+$  ( $r=0.68$ , significant at  $p<0.01$ ) indicates that these cations are provided from a common source. An important aspect that may be pointed out here is that the regional rock formation is mainly constituted of granulites, charnockites and migmatites, which present  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  in most of their constituents. This fact can clearly explain the source of those cations.

Positive correlations (0.40–0.70, significant at  $p<0.01$ ) of  $\text{SO}_4^{2-}$  with  $\text{NH}_4^+$  and  $\text{NO}_3^-$  suggest the contribution of  $\text{SO}_4^{2-}$  from anthropogenic sources, such as automobile exhaust, incinerators, waste burning and ZnS combustion, used as a Zn source by a local factory.

### 3.7. Principal components analysis

Principal components analysis (PCA) was performed on the data set comprised of major ions in the precipitation samples with a view to identify and associate their possible sources. Factors with an eigenvalue  $>1$  were retained. PCA yielded in total four significant factors, explaining about 81.8% of the total data variance. Loadings of the Varimax rotated factors are presented in Table 2.

Factor 1 explained about 37% of the total variance, with strong positive loadings for  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , showing a high influence of crustal contribution at JFC atmosphere, as all those

ions were mostly provided by soil and road dust, especially due to the regional rock formation. The higher  $\text{HCO}_3^-$  loading at this factor can be associated to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  neutralization process of rain acids, by suspended  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in air, originated mostly from roadside dust (Shrestha et al., 2013).

Factor 2, which explained 24.3% of the total variance, showed strong positive loading for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{H}_3\text{O}^+$ .  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are mainly provided by anthropogenic sources, such as automobile exhaust, incinerators, waste burning and industrial processes. However,  $\text{SO}_4^{2-}$  was found to have also a sea salt source, as already discussed. It was also observed that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are directly associated to the pH of JFC rainwater. This was also expected as those ions are the main contributors for acid rains (Kumar et al., 2002).

Factor 3 with strong positive loading for  $\text{Cl}^-$  and  $\text{Na}^+$ , both mainly originated by sea salt breeze.  $\text{Na}^+$  was also found to have a crustal origin, confirmed by a strong positive correlation between this ion and  $\text{Mg}^{2+}$  ( $r=0.62$ , significant at  $p<0.01$ ) (Migliavacca et al., 2005).

Factor 4 presented a strong positive loading for  $\text{NH}_4^+$ , commonly associated to biomass decomposition, probably originated from agricultural and cattle farming. This can also be explained by the positive correlation found between  $\text{K}^+$  and  $\text{NH}_4^+$  ( $r=0.68$ , significant at  $p<0.01$ ), as  $\text{K}^+$  can indicate the influence of agricultural tillage practices, which enhances the suspension of soil-derived particles in the atmosphere (Kulshrestha et al., 2003).

## 4. Conclusion

The total amount of wet precipitation measured during the sampling period (February, 2010 to February, 2011) for the JFC region was 1 505 mm. The mean pH showed that samples had on their majority acidic properties. This acidity was directly associated with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , where  $\text{NO}_3^-$  was found to be the main contributor to this characteristic. On the other hand, the neutralization process mainly originated from the presence of  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , primarily  $\text{NH}_4^+$ .

Major ions evaluation was also made.  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  showed marine contribution, but  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  showed also non-marine contributions.  $\text{SO}_4^{2-}$  non-marine contribution was found to be from anthropogenic sources, while  $\text{Na}^+$  non-marine contribution was associated to soil contribution. With respect to soil contribution  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  were seen to be based originated from this kind of contribution.  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were found to be mainly originated from anthropogenic sources.

**Table 2.** Factor loadings matrix obtained from atmospheric wet precipitation at JFC region, Minas Gerais, Brazil, from February/2010 to February/2011

Variable	Factor 1	Factor 2	Factor 3	Factor 4
$[\text{H}_3\text{O}^+]$	-0.186	0.676 <sup>a</sup>	0.081	0.475
$[\text{Cl}^-]$	-0.035	0.346	0.793 <sup>a</sup>	0.183
$[\text{SO}_4^{2-}]$	0.043	0.892 <sup>a</sup>	0.213	0.238
$[\text{NO}_3^-]$	0.170	0.912 <sup>a</sup>	0.104	-0.041
$[\text{HCO}_3^-]$	0.863 <sup>a</sup>	0.099	-0.137	0.081
$[\text{NH}_4^+]$	0.152	0.229	0.178	0.841 <sup>a</sup>
$[\text{K}^+]$	0.723 <sup>a</sup>	-0.041	0.073	0.480
$[\text{Ca}^{2+}]$	0.890 <sup>a</sup>	0.129	0.081	-0.091
$[\text{Mg}^{2+}]$	0.675 <sup>a</sup>	-0.194	0.533	0.058
$[\text{Na}^+]$	0.072	0.167	0.917 <sup>a</sup>	0.099
Total variance	36.5%	24.3%	12.7%	8.3%
Probable origin	Soil	Anthropogenic	Sea Salt	Anthropogenic

<sup>a</sup> Factors  $>0.50$  are considered significant.

The hydrogen peroxide levels were higher in summer and lower in spring and autumn, the reverse of what was observed for the  $\text{H}_3\text{O}^+$  concentration. With respect to trace metals, it was found that the amount of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  found were within the range of other studied areas. No significant levels of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were found. It was also observed that the amount of dissolved trace metals in local rainwater was directly related to its pH and redox potential.

### Acknowledgments

The authors would like to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico – Edital MCT/CNPq/CT-Hidro 21/2009 – Tecnologias Poupadoras de Água – Processo 556034/2009–0), FAPEMIG (Fundação de Amparo a Pesquisa do Estado de Minas Gerais – Edital 01/2011 – Demanda Universal – Processo CEX – APQ–00173–11), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) and PROPESQ/UFJF (Pro-Reitoria de Pesquisa e Pós-Graduação da Universidade Federal de Juiz de Fora) for their financial support and grants.

### Supporting Material Available

Location of sample collection points (Figure S1). This information is available free of charge via the internet at <http://www.atmospolres.com>

### References

- Ahmed, M.F., Rahman, M.M., 2000. *Water Supply and Sanitation: Rural and Low Income Urban Communities*, ITN–Bangladesh, Centre for Water Supply and Waste Management, BUET.
- Alastuey, A., Querol, X., Chaves, A., Ruiz, C.R., Carratala, A., Lopez–Soler, A., 1999. Bulk deposition in a rural area located around a large coal–fired power station, northeast Spain. *Environmental Pollution* 106, 359–367.
- Al–Khashman, O.A., 2009. Chemical characteristics of rainwater collected at a western site of Jordan. *Atmospheric Research* 91, 53–61.
- Al–Momani, I.F., 2003. Trace elements in atmospheric precipitation at Northern Jordan measured by ICP–MS: Acidity and possible sources. *Atmospheric Environment* 37, 4507–4515.
- Baron, J., Denning, A.S., 1993. The influence of mountain meteorology on precipitation chemistry at low and high elevations of the Colorado Front Range, USA. *Atmospheric Environment Part A–General Topics* 27, 2337–2349.
- Brandt, C., Vaneldik, R., 1995. Transition–metal–catalyzed oxidation of sulfur(IV) oxides – atmospheric–relevant processes and mechanisms. *Chemical Reviews* 95, 119–190.
- Bravo, H.A., Saavedra, M.I.R., Sanchez, P.A., Torres, R.J., Granada, L.M.M., 2000. Chemical composition of precipitation in a Mexican Maya region. *Atmospheric Environment* 34, 1197–1204.
- Byron, E.R., Axler, R.P., Goldman, C.R., 1991. Increased precipitation acidity in the central Sierra–Nevada. *Atmospheric Environment Part A–General Topics* 25, 271–275.
- Campos, M.L.A.M., Bendo, A., Viel, F.C., 2002. Low cost methods to purify low grade reagents and to control contamination for trace metal determination in natural waters. *Quimica Nova* 25, 808–813.
- Campos, V.P., Costa, A.C.A., Tavares, T.M., 1998. Comparison of two types of rain sampling: Total deposition and wet only deposition. *Quimica Nova* 21, 418–423.
- Cao, Y.Z., Wang, S.Y., Zhang, G., Luo, J.Y., Lu, S.Y., 2009. Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. *Atmospheric Research* 94, 462–469.
- Ceron, R.M., Ceron, J.G., Muriel, M., Cardenas, B., 2008. Identification of ion sources in rainwater of a coastal site impacted by the gas and oil industry in the southeast of Mexico. *Global Nest Journal* 10, 92–100.
- de Mello, W.Z., 2001. Precipitation chemistry in the coast of the Metropolitan Region of Rio de Janeiro, Brazil. *Environmental Pollution* 114, 235–242.
- Flues, M., Hama, P., Lemes, M.J.L., Dantas, E.S.K., Fornaro, A., 2002. Evaluation of the rainwater acidity of a rural region due to a coal–fired power plant in Brazil. *Atmospheric Environment* 36, 2397–2404.
- Fung, Y.S., Lau, K.M., 1998. Development and validation of analytical methodology using capillary electrophoresis for separation and determination of anions in rainwater. *Talanta* 45, 641–656.
- Gromping, A.H.J., Ostapczuk, P., Emons, H., 1997. Wet deposition in Germany: Long–term trends and the contribution of heavy metals. *Chemosphere* 34, 2227–2236.
- Halstead, M.J.R., Cunningham, R.G., Hunter, K.A., 2000. Wet deposition of trace metals to a remote site in Fiordland, New Zealand. *Atmospheric Environment* 34, 665–676.
- Hontoria, C., Saa, A., Almorox, J., Cuadra, L., Sanchez, A., Gasco, J.M., 2003. The chemical composition of precipitation in Madrid. *Water Air and Soil Pollution* 146, 35–54.
- INMET (Instituto Nacional de Meteorologia), 2013. Rainfall Variation over A518 Station (Juiz de Fora), [http://www.inmet.gov.br/portal/index.php?r=home/page&page=rede\\_estacoes\\_auto\\_graf](http://www.inmet.gov.br/portal/index.php?r=home/page&page=rede_estacoes_auto_graf), accessed in January 2013.
- Koulousaris, M., Aloupi, M., Angelidis, M.O., 2009. Total metal concentrations in atmospheric precipitation from the Northern Aegean Sea. *Water Air and Soil Pollution* 201, 389–403.
- Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R., Vairamani, M., 2003. Chemical characteristics of rainwater at an urban site of south–central India. *Atmospheric Environment* 37, 3019–3026.
- Kumar, R., Rani, A., Singh, S.P., Kumari, K.M., Srivastava, S.S., 2002. A long term study on chemical composition of rainwater at Dayalbagh, a suburban site of semiarid region. *Journal of Atmospheric Chemistry* 41, 265–279.
- Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Victoria, R.L., Camargo, P.B., Krusche, A., Ayers, G.P., Ferraz, E.S.B., Ballester, M.V., 2001. Chemical composition of rainwater and anthropogenic influences in the Piracicaba River Basin, Southeast Brazil. *Atmospheric Environment* 35, 4937–4945.
- Liljestrand, H.M., 1985. Average rainwater pH, concepts of atmospheric acidity, and buffering in open systems. *Atmospheric Environment* 19, 487–499.
- Matos, R.C., Coelho, E.O., de Souza, C.F., Guedes, F.A., Matos, M.A., 2006. Peroxidase immobilized on Amberlite IRA–743 resin for on–line spectrophotometric detection of hydrogen peroxide in rainwater. *Talanta* 69, 1208–1214.
- Matos, R.C., Pedrotti, J.J., Angnes, L., 2001. Flow–injection system with enzyme reactor for differential amperometric determination of hydrogen peroxide in rainwater. *Analytica Chimica Acta* 441, 73–79.
- Melidis, P., Akrotas, C.S., Tsihrintzis, V.A., Trikilidou, E., 2007. Characterization of rain and roof drainage water quality in Xanthi, Greece. *Environmental Monitoring and Assessment* 127, 15–27.
- Migliavacca, D.M., Teixeira, E.C., Gervasoni, F., Conceicao, R.V., Rodriguez, M.T.R., 2009. Characterization of wet precipitation by X–ray diffraction (XRD) and scanning electron microscopy (SEM) in the metropolitan area of Porto Alegre, Brazil. *Journal of Hazardous Materials* 171, 230–240.
- Migliavacca, D., Teixeira, E.C., Wiegand, F., Machado, A.C.M., Sanchez, J., 2005. Atmospheric precipitation and chemical composition of an urban site, Guaiba hydrographic basin, Brazil. *Atmospheric Environment* 39, 1829–1844.
- Migliavacca, D., Teixeira, E.C., Pires, M., Fachel, J., 2004. Study of chemical elements in atmospheric precipitation in South Brazil. *Atmospheric Environment* 38, 1641–1656.



- Morselli, L., Brusori, B., Passarini, F., Bernardi, E., Francaviglia, R., Gataleta, L., Marchionni, M., Aromolo, R., Benedetti, A., Olivieri, P., 2004. Heavy metals monitoring at a Mediterranean natural ecosystem of Central Italy. Trends in different environmental matrixes. *Environment International* 30, 173–181.
- Muezzinoglu, A., Cizmecioglu, S.C., 2006. Deposition of heavy metals in a Mediterranean climate area. *Atmospheric Research* 81, 1–16.
- Ozsoy, T., Ornektekin, S., 2009. Trace elements in urban and suburban rainfall, Mersin, Northeastern Mediterranean. *Atmospheric Research* 94, 203–219.
- Panyakapo, M., Onchang, R., 2008. A four-year investigation on wet deposition in western Thailand. *Journal of Environmental Sciences–China* 20, 441–448.
- Pena, R.M., Garcia, S., Herrero, C., Lucas, T., 2001. Measurements and analysis of hydrogen peroxide rainwater levels in a Northwest region of Spain. *Atmospheric Environment* 35, 209–219.
- Sakata, M., Asakura, K., 2009. Factors contributing to seasonal variations in wet deposition fluxes of trace elements at sites along Japan Sea Coast. *Atmospheric Environment* 43, 3867–3875.
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, Inc, Canada.
- Sekabira, K., Origa, H.O., Basamba, T.A., Mutumba, G., Kakudidi, E., 2010. Heavy metal assessment and water quality values in urban stream and rain water. *International Journal of Environmental Science and Technology* 7, 759–770.
- Seto, S., Oohara, M., Ikeda, Y., 2000. Analysis of precipitation chemistry at a rural site in Hiroshima Prefecture, Japan. *Atmospheric Environment* 34, 621–628.
- Shrestha, S., Pandey, V.P., Yoneyama, Y., Shrestha, S., Kazama, F., 2013. An evaluation of rainwater quality in Kathmandu Valley, Nepal. *Sustainable Environment Research* 23, 341–350.
- Tanner, P.A., 1999. Analysis of Hong Kong daily bulk and wet deposition data from 1994 to 1995. *Atmospheric Environment* 33, 1757–1766.
- Xu, H., Bi, X.H., Feng, Y.C., Lin, F.M., Jiao, L., Hong, S.M., Liu, W.G., Zhang, X.Y., 2011. Chemical composition of precipitation and its sources in Hangzhou, China. *Environmental Monitoring and Assessment* 183, 581–592.