



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 (H_3O^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) and anions (NO_3^- , SO_4^{2-} , Cl^- and HCO_3^-), hydrogen peroxide (H_2O_2), some trace metals (Cu^{2+} , Zn^{2+} , Cd^{2+} and 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 $7.12 \mu\text{Eq L}^{-1}$ (K^+) to $39.6 \mu\text{Eq L}^{-1}$ (Ca^{2+}). Principal Component Analysis (PCA) with Varimax normalized rotation was performed, grouping the major analyzed cations and anions into different factors. Mg^{2+} , K^+ , Ca^{2+} and HCO_3^- were assigned to soil contribution, Na^+ and Cl^- to sea-salt contribution and NO_3^- , SO_4^{2-} and 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 H_3O^+ levels. Zn^{2+} (7.31 ± 2.74) $\mu\text{g L}^{-1}$ and Cu^{2+} (4.07 ± 0.74) $\mu\text{g L}^{-1}$ were within the range of other studied areas, while Cd^{2+} and 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

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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 SO_2 and 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 Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ , anions Cl^- , NO_3^- and SO_4^{2-} , hydrogen peroxide and trace metals Cu^{2+} , Pb^{2+} , Cd^{2+} and 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^2 , with 446 551 km^2 of urban area and 983 324 km^2 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), NH_4Cl (Impex, Sao Paulo, SP, Brazil), NH_4OH (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 mol L^{-1} acetic acid (Merck, Darmstadt, Germany) stock solution was used for electrolyte pH adjustments. Stock solutions of a mixture of Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ were prepared by diluting standards acquired from Vetec (Rio de Janeiro, RJ, Brazil). A 0.10 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 mmol L^{-1} CrO_4^{2-} (Vetec, Rio de Janeiro, RJ, Brazil), which absorbs in the UV range, and 0.25 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 Cl^- , NO_3^- and SO_4^{2-} were prepared by diluting standards acquired from Vetec (Rio de Janeiro, RJ, Brazil). A 3.00 mg L^{-1} 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 U mg^{-1}) was obtained from Sigma (St. Louis, MO, USA).

Zn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Ga^{2+} and 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°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°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.

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 H_2CO_3 , $S = 3.05 \times 10^{-2} \text{ mol L}^{-1}$ is the solubility of CO_2 in water at 25°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 K^+ , $1.50 \mu\text{Eq L}^{-1}$ and $5.00 \mu\text{Eq L}^{-1}$ for NH_4^+ , $1.30 \mu\text{Eq L}^{-1}$ and $4.33 \mu\text{Eq L}^{-1}$ for Na^+ , $0.60 \mu\text{Eq L}^{-1}$ and $2.00 \mu\text{Eq L}^{-1}$ for Mg^{2+} , $0.45 \mu\text{Eq L}^{-1}$ and $1.50 \mu\text{Eq L}^{-1}$ for Ca^{2+} , $0.70 \mu\text{Eq L}^{-1}$ and $2.30 \mu\text{Eq L}^{-1}$ for Cl^- , $0.25 \mu\text{Eq L}^{-1}$ and $0.85 \mu\text{Eq L}^{-1}$ for SO_4^{2-} and $0.60 \mu\text{Eq L}^{-1}$ and $2.00 \mu\text{Eq L}^{-1}$ for 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 H_2O_2 were of $0.70 \mu\text{mol L}^{-1}$ and

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