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Chemical composition monitoring of tropical rainwater during an atypical dry year

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ABSTRACT

The effects of an atypical dry year on the rainwater chemical composition were investigated. Conductivity, pH, major inorganic ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, H^+, Cl^-, NO_3^-, SO_4^{2-} and HCO_3^-) and trace-elements (As, Cd, Cu, Mn and Pb) were determined in 53 rainwater samples, which were collected on a daily basis over 12 months, in a meteorological station from Juiz de Fora city, Southeast Brazil. The rainwater conductivity ranged from 3.9 a 46.5 μS cm^{-1} and the pH ranged from 5.04 to 7.10. The analytes concentrations decreased in the following order: $Ca^{2+} > Na^+ > K^+ > Mg^{2+} > H^+$ for cations, $NO_3^- > Cl^- > HCO_3^- > SO_4^{2-}$ for anions and Cu > Mn > Pb > Cd > As for trace-elements. In general, higher analytes concentrations were observed during the dry season. The total annual rainfall in 2014 was 964.4 mm. This value is significantly lower than the historic annual mean of Juiz de Fora, which is 1550 mm. Therefore, the year 2014 was characterized as a very dry year.

1. Introduction

Water is a renewable natural resource, fundamental for the survival of living beings. On the water cycle, rain is the most effective scavenging factor for cleaning the atmosphere. During the condensation (rainout) and precipitation (washout), the gases and particulate materials present in the atmosphere are dissolved in raindrops and deposited. Thus, many substances from air pollution are present in rainwater, changing its chemical composition and the pH (Conceição et al., 2011; Flues et al., 2002; Oliveira et al., 2012).

Rainwater chemical constituents come from marine and biogenic aerosols, soil particles and volcanic emissions. Anthropogenic activities, like the use of fossil fuel, industrial emissions, waste incineration, agriculture and mining also contributes to the rainwater composition. The rainwater chemical composition can reflect the atmospheric quality of a specific region and depends on the emission site, on the sea level elevation and on the meteorological conditions (Flues et al., 2002; Santos et al., 2011). The chemical elements and compounds in atmosphere can be transported by wind as aerosols and travel long distances before being deposited by rain, affecting soil, superficial water and vegetation (Honório et al., 2010; Niu et al., 2014). Thus, the chemical investigation of rainwater is useful to trace different sources of atmospheric pollutants (Oliveira et al., 2012).

Southeast Brazil is a tropical area with increase of urbanization and large industrial expansion. This region has been highlighted as an area susceptible to emissions from urban and industrial activities (Lara et al., 2001; Mello and Almeida, 2004). As noted by Lara et al. (2001), numerous studies on atmospheric chemistry have been published in the Northern Hemisphere, but there are few works on rainwater chemistry in Brazil. Furthermore, studies of rainwater composition in the Southeast Brazil are mainly performed in São Paulo (SP) and Rio de Janeiro (RJ) states.

Thus, the purpose of this study was to investigate the rainwater chemical composition in Juiz de Fora, a city of Minas Gerais (MG) state, during a dry year and discuss the results relating them to the meteorological conditions in this period.

2. Experimental

2.1. Sampling site

The rainwater samples were collected in an open area, in the Universidade Federal de Juiz de Fora (UFJF) meteorological station (latitude: 21° 41′ 40″ S, longitude: 43° 20′ 40″ W, altitude: 937 m), (Fig. 1), which has been operated since 1972. Juiz de Fora is a city with approximately 550,000 inhabitants, 1430 km^2 area and is the third more populated city of the MG state (Prefeitura de Juiz de Fora, 2015; Cerqueira et al., 2014). The city has high-altitude tropical climate, with two defined seasons: wet (October to April) and dry (May to September).

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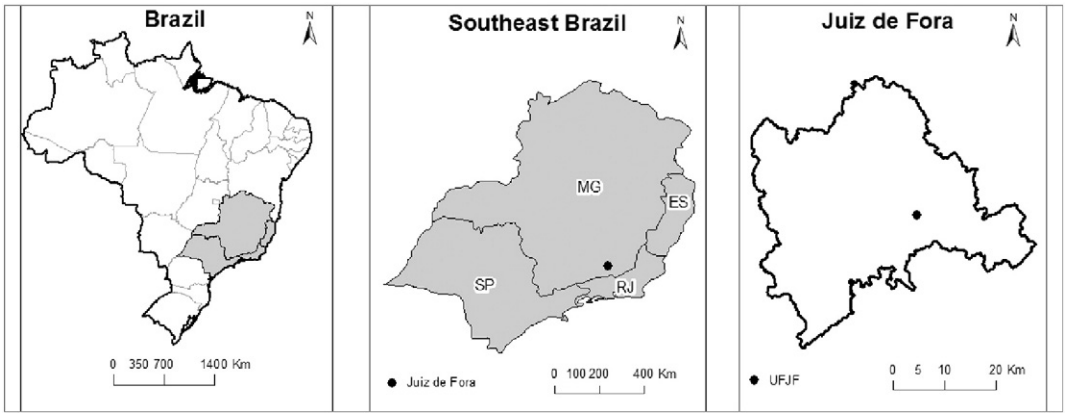

Fig.1. Map of Brazil with the geographical location of sampling site.

The wind predominant direction is North (N). According to UFJF meteorological station data, the historical mean annual rainfall is 1550 mm and the historical mean annual air temperature is 19.3 °C, ranging from 3.1 °C to 34.4 °C.

Rainwater samples (n = 53) were collected on a daily basis over 12 months (from January to December, 2014). Events of precipitation less than 2 mm were not collected. Sampling was carried out in a total deposition sampler (bulk collector), composed of a polyethylene funnel with approximately 10 cm diameter attached to a 2 L vessel of the same material, at approximately 1.5 m above the ground. The samples were transferred into polyethylene bottles and then transported to the laboratory. pH and conductivity were measured as soon as possible. Then, the samples were filtered to remove the insoluble particles, and stored at about 4 °C until analysis. In order to avoid trace-element contamination, the funnel and bottles used for sampling and storing the water were cleaned in an acid bath containing 10% v/v HNO_3 for 24 h and rinsed with deionized water. A blank was evaluated for all analytes and no contamination from the acid was detected.

2.2. Reagents and solutions

The standards used for calibration were prepared from stock solutions of Na (2000 mg L^{-1}, Carlo Erba, São Paulo, Brazil); K (Ultra Scientific, São Paulo, Brazil); Mn (Merck, São Paulo, Brazil); As, Ca, Cd and Pb (Qhemis, Joinville, Brazil); Mg and Cu (Vetec, São Paulo, Brazil) with concentration of 1000 mg L^{-1} and kept in 1.0% v/v HNO_3 (Vetec, São Paulo, Brazil). The bottles and glassware used were immersed in acid bath containing 10% v/v HNO_3 for 24 h and rinsed with deionized water. All solutions were prepared using purified water at 18 MΩ cm in a Milli-Q® system (Millipore, Direct-Q UV MA, USA). For anions analysis, the electrolyte solution was composed by a chromophore group 50.0 mmol L^{-1} CrO_4^{2-}, prepared from sodium chromate (Na_2CrO_4) (Vetec, São Paulo, Brazil) and 0.20 mmol L^{-1} hexadeciltrimetylammonium bromide (CTAB — Sigma, St. Louis, MO, USA). Sodium hydroxide (NaOH) (Synth, São Paulo, Brazil) was used for electrolyte pH adjustment to 11.0. The standards were prepared from sodium nitrate ($NaNO_3$) (Vetec, São Paulo, Brazil), sodium sulfate (Na_2SO_4), potassium chloride (KCl) and sodium bicarbonate ($NaHCO_3$) (Isofar, São Paulo, Brazil). NO_2^- (Fluka, São Paulo, Brazil) was used as internal standard.

2.3. Instrumentation

The determination of Na and K was performed by flame atomic emission spectrophotometry (F AES), using Digimed-DM 61 photometer (São Paulo, Brazil). As, Ca, Cd, Cu, Mn, Mg and Pb determination was carried out using an atomic absorption spectrometer (Thermo Scientific, Solaar M5 Series, Cambridge, United Kingdom) equipped with deuterium background corrector. Ca and Mg were determined by flame atomic absorption spectrometry (F AAS), using N_2O/C_2H_2 flame for Ca and air/C_2H_2 flame for Mg. The determination of As, Cd, Cu, Mn and Pb was performed by graphite furnace atomic absorption spectrometry (GF AAS). The used wavelengths were: 422.5, 285.2, 193.7, 228.8, 324.8, 279.5 and 217.0 nm for Ca, Mg, As, Cd, Cu, Mn and Pb, respectively. The major anions (Cl^-, NO_3^-, SO_4^{2-} and HCO_3^-) were determined using a capillary electrophoresis (CE) system (HP3d CE, Agilent Technologies, Palo Alto, CA, USA) equipped with a diode array detector (DAD), with ultraviolet (UV) indirect detection, at 250 nm, a temperature control device (set at 25 °C), inverted polarity and constant voltage (−10 kV). A fused-silica capillary tube of 48.5 cm long (40 cm effective length), 75 μm of internal diameter and 375 μm of outer diameter with fluoropolymer external coating (TSU — Polymicro Technologies, Phoenix, AZ, USA) was used. The samples were pre-concentrated 10-fold for anions analysis. The limits of detection were: 0.046 to 3.5 μeq L^{-1}, 4.47 to 16.0 μeq L^{-1} and 0.25 to 5.38 nmol L^{-1} for cations, anions and trace-elements, respectively. The pH was measured with pHmeter Digimed, DM-22, calibrated with pH 4.00 and 7.00 standard buffer solutions (Vetec, São Paulo, Brazil). The H^+ concentration was calculated through pH measurements. Conductivity was measured with equipment QUIMIS Q405M and turbidity measurements were performed with Turbidity Meter Instrutherm TD-300.

2.4. Statistical analysis

Statistical tests were performed in Microsoft Office® Excel 2007 software (correlation matrix) and QualiGraf ® software (Piper diagram).

3. Results and discussion

3.1. Climatological conditions in Juiz de Fora city during 2014

The data obtained from the UFJF meteorological station in 2014 allowed a climate characterization of this period under an unusual water shortage. The mean annual value for relative humidity was 75.3%, ranged from 18 to 98%. The air pressure annual mean was 912.4 hPa. The mean solar radiation was 830 kJ m^{-2} and the summer months (January, February and December) showed highest solar radiation (above 1000 kJ m^{-2}). Table 1 presents the other weather parameters (temperature, wind and precipitation), also obtained in UFJF meteorological station for the year 2014. About air temperature, the mean value was 19.6 °C, ranging from 8.7 °C to 35.0 °C. The wind speed annual mean was 2.8 m s^{-1}, with wind gusts up to 24.8 m s^{-1}, in 2014. The wind profile was also analyzed during diurnal and nighttime period. The data showed that N direction is predominant in the diurnal period, and NE direction in the nighttime period. These wind directions are associated with the configuration of the urban area which the city is located, combined with secondary circulation. The complex terrain of this region, with large