

COMPOSITION AND SOURCES OF MAJOR INORGANIC CONSTITUENTS IN RAINWATER FROM THE CITY OF RIO DE JANEIRO, SOUTHEASTERN BRAZIL



Revista
Desafios

Artigo Original
Original Article
Artículo Original

Composição e fontes dos constituintes inorgânicos majoritários na água da chuva da cidade do Rio de Janeiro, sudeste do Brasil.

Composición y fuentes de los principales componentes inorgánicos en el agua de lluvia de la ciudad de Río de Janeiro, sureste de Brasil.

Patricia Alexandre de Souza^{*1,2}, William Zamboni de Mello², John Edmund Lewis Maddock²

¹Curso de Engenharia Florestal, Universidade Federal do Tocantins, Gurupi (TO), Brasil.

²Laboratório de Biogeoquímica Ambiental, Departamento de Geoquímica, Instituto de Química, Universidade Federal Fluminense, Niterói (RJ), Brasil.

*Correspondência: Curso de Engenharia Florestal, Universidade Federal do Tocantins, Rua Badejós, Lote 07, S/N – Jardim Servilha, Gurupi, Tocantins, Brasil. CEP:77.404-070. e-mail: pasouza.geoq@gmail.com.

Artigo recebido em 23/03/2020 aprovado em 04/11/2020 publicado em 10/03/2021.

RESUMO

Amostras de água da chuva foram coletadas em dois locais (Maracanã e Deodoro) na cidade do Rio de Janeiro, no período de junho de 1999 a março de 2000. As amostras foram analisadas quanto aos constituintes inorgânicos majoritários (H^+ , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- e SO_4^{2-}) para determinação de suas concentrações e fontes potenciais. As concentrações médias ponderadas pelo volume (MPV) dos íons inorgânicos não diferiram estatisticamente entre os locais de amostragem, exceto o H^+ . Cloreto e Na^+ foram os constituintes mais abundantes na água da chuva em ambos os locais. As frações não-marinhas (nss-) de K^+ , Ca^{2+} , Mg^{2+} e SO_4^{2-} compreenderam 54–83% de suas concentrações. Amônio excedeu a concentração do NO_3^- por um fator de 1,5, indicando predominância da forma reduzida de nitrogênio para o total de nitrogênio inorgânico. As correlações significativas entre as concentrações de NH_4^+ , nss- Ca^{2+} , nss- SO_4^{2-} e NO_3^- (dados combinados; $n = 41$), sugerem que a dissolução dos seus precursores (NH_3 , H_2SO_4 , HNO_3 , $(NH_4)_2SO_4$, NH_4HSO_4 , NH_4NO_3 and CaC_2O_4), controlaram a acidez da água da chuva. A composição química da precipitação nessa região é provavelmente governada por aerossóis de sal marinho e por múltiplas fontes naturais e antrópicas locais e/ou regionais.

Palavras-chave: Precipitação química, poluição atmosférica, química da atmosfera.

ABSTRACT

Rainwater samples were collected at two sites (Maracanã and Deodoro) in the city of Rio de Janeiro, from June 1999 to March 2000. The samples were analyzed for major inorganic constituents (H^+ , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-}) in order to determine their concentrations and potential sources. The volume-weighted mean (VWM) concentrations of inorganic ions did not differ statistically between the sampling sites, excepted H. Chloride and Na^+ were the most constituents in the rainwater in both sites. The non-sea-salt (nss-) fractions of K^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} comprised 54–83% of their total concentrations. Ammonium exceeded NO_3^- concentration by a factor of 1.5, indicating predominance of the reduced nitrogen form for the total of inorganic nitrogen. The significant correlations between NH_4^+ , nss- Ca^{2+} , nss- SO_4^{2-} and NO_3^- concentrations (combined data; $n=41$) indicate that dissolution of their precursors (NH_3 , H_2SO_4 , HNO_3 , $(NH_4)_2SO_4$, NH_4HSO_4 , NH_4NO_3 and CaC_2O_4) controlled the rainwater acidity. The chemical composition of precipitation in this region is probably governed by sea-salt aerosols and by multiple local and/or regional natural and anthropogenic sources.

Keywords: Chemical precipitation, atmospheric pollution and atmospheric chemistry.

RESUMEN

Muestras de agua de lluvia han sido recogidas en dos sitios en la ciudad de Rio de Janeiro (Maracanã y Deodoro), desde junio de 1999 hasta marzo de 2000. Se hizo las analisis para determinar las concentraciones de sus componentes inorgánicos (H^+ , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- y SO_4^{2-}) y posibles fuentes. No fueron encontradas distinciones en los sitios cuanto a las concentraciones promedio ponderadas en volumen (PPV) de iones inorgánicos, excepto para H^+ . Cloruro y Na^+ fueron los componentes más abundantes en el agua de lluvia en ambos lugares. Las fracciones no marinas (nss-) de K^+ , Ca^{2+} , Mg^{2+} y SO_4^{2-} comprendieron 54-83% de sus concentraciones. Amonio excedió la concentración de NO_3^- en un factor de 1.5, indicando predominio de la forma reducida del nitrógeno para el total de nitrógeno inorgánico. Las correlaciones fueran significativas en las concentraciones de NH_4^+ , nss- Ca^{2+} , nss- SO_4^{2-} y NO_3^- (datos combinados; $n=41$) indicando que la disolución de sus precursores (NH_3 , H_2SO_4 , HNO_3 , $(NH_4)_2SO_4$, NH_4HSO_4 , NH_4NO_3 y CaC_2O_4), controlaron la acidez en la lluvia. La composición química de la precipitación es probablemente gobernada por aerosoles de la sal marina y por múltiples fuentes naturales y antrópicas locales y/o regionales.

Descriptor: Precipitación química, contaminación del aire, química de la atmósfera.

INTRODUCTION

Precipitation plays an important role in the removal processes (in-cloud and below-cloud) of soluble substances from the atmosphere. Rainwater contains trace amounts of inorganic (H^+ , Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , NO_2^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} and transition elements) and organic (organic acids, semi-volatile organic compounds, amino acids and urea) constituents (MOPPER and ZICA, 1987; GALLOWAY and KEENE, 1989; CORNELL *et al.*, 1998; VET *et al.*, 2014). Its composition varies locally and regionally due to natural and anthropogenic emissions of gases and aerosol particles, and their chemical transformations in the atmosphere (SEINFELD and PANDIS, 2006; VET *et al.*, 2014). Therefore, rainwater is a useful tool to evaluate the levels of impact caused by human activities on the atmosphere (VET *et al.*, 2014).

Investigations on rainwater chemistry have been subject of research since the mid-20th century due to the effects of acid rain on the environment and its ecological consequences (BARRETT and BRODIN, 1955; ODÉN, 1976; GORHAM, 1998; BURNS *et al.*, 2016; GRENNFELT *et al.*, 2020). In Brazil, studies of chemical composition of rainwater and bulk precipitation (rainwater and dry deposition of settling particles; DE SOUZA *et al.*, 2017) have been conducted

in (coastal and inland) urban áreas (CAMPOS *et al.*, 1998; FIGUERÊDO, 1999; DE MELLO, 2001; LARA *et al.*, 2001; FORNARO and GUTZ, 2003; LEAL *et al.*, 2004; MIGLIAVACCA, 2005; FORTI *et al.*, 2007; DE SOUZA *et al.*, 2015); locations of coal mining, coal-fired power plant and cement industry (FLUES *et al.*, 2003; MIGLIAVACCA, 2004); rural and agricultural áreas (CARVALHO and LEPRUN, 1991; LARA *et al.*, 2001; CASARTELLI *et al.*, 2008; OLIVEIRA *et al.*, 2012); industrial locations (CASARTELLI *et al.*, 2008; VIEIRA-FILHO *et al.*, 2015) and tropical forest sites (SILVA-FILHO, 1985; BROWN *et al.*, 1989; WILLIAMS *et al.* 1997; FILOSO *et al.*, 1999; DE MELLO and ALMEIDA, 2004; FORTI *et al.*, 2007; ABREU, 2005; DE SOUZA *et al.*, 2015).

In the Metropolitan Region of Rio de Janeiro (MRRJ), the second largest urban and industrial center of Brazil, studies on precipitation chemistry started in the early 1980s in a 40-km² urban forest reserve (Tijuca National Park) located within the city of Rio de Janeiro by Silva-Filho (1985) and Brown *et al.* (1989) with measurements of pH and some major inorganic constituents (Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Cl^-). These authors reported a low mean pH value (4.7), however, the controlling factors which influenced the free acidity could not be properly discussed due to the lack of NH_4^+ ,

NO_3^- and SO_4^{2-} data. If they had calculated the volume-weighted mean (VWM), based on the weekly H^+ concentration data, instead of mean pH, the former would possibly be lower, as emphasized by Fornaro and Gutz (2006).

De Mello (2001) investigated the major inorganic constituents of rainwater in the late 1980s in the city of Niterói, southeastern MRRJ, approximately 17 km east-northeast of Tijuca National Park. He found a VWM pH of 4.8, very similar to the mean value reported by Silva-Filho (1985) and Brown *et al.* (1989). De Mello (2001) also revealed that, based on the VWM concentrations of SO_4^{2-} and Na^+ , the non-sea-salt sulfate fraction (nss-SO_4^{2-}) corresponded to 82% of the total SO_4^{2-} and the equivalent proportion of $\text{nss-SO}_4^{2-}:\text{NH}_4^+:\text{NO}_3^-$ was 2.1:1.2:1.0.

Fornaro and Gutz (2006) showed that the mean annual concentration of SO_2 in the city of São Paulo, Brazil's largest urban and industrial center, dropped about 72% from 1983 to 2004, being more pronounced in the first 10 years. No monitoring data for the same period is available in the literature for the MRRJ.

Studies on chemical composition of rainwater within the MRRJ are still poorly documented. In this article we present the concentration of major inorganic constituents in rainwater sampled at two locations in the city of Rio de Janeiro from mid-1999 to March 2000 and examine their major natural and anthropogenic sources. The surroundings of these two sites are characterized by areas of high traffic flow and poor ventilation due to the presence of Tijuca and Pedra Branca massifs, topographical barriers against the prevailing southerly winds. Our work focused on determining the major natural and human-related factors controlling the chemical composition of rainwater in this region.

MATERIAL AND METHODS

Study area

This study was conducted at two sampling sites in the city of Rio de Janeiro (Fig.1). One located at the campus of Universidade Estadual do Rio de Janeiro (22°54'42" S; 43°14'04" W), in Maracanã district. Another, located at a military base in Deodoro district (22°51'43" S; 43°23'28" W). The Maracanã and Deodoro sites, characterized as coastal urban areas, are located respectively 9 and 17 km north of the Atlantic coastline. Between the Atlantic and these sampling sites lie the Tijuca and Pedra Branca massifs.

The city of Rio de Janeiro is bounded by the Gericinó-Mendanha massif to the northwest, Tijuca massif to the south and Pedra Branca massif to the midwest (Fig.1). The city has an area of 1.225 km², of which 45% are built up, 43% is covered by vegetation, 3% by industries, 2% by agricultural areas and the remainder is occupied by rocky outcrops and flooded areas (IPP, 2013). In 2000, its population comprised 5.9 million inhabitants (IBGE, 2000); and the active vehicle fleet was about 1.6 million, of which 84% were made up of cars (DETRAN, 2001). Soils in the city of Rio de Janeiro are classified as red-yellow latosol and red-yellow podzolic (IPP, 2013).

The mean annual precipitation in the city of Rio de Janeiro presents a spatial variation due to the topography. At higher altitudes, precipitation ranges from 1200 to 2200 mm and decreases to a minimum of 900 mm at lower elevations (DERECZYNSKI *et al.*, 2009). Based on the Köppen climate classification system, climate is tropical monsoon (Am) (ALVARES *et al.*, 2013).

Atmospheric circulation in this region is under influence of the sea breeze with prevailing winds from south and southeast (at the day and early evening) and of the mountain breeze with winds from north (at dawn and early morning). During the passage of cold fronts, winds

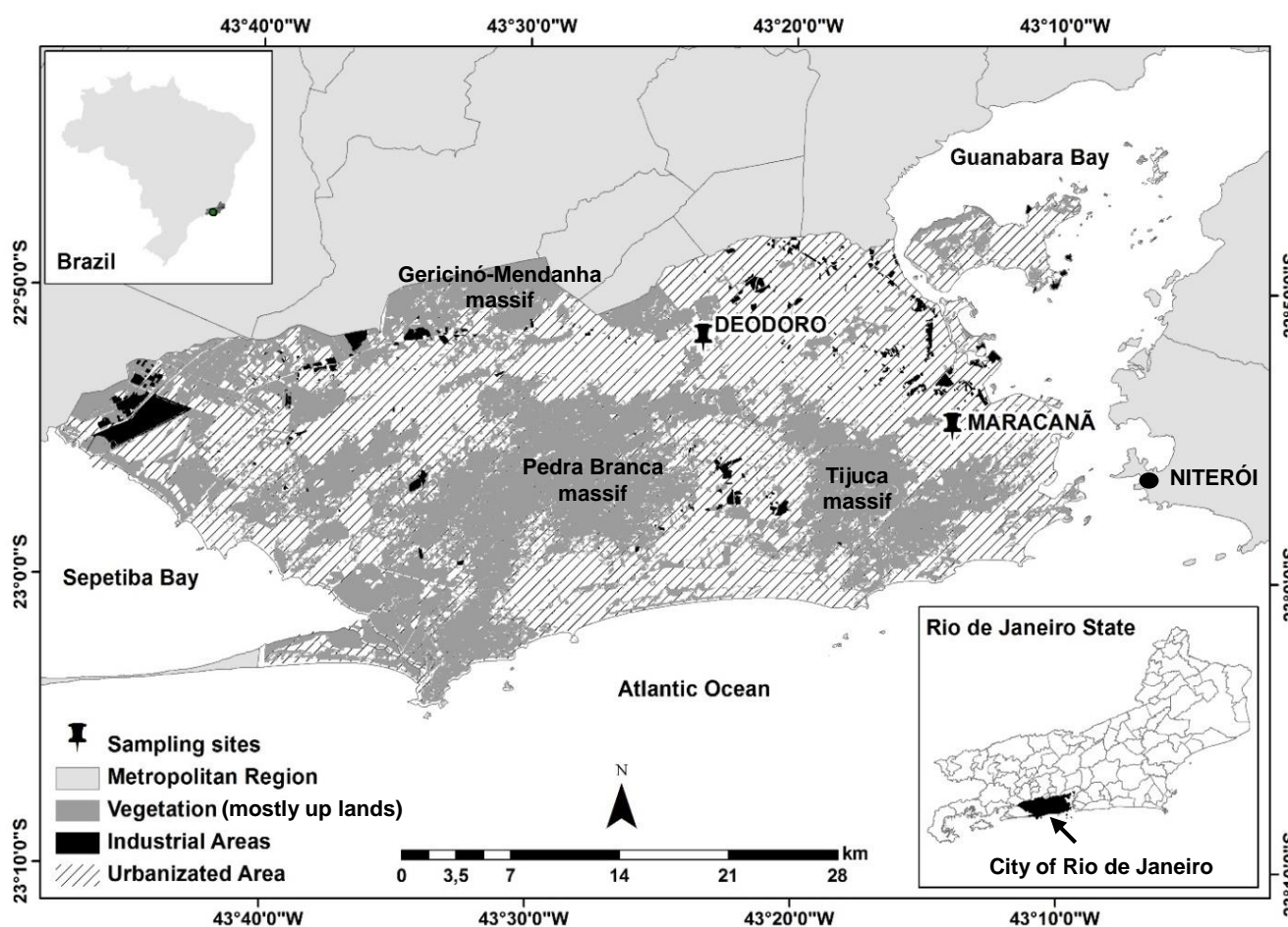
are from south and southwest (DE SOUZA *et al.*, 2015). However, the two sampling locations are characterized by poor ventilation due to the mountainous relief between them and the coastline, which form a barrier for the prevailing southerly winds. At these sites, daily average calm wind conditions (wind speed $< 0.5 \text{ m s}^{-1}$) is 8% for Maracanã and 26% for Deodoro, with high stagnation conditions occurring at dawn, reaching 15% and 46%, respectively (PIMENTEL *et al.*, 2014).

In the MRRJ (6,745 km^2), at the turn of the 21st century, the anthropogenic emissions of NO_x and SO_2

were 28 Gg N yr^{-1} ($G = 10^9$) and 32 Gg S yr^{-1} , respectively, of which mobile and fixed (mainly petrochemical industry and power plants) sources comprised respectively 66% and 33% of NO_x and 12% and 88% of SO_2 emissions (LOUREIRO, 2005).

The airports and the port zone of the city of Rio de Janeiro contribute with less than 1% of NO_x and SO_2 . Emissions of H_2S , from polluted mangrove sediments in Guanabara Bay have never been estimated, but because their rapid oxidation rate in the atmosphere, they might represent an important local source of SO_2 .

Figure 1. Location of study area and sampling sites, the Maracanã and Deodoro districts, in the city of Rio de Janeiro, southeastern of Brazil.



By the beginning of the 21st century, the surface waters of Guanabara Bay emitted about 1.4 Gg N yr^{-1} (or 3.6 t N d^{-1}) of NH_3 to the atmosphere,

attributed to discharges of untreated sewage into the bay (GUIMARÃES and DE MELLO, 2006). In addition, we consider municipal landfills, biomass

burning, vehicles and a petrochemical industry as potentially important local sources of NH_3 to the local atmosphere, though unquantified as yet.

Sampling

Rainwater samples were collected weekly during 10 months (from 1999 to March 2000) in the Maracanã district and during 8 months (from August 1999 to March 2000) in the Deodoro district. The collections of rainwater samples were performed using a Graseby /GMW automatic sampler (model APS 78–100, Village of Cleves, Ohio). This sampler was equipped with two 13-L buckets (with 28.5 cm diameter), one for wet deposition (rainwater collection) and one for dry deposition (collection of settling particles), whose opening and shutting were controlled by a precipitation detector. In this study, only wet deposition was used.

One-liter polyethylene bottles were used for sample collections from buckets and 250-mL polyethylene bottles for storage of filtered samples. They were previously cleaned using Milli-Q water (ultrapure; $< 1 \mu\text{S cm}^{-1}$) and soaked for 24 h. Then were dried and stored in plastic seal bags. After the samples retrieval, the volume of rainwater was recorded for further calculation of precipitation. A total of 48 rainwater samples (27 from Maracanã and 21 from Deodoro) were collected during the study period.

No biocide was added to the sample before or after collection. Previous studies showed no alteration in the chemical composition of rainwater samples treated or not with thymol (biocide) after 7 days of storage at room temperature (HADI and CAPE 1995; AYERS *et al.*, 1998).

After collection, the rainwater samples were taken to the Laboratory of Environmental Geochemistry at the Chemistry Institute of Universidade Federal Fluminense and immediately

filtered through Millipore 0.22 μm pore size cellulose acetate membranes (diameter of 47 mm) and stored in a freezer ($-22 \text{ }^\circ\text{C}$). In unfiltered aliquots, electrical conductivity and pH measurements were carried out using a conductivity meter WTW model LF330 and a pH meter WTW model pH330. The former was calibrated with 0.01 and 0.05 $\mu\text{mol L}^{-1}$ KCl solutions and the latter with pH 6.86 and 4.01 standard buffer solutions (APHA, 1985).

Chemical Analysis

Ammonium was determined spectrophotometrically using the indophenol blue methods with absorbance measured at 630 nm in a Hitachi spectrophotometer model U-1100 (GRASSHOFF *et al.*, 1983). Calcium and Mg^{2+} were analyzed by atomic absorption spectrometry, and Na^+ and K^+ by flame emission spectrometry in a spectrophotometer Baird Atomic 4200. Nitrate, Cl^- and SO_4^{2-} anions were determined by ion chromatography (Shimadzu model LC-10 AD), with a conductivity detector, using a Shim-pack IC-GA1 pre-column and a Shim-pack IC-A1 (4.6 mm x 10 cm) chromatographic column (with no suppression system). The temperature of the column was maintained at $40 \text{ }^\circ\text{C}$ during analysis. The mobile phase consisted of a solution of 2.4 mmol L^{-1} potassium hydrogenphthalate, prepared with Milli-Q ultrapure water ($< 1 \mu\text{S cm}^{-1}$), with a flow rate of 1.4 mL min^{-1} . The samples (or standards solutions and blanks) were injected manually through a loop of 1 mL. The detection limits were (in $\mu\text{mol L}^{-1}$): Na^+ (0.74), K^+ (0.55), Mg^{2+} (0.61), Ca^{2+} (1.0), NH_4^+ (1.7), Cl^- (0.61), NO_3^- (0.36) and SO_4^{2-} (0.40). The precision of analysis was $\pm 5\%$.

Data treatment

The analytical results were evaluated by comparing the relation between measured electrical

conductivity and electrical conductivity calculated by ionic balance, according to the guidelines of the World Meteorological Organization (WMO/GAW, 2004). Following this criteria, 3 rainwater samples from Maracanã and 4 from Deodoro were rejected.

In this study, we applied non-parametric statistics on the precipitation chemistry data because most of the variables did not show normal distribution based on the Shapiro-Wilk test (CONOVER, 1980). Mann-Whitney test was used to evaluate the spatial differences between the variables, while the Spearman rank test and linear regressions were used to verify correlations between them. Factor Analysis with Varimax normalized rotation was applied to the results to identify the potential origins of the variables. The statistical tests were performed to significance equal or less than 0.05 using Statistic Program 7.0.

RESULTS AND DISCUSSION

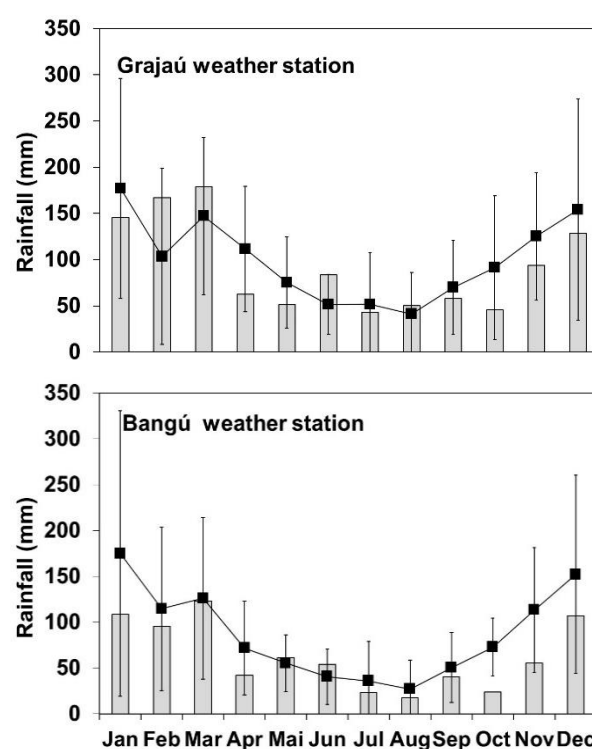
Rainfall

The total accumulated precipitation sampled in Maracanã (from June 1999 to March 2000) and Deodoro (from August 1999 to March 2000) were 710 mm and 507 mm, respectively. For Maracanã, this value corresponded to 64% of the 12-month records (from April 1999 to March 2000) from the Grajaú (1107 mm) weather station located ca. 3 km southwest (22°55'00" S, 43°16'03" W; 112 m elevation) of that sampling site. For Deodoro, the precipitation amount comprised 67% of the 12-month record (from April 1999 to March 2000) from the Bangú weather station (752 mm), located ca. 8 km southwest (22°52'49" S; 43°27'57" W; 50 m elevation) of that sampling site. All precipitation data from meteorological stations were compiled from the website of the FUNDAÇÃO GEORio (2020a).

The monthly precipitation values during the study period (12-month record; April 1999–March 2000) were mostly below the long term monthly

means (period 1997–2016), especially from October to December, from both meteorological stations (Figure 2). This could be attributed to severe drought that affected southeastern Brazil, due to strong El Niño events that took place during the period 1997–1999 (INPE, 2020a).

Figure 2. Comparison between twelve-month record rainfall (April 1999–March 2000; \blacksquare) and long term mean monthly rainfall (period 1997–2016; \square) from Grajaú and Bangú weather stations in the city of Rio de Janeiro. The vertical lines represent the standard deviations. Precipitation data were compiled from the website of the FUNDAÇÃO GEORio (2020a).



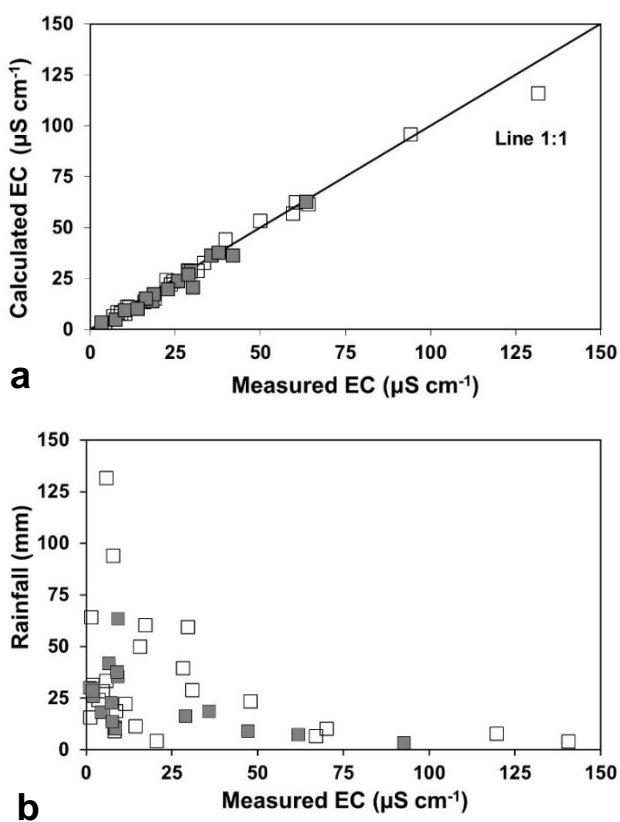
Electrical conductivity and pH

The measured electrical conductivities (EC) were comparable to the calculated EC at both sampling sites (Figure 3a). The distribution of these values fits quite well to the 1:1 line, indicating good agreement between them.

The volume-weighted mean (VWM) measured electrical conductivity (EC) of rainwater in Maracanã and Deodoro were respectively $18.4 \mu\text{S cm}^{-1}$ ($4.20\text{--}132 \mu\text{S cm}^{-1}$; $n = 24$) and $13.4 \mu\text{S cm}^{-1}$ (from $3.20\text{--}63.6 \mu\text{S cm}^{-1}$; $n = 17$), with greater amplitude of

values found in the former. There is an inverse relationship between the measured EC and rainfall amount, which is basically attributed to dilution effect (Figure 3b). Maracanã is subjected to greater influence of sea-salt aerosols due to its shorter distance from the coast, which explains the highest measured EC values in the rainwater from this site.

Figure 3. Correlations between measured electrical conductivity (measured EC) and calculated electrical conductivity (calculated EC) (a) and measured EC and rainfall (b) in rainwater at the two sampling sites in the city of Rio de Janeiro (Maracanã □ and Deodoro ■).



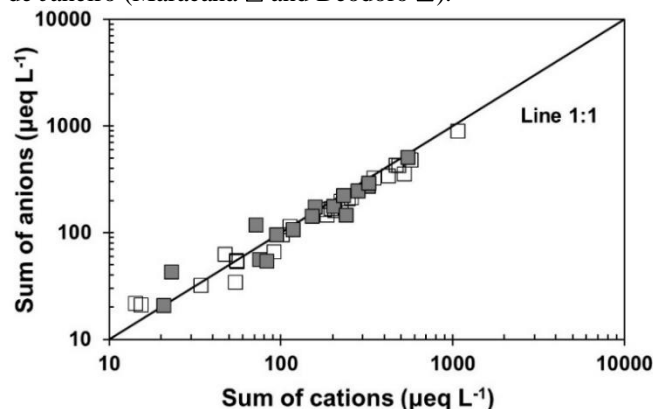
The VWM pH of rainwater, calculated from the VWM H^+ concentrations, were 5.1 (3.8–6.5; $n = 24$) for Maracanã and 5.5 (4.8–6.1; $n = 17$) for Deodoro, corresponding to free acidities (H^+ ions) of 8.4 and of $3.4 \mu\text{eq L}^{-1}$, respectively (Table 1). These VWM pH values are smaller than that resulting from the dissolution of atmospheric CO_2 ($p\text{CO}_2 = 3.7 \times 10^{-2}$ atm at 298 K) and partial ionization of H_2CO_3 in pure water ($\text{pH} = 5.6$ or $H^+ = 2.3 \mu\text{eq L}^{-1}$). Galloway *et al.*

(1982) considered $\text{pH} = 5.0$ as the lower limit of natural contribution of acids in rainwater.

We found that 63% and 29% of the pH values in Maracanã and 23% and 6% of those in Deodoro were below 5.6 and 5.0, respectively. The VWM pH values from Maracanã and Deodoro were higher than those reported in previous studies conducted in the MRRJ during the 1980s (SILVA-FILHO, 1985; BROWN *et al.*, 1989; DE MELLO, 2001) and similar to the range of values (5.1 – 5.3) reported in the early 2000s (ABREU, 2005; SILVA, 2009).

The difference between the sum of anions (Cl^- , NO_3^- and SO_4^{2-}) and the sum of cations (H^+ , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) displays a VWM anion deficit of $15.7 \mu\text{eq L}^{-1}$ for Maracanã and of $2.5 \mu\text{eq L}^{-1}$ for Deodoro (Figure 4). This fact has been observed in remote, urban, rural and industrial areas and is usually attributed to undetermined carboxylate anions, such as formate, acetate and oxalate (FORNARO and GUTZ, 2006; CASARTELLI *et al.*, 2008; CONCEIÇÃO *et al.*, 2013; VET *et al.*, 2014)

Figure 4. Correlation between sum of cations and sum of anions in rainfall at the two sampling sites in the city of Rio de Janeiro (Maracanã □ and Deodoro ■).



Concentrations of major inorganic ions

There was no significant spatial difference between the VWM concentrations of major inorganic

constituents in rainwater, except H^+ , which was about 2.5 fold higher in Maracanã compared to Deodoro (Table 1; Mann–Whitney test; $p < 0.05$). In this study, the VWM concentrations of NH_4^+ , Na^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} were within the range of the VWM values reported for other large urban areas in Southeast Brazil, except K^+ and NO_3^- which fit in the lower end of their ranges (DE MELLO, 2001; LARA *et al.*, 2001; ROCHA *et al.*, 2003; LEAL *et al.*, 2004; SANTOS *et al.*, 2007).

Table 1. Arithmetic mean (AM \pm SD) and volume-weighted mean (VWM) concentrations ($\mu eq L^{-1}$) of major inorganic constituents in rainwater at the Maracanã and Deodoro sites.

SD: Standard deviation.

Sampling site	AM \pm SD	VWM
Maracanã (n = 24)		
H^+	13.0 \pm 34.0	8.37
NH_4^+	50.8 \pm 41.4	26.1
Na^+	109 \pm 128.6	52.9
K^+	7.00 \pm 14.2	4.06
Ca^{2+}	26.1 \pm 41.4	13.4
Mg^{2+}	50.7 \pm 29.1	27.8
NO_3^-	31.1 \pm 32.8	17.2
Cl^-	121 \pm 151	66.5
SO_4^{2-}	60.0 \pm 27.8	33.3
Deodoro (n = 17)		
H^+	2.79 \pm 3.50	3.37
NH_4^+	51.2 \pm 57.70	24.7
Na^+	72.2 \pm 90.0	33.6
K^+	3.90 \pm 2.57	2.56
Ca^{2+}	12.6 \pm 4.32	6.71
Mg^{2+}	36.7 \pm 21.4	16.5
NO_3^-	25.5 \pm 23.4	16.4
Cl^-	94.8 \pm 114	44.9
SO_4^{2-}	40.9 \pm 11.6	23.7

The relative distribution of inorganic ions in rainwater (based on equivalent concentrations) decreased as follows: Cl^- (27%) > Na^+ (21%) > SO_4^{2-} (13%) > Mg^{2+} (11%) = NH_4^+ (11%) > NO_3^- (7%) > Ca^{2+} (5%) > H^+ (3%) > K^+ (2%) for Maracanã and Cl^- (26%) > Na^+ (19%) > SO_4^{2-} (14%) = NH_4^+ (14%) > Mg^{2+} (10%) = NO_3^- (10%) > Ca^{2+} (4%) > H^+ (2%) > K^+ (1%) for Deodoro. Chloride and Na^+ together accounted to approximately half of the total major inorganic constituents dissolved in rainwater and were highly correlated (Spearman rank test, $p < 0.01$; $r =$

0.99, $n = 24$ for Maracanã; $r = 0.98$, $n = 17$ for Deodoro), indicating that at both sites the chemical composition of rainwater is strongly influenced by sea–salt aerosol. Likewise, the chemical composition of rainwater in an urban coastal site and in a montane forest area, both in the MRRJ, has shown to be quite affected by marine sources (DE MELLO, 2001; ABREU, 2005).

Using Na^+ as a sea–salt tracer (KEENE *et al.*, 1996; MILLERO, 2006), non–sea–salt fractions of Cl^- , Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} comprised respectively 7%, 57%, 72%, 83% and 81% of their total VWM concentrations for Maracanã and 13%, 54%, 71%, 78% and 83% for Deodoro. In general, most of K^+ , Ca^{2+} and SO_4^{2-} and little more than half of Mg^{2+} originated from natural and/or anthropogenic sources other than sea–salt aerosol particles, whereas Cl^- is predominantly of sea salt origin.

Inorganic ions sources in rainwater

Non–sea–salt potassium, calcium and magnesium

The non–sea–salt fractions of K^+ , Ca^{2+} and Mg^{2+} in rainwater varies significantly from coastal to inland sites and also with altitude. In a southern shore of Ilha Grande (ca. 100 km southwest from our study sites), a coastal island in southwestern Rio de Janeiro state, De Souza *et al.* (2006) found that the non–sea–salt fractions of K^+ , Ca^{2+} and Mg^{2+} comprised respectively 56%, 32% and 20% of their total concentrations.

Using rainwater chemical composition data from central Amazon reported by Williams *et al.* (1997), we calculated non–sea–salt contributions of 93%, 96% and 40% for those K^+ , Ca^{2+} and Mg^{2+} , respectively. At the Itatiaia massif (a conservation area of the Atlantic Forest Biome), a mountain range ca. 160 km northwest from our study sites, the non–sea–salt fractions of K^+ , Ca^{2+} and Mg^{2+} comprised 93% and 97%, 96% and 98%, and 60% and 64% for 820 m and

2460 m altitude, respectively (DE MELLO and ALMEIDA, 2004).

The excesses (non-sea-salt fractions) of K^+ , Ca^{2+} and Mg^{2+} with respect to sea-salt are usually attributed to terrestrial biogenic sources, such as leaf fragments, pollen grains, fungi, algae and *al.*, 1990; ARTAXO and HANSSON, 1995). The proportions of K^+ , Ca^{2+} and Mg^{2+} in terrestrial plants are variable in tropical forests according to sazonality, leaf age, successional stage, nutrient availability, topography and soil types (SOBRADO and MEDINA, 1980; VITOUSEK and SANFORD, 1986; VITOUSEK *et al.*, 1995; MORAES and DOMINGO, 1997; KLUMP *et al.*, 2002; BOEGER *et al.*, 2005).

Some studies suggest enrichments of Ca^{2+} and Mg^{2+} (GASTON *et al.*, 2011; SALTER *et al.*, 2016; and references therein), with respect to sea-salt composition, in natural submicrometer marine aerosol particles generated by bursting bubble process in marine environment.

Chloride and sodium

The Cl^-/Na^+ equivalent ratios (based on their VWM concentrations) in rainwater in Maracanã and Deodoro were respectively 1.26 and 1.34. No significant difference was found between them when the entire individual data sets are compared (Mann-Whitney test, $p < 0.01$). These values are slightly greater (8.3% and 15%, respectively) than the sea-salt Cl^-/Na^+ ratio (1.16; MILLEIRO, 2006). A 7.6 % Cl^- enrichment with respect to sea-salt was reported by de Souza *et al.* (2006) in rainwater collected at the southern coast of Ilha Grande. A slightly higher enrichment value (17%) was reported by Andrade (2005) in rainwater at the Pedra Branca massif, a forest reserve within the urban area of the city of Rio de Janeiro. Interestingly, de Mello and Almeida (2004) found a significant altitudinal variation at the Itatiaia

massif, with Cl^- enriching from 15% at 820 m to 160% at 2460 m altitude.

In contrast, Cl^- depletion has been observed in bulk precipitation (rainwater and soluble particles deposited by gravitational settling) samples (DE MELLO, 2001; ARAUJO *et al.*, 2015) and in atmospheric aerosol particles (MARIANI and DE MELLO, 2007; DE SOUZA *et al.* 2010; 2011) in coastal urban areas of Brazil. A possible mechanism to explain the Cl^- in rainwater and aerosol particles is the volatilization of HCl after heterogeneous reactions of gaseous HNO_3 and H_2SO_4 on the surface of NaCl particles as proposed by Keene *et al.* (1986) (Equation 1):



In a costal urban area of Hong Kong, Zhuang *et al.* (1999) estimated that the loss of Cl^- from atmospheric aerosols increased from 10% to 98% as particles decrease in size from 18 μm to 1.8 μm , due to the larger surface area and longer residence time in the atmosphere of the smallest particles. In Niterói, ca. 10–20 km east-southeast from our sampling sites (Figure 1), and in São José dos Campos, a urban and industrial area of São Paulo state, ca. 60 km north from the Atlantic coast and 270 km southwest from our study sites, Cl^- deficits were found in both fine (41%) and coarse (39%) fractions of PM_{10} (particulate matter $\leq 10 \mu m$ in diameter), with a more pronounced enrichment in dry season (DE SOUZA *et al.*, 2010).

In remote area of Asia (Himalaya Mountainous), Shrestha *et al.* (2002) reported Cl^- enrichment relative to seawater Cl^-/Na^+ ratio in rainwater and snow, and Cl^- deficit in aerosol particles. They believe that Cl^- enrichment is due to scavenging of gaseous HCl by rain droplets and incorporation during growth of snowflakes.

Chloride enrichment in rainwater and deficit in particulate matter were also found in central

Amazon during dry season, being the former attributed to scavenging of gaseous HCl and biogenic KCl particles from biomass burning (ANDREAE *et al.*, 1990, ARTAXO *et al.*, 1998). Therefore, we believe that Cl⁻ enrichment in rainwater in the MRRJ results from the scavenging of gaseous HCl volatilized from sea-salt particles, but possibly also from gaseous HCl and KCl particles both from biomass burning. However, no significant correlation (Spearman rank test, $p > 0.05$) was found between nss-Cl⁻ and nss-K⁺ in the rainwater samples from Maracanã ($r = 0.21$, $n = 24$) and Deodoro ($r = 0.08$, $n = 17$).

Non-sea-salt sulfate, nitrate and ammonium

Volume-weighted mean concentrations of SO₄²⁻ in rainwater samples in Maracanã and Deodoro were respectively 33.3 and 23.7 µeq L⁻¹, which are lower than the VWM concentration of SO₄²⁻ (41.3 µeq L⁻¹) found by de Mello (2001) in rainwater from Niterói by the late 1980s. The rainwater SO₄²⁻ concentration reported by Abreu (2005) in the Pedra Branca massif (32 µeq L⁻¹) is very similar to the value observed in Maracanã, but higher than the that determined in Deodoro. The distances between sampling sites and the Atlantic coast (Figure 1), as well as topography, explain the differences, although small, of VWM sea-salt sulfate concentrations for Deodoro (4.1 µeq L⁻¹), Maracanã (6.4 µeq L⁻¹), Pedra Branca (7.2 µeq L⁻¹) and Niterói (7.4 µeq L⁻¹).

Their non-sea-salt sulfate fractions were similar comprising respectively 82, 81, 77 and 83%, suggesting that no significant changes in anthropogenic SO₂ emissions took place in the MRRJ between the late 1980s and the early 2000s, when the study in Niterói and those in Rio the city of Rio de Janeiro (Deodoro, Maracanã and Pedra Branca) took place, respectively. However, there are no data available in the literature regarding SO₂ concentrations in RMRJ during that period. In the city of São Paulo,

Fornaro and Gutz (2006) showed an expressive drop of SO₂ concentrations between 1983 (~ 64 µg m⁻³) and 1992 (~ 15 µg m⁻³) and much less pronounced changes from 1993 to 2003, when concentrations oscillated from around 13 to 20 µg m⁻³.

Using data compiled from different studies of SO₄²⁻ in rainwater, they showed a concomitant decrease of SO₄²⁻ concentrations in rainwater between 1983 and 2003. In the MRRJ, the anthropogenic emissions of SO₂ from fixed and mobile sources might have decreased due to use of fuel with lower sulfur contents following the regulations established by PRONAR (National Air Quality Control Program) and PROCONVE (National Vehicular Emissions Control Program) in the mid-1980s, however, the vehicular fleet have doubled between 1994 and 2004, going from 980 thousand to 1.9 million vehicles (FUNDAÇÃO GeoRIO, 2020b).

Volume-weighted mean concentrations of NO₃⁻ in Maracanã (17.2 µeq L⁻¹) and Deodoro (16.4 µeq L⁻¹) were similar to that reported by de Mello (2001) in Niterói (15.8 de µeq L⁻¹) in the late 1980s. These values are closer to the lower end of the range of rainwater NO₃⁻ compiled by Fornaro and Gutz (2006) from several studies conducted in São Paulo, 12.6–30.0 µeq L⁻¹, between the early 1980s to the early 2000s.

The VWM concentrations of NH₄⁺ in Maracanã and Deodoro (26.1 and 24.7 µeq L⁻¹, respectively) were greater than those reported by de Mello (2001), 18.8 µeq L⁻¹, in Niterói in the late 1980s and by Abreu (2005), 22,4 µeq L⁻¹, at the Pedra Branca massif, early 2000s. However, they fit at the lower end of the range of NH₄⁺ data compiled by Fornaro and Gutz (2006) for the Metropolitan Region of São Paulo (26.1–37.8 µeq L⁻¹).

The median NH₄⁺/NO₃⁻ ratio for Maracanã and Deodoro together is 2.0, indicating a predominance of ammonium to the total inorganic nitrogen in rainwater.

This value is slight higher to the median value of $\text{NH}_4^+/\text{NO}_3^-$ (1.4) calculated from the data compiled by Fornaro and Gutz (2006). Basically, the major atmospheric sink for ammonia is neutralization of acids, specially sulfuric and nitric, give rise to dissolved ammonium. In rainwater, NH_4^+ originates from dissolution of gaseous NH_3 and NH_4^+ -containing aerosol particles, such as $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4NO_3 . Gas phase reaction with hydroxyl radicals (OH) is not a significant sink for NH_3 in the atmosphere due to the low reaction rate (rate constant: $k = 1.6 \times 10^{-13} \text{ cm}^3 \text{ moléculas}^{-1} \text{ s}^{-1}$) for the usual mixing ratio of OH radical in the troposphere, ca. 0.04 ppt (SEINFELD and PANDIS, 2006).

There is no available data of atmospheric NH_3 in the MRRJ. Given that it is not a pollutant legislated by CONAMA (National Council for the Environment), its air concentrations are not regularly monitored by state environmental agencies in Brazil. However, there are several potential anthropogenic sources of NH_3 that might have contributed to the intensification of its emissions over the 1990s, and consequently the raise of NH_4^+ in rainwater: uncollected and untreated urban sewage, release of under-treated and untreated sewage into Guanabara Bay, municipal landfills, cattle breeding farms and biomass burning (including long-range transport of small particles and gases from slash and burn agriculture and deforestation activities).

In 2000, the daily production of waste by the population of the MRRJ (ca. 10.1 million inhabitants) was ca. 13 thousand tones, of which 73% were disposed in landfills and the remainder (25%) in open municipal dumping grounds (IBGE, 2000). Jardim Gramacho landfill, the largest municipal landfill (130 ha) in Latin America, inactive since 2012 after 3 decades of operation, received ca. 7 thousand tones day^{-1} of waste (GUEDES, 2007). The high

concentrations of total ammonia ($\text{NH}_3 + \text{NH}_4^+$, up to 60 mmol L^{-1}) in the leachate produced by the Gramacho landfill associated to its alkaline pH (8.1) (SILVA, 2002) represented favorable conditions to promote NH_3 emissions.

We believe that the eutrophic waters of Guanabara Bay are an important source of NH_3 to the atmosphere of the MRRJ, basically due to elevated discharge of under-treated and untreated sewage into the bay. From 1990 to 2000, the release of sewage into the bay increased from 19.2 to $23.5 \text{ m}^3 \text{ s}^{-1}$, of which a small fraction was treated, 12 and 20%, respectively (COELHO, 2007). Guimarães and de Mello (2006) estimated an average NH_3 emission of $42 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from the bay's surface waters (328 km^2), eight times higher than the local total inorganic nitrogen deposition ($\text{NH}_4^+ + \text{NO}_3^-$) estimated by de Mello (2001), $5.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$.

Based on the inventory livestock data from the Brazilian Institute of Geography and Statistics (IBGE, 1988,1998) and the emission factors of NH_3 provided by Bouwman and Van der Hoek (1997), we estimated that NH_3 emissions from cattle excreta in the MRRJ (6745 km^2) increased almost 70% from 1988 ($3.5 \text{ N kg ha}^{-1} \text{ yr}^{-1}$) to 1998 ($5.9 \text{ N kg ha}^{-1} \text{ yr}^{-1}$). We also believe that biomass burning during the dry season is an important source of NH_3 to the atmosphere. It is important to highlight that during our study period (1999–2000), characterized by very low rainfall regimes, 356 occurrences of vegetation fires were detected in the Rio de Janeiro state (INPE, 2020b) most (87%) during the dry season, three times higher than that for the same period in 1998.

Our results show that from the late 1980s (DE MELLO, 2001) to the late 1990s the rainwater $\text{NH}_4^+/\text{NO}_3^-$ ratio increased from 1.2 to 1.5 and the $\text{NH}_4^+/\text{nss-SO}_4^{2-}$ ratio increased from 0.6 to 1.1 (Maracanã–Deodoro rainwater data together), which certainly explains the increase of pH in rainwater from

4.7–4.8 (SILVA-FILHO, 1985; BROWN *et al.*, 1989; DE MELLO, 2001) in the 1980s to 5.1–5.5 (Maracanã–Deodoro) in the late 1990s. The Abreu (2005) report reveals similar values of these ratios (2.3 and 0.9, respectively) and pH (5.0) in rainwater, in the early years of the 2000s, corroborating this supose.

Rainwater neutralization acidity

Highly and significant correlations (Spearman rank test, $p < 0.01$) were found for NH_4^+ and NO_3^- ($r = 0.71$), NH_4^+ and nss-SO_4^{2-} ($r = 0.71$), nss-SO_4^{2-} and NO_3^- ($r = 0.89$), nss-Ca^{2+} and NO_3^- ($r = 0.78$), and nss-Ca^{2+} and nss-SO_4^{2-} ($r = 0.86$) in rainwater obtained by combining all values from Maracanã and Deodoro sites ($n = 41$), given that statistically there was no spatial difference between them.

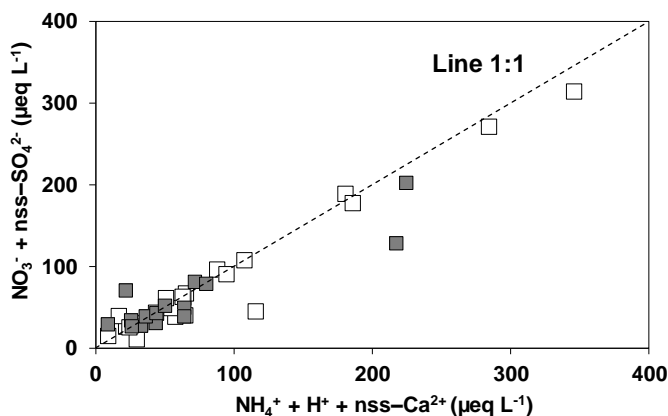
The $[\text{NH}_4^+ + \text{H}^+ + \text{nss-Ca}^{2+}]/[\text{NO}_3^- + \text{nss-SO}_4^{2-}]$ ratio was 1.0 for Maracanã and Deodoro altogether. Figure 5 shows the relationship between $[\text{NH}_4^+ + \text{H}^+ + \text{nss-Ca}^{2+}]$ and $[\text{NO}_3^- + \text{nss-SO}_4^{2-}]$, whose coefficient of determination is $r^2 = 0.91$, indicating that 91% of the acidity in rainwater are controlled by dissolution of H_2SO_4 , HNO_3 , NH_3 gaseous and their salts particles, such as $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4NO_3 , with a smaller contribution from the dissolution of calcium-containing salts, as calcium oxalate (CaC_2O_4). Oxalate is the most abundant carboxylate that has been found in aerosol particles in urban and forest area of São Paulo (VASCONCELOS *et al.*, 2010), and in aerosol particles (DECESARI *et al.*, 2006) and in rainwater in the Amazon forest (PAULIQUEVIS *et al.*, 2012).

Factor Analysis with Varimax rotation

Factor analysis with Varimax rotation was applied to the set of all rainwater samples ($n = 41$) because there was no statistically significant difference between the sampling sites. Only the excesses of Mg^{2+} , Ca^{2+} , K^+ and SO_4^{2-} concentrations

were considered, since the sea-salt contribution has been already discussed. In addition, we included the total concentration of Cl^- because of its low enrichment regarding sea-salt Cl^- .

Figure 5. Relationship between $[\text{NH}_4^+ + \text{H}^+ + \text{nss-Ca}^{2+}]$ and $[\text{NO}_3^- + \text{nss-SO}_4^{2-}]$ concentrations in rainwater samples for Maracanã (□) and Deodoro (■) districts, together.



Three factors were obtained which explained 91% of the total variance (Table 2). The factor 1 accounted for 49% of the total variance with high loading for Na^+ , Cl^- , and nss-Mg^{2+} . This factor is attributed to a marine source and supports the assumption that nss-Mg^{2+} could have a marine component other than sea-salt spray. The factor 2 showed high loaded values for H^+ , NH_4^+ , NO_3^- and nss-SO_4^{2-} , that encompasses 30% of the total variance, which is interpreted as ions resulting from dissolution of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4NO_3 aerosols particles and their base and acid precursors in rainwater. They were found to be the major substances controlling free acidity of rainwater in the study area.

Finally, in factor 3, we identified higher loaded values for nss-K^+ and nss-Ca^{2+} , corresponding to 12% of the variance of results, suggesting as discussed early that their potential sources comprise terrestrial vegetation, including biomass burning emissions.

Table 2. Varimax-rotated factor loading matrix for rainwater samples combined from Maracanã and Deodoro sites (n = 41).

Variables	Factor 1	Factor 2	Factor 3
H ⁺	0.04	0.83 ^a	-0.32
NH ₄ ⁺	-0.07	0.80 ^a	0.18
Na ⁺	0.97 ^a	0.05	0.20
NO ₃ ⁻	0.00	0.90 ^a	0.37
Cl ⁻	0.97 ^a	0.05	0.21
nss-K ⁺	0.38	0.16	0.86 ^a
nss-Ca ²⁺	0.27	0.23	0.92 ^a
nss-SO ₄ ²⁻	0.16	0.84 ^a	0.47
nss-Mg ²⁺	0.95 ^a	0.19	0.19
Var. expl. %	49	30	12
Eigenvalues	4.4	2.7	1.1

Var. expl. %: Variance explained %.

^aValues > 0.70.

CONCLUSION

The major inorganic ions concentrations in rainwater did not differ except H⁺ between the two study sites, characterized by areas of heavy traffic flow and poor ventilation in the city of Rio de Janeiro. Rainwater chemistry is strongly influenced by sea-salt aerosols, with Cl⁻ and Na⁺ comprising half of the total concentration of inorganic ions. The non-sea-salt fractions of the K⁺, Mg²⁺, Ca²⁺ and SO₄²⁻ comprised 54–83% of their concentrations in rainwater owing to unidentified natural and anthropogenic sources.

Ammonium is the predominant inorganic form of nitrogen in the rainwater and was well correlated with nss-SO₄²⁻ and NO₃⁻, indicating dissolution of secondary aerosols and their base and acid precursors, which are major components controlling the local rainwater acidity. The VWM pH of rainwater increased by at least 0.3 pH units compared to those reported in the literature from studies performed in the metropolitan regions of Rio de Janeiro and São Paulo during the 1980s. We believe that this change can be attributed to an increase in ammonium concentrations and a decrease in sulfate concentrations in relation to the reported concentrations of studies carried out in the 1980s.

Factor analysis with varimax rotation identified three potential sources for inorganic ions:

marine, secondary aerosols and terrestrial vegetation including natural processes and biomass burning activities.

These findings suggest that rainwater chemistry in the city of Rio de Janeiro is governed largely by sea-salt aerosols, but also by multiple local and regional natural and anthropogenic sources. It also shows indications that it is changing over time due to effective implementation of SO₂ emission controls and, on the other hand, insufficient basic sanitation infrastructure and inefficient environmental management practices to control biomass burning.

ACKNOWLEDGMENTS

This research was supported by FNMA (n.: 1108/94), CNPq and CAPES-PROEX. CAPES also provided the post-doctoral fellowship to Patricia A. de Souza. We would like to thank Carla Araujo Vilardo for assistance with the chemical analysis and Mrs. Ricardo Sierpe for assistance with the map.

Todos os autores declararam não haver qualquer potencial conflito de interesses referente a este artigo.

REFERENCES

- ABREU, M. L. 2005. Ocorrência de chuva ácida em unidades de conservação da natureza urbana- Estudo de caso no Parque Estadual da Pedra Branca- Rio de Janeiro-RJ. **Dissertação de Mestrado**. Universidade Estadual do Rio de Janeiro- UERJ, 2005.
- ALVARES, C.A.; STAPE, J.L.; SENTELHAS, P.C.; GONÇALVES, J.L.M.; SPAROVEK, G. Köppen's climate classification map for Brazil. **Meteorologische Zeitschrift**, v. 22, n.6, p.711–728, 2013. doi:10.1127/0941–2948/2013/0507.
- ANDREAE, M.O.; TALBOT, R.W.; BERRESHEIM, H; BEECHER, K.M. Precipitation Chemistry in Central Amazonia. **Journal of Geophysical Research**, v.95, n.D10, p.16987–16999, 1990. <https://doi.org/10.1029/JD095iD10p16987>.
- APHA. Standard Methods for the Examination of Wastewater and Water. 19 ed., American Public Health Association, Washington DC.,1985.

- ARAUJO, T.G.; SOUZA, M.F.L.; DE MELLO, W.Z.; SILVA, D.M.L. Bulk Atmospheric Deposition of Major Ions and Dissolved Organic Nitrogen in the Lower Course of a Tropical River Basin, Southern Bahia, Brazil. **Journal of Brazilian Chemical Society**, v.26, n.8, p.1692–1701, 2015. <https://doi.org/10.5935/0103-5053.20150143>.
- ARTAXO, P.; FERNANDES, E.T.; MARTINS, J.V.; YAMASOE, M.A.; HOBBS, P.V.; MAENHAUT, W., LONGO, K.M.; CASTANHO, A. Large-scale aerosol source apportionment in Amazonia. **Journal Geophysical Research**, v.103, n.D24, p.31837–31847, 1998. <http://dx.doi.org/10.1029/98JD02346>.
- ARTAXO, P.; HANSSON, H-C. Size distribution of biogenic aerosol particles from the Amazon basin. **Atmospheric Environment**, v.29, n.3, p. 393–402, 1995. [https://doi.org/10.1016/1352-2310\(94\)00178-N](https://doi.org/10.1016/1352-2310(94)00178-N).
- ARTAXO, P.; MAENHAUT, W.; STORMS, H.; VAN GRIEKEN, R. Aerosol characteristics and sources for the Amazon basin during wet season. **Journal Geophysical Research**, v.95, n.D10, p.16971–16985, 1990. <https://doi.org/10.1029/JD095iD10p16971>.
- ARTAXO, P.; STORMS, H.; BRUYNSEELS, F.; VAN GRIENKEN, R. Composition and sources of aerosol from the Amazon Basin. **Journal Geophysical Research**, v.93, n.D2, p.1605–1615, 1988. <http://dx.doi.org/10.1029/JD093iD02p01605>.
- AYERS, G.P.; FUKUZAKI, N.; GILLETT, R.W.; SELLECK, P.W.; POWELL, J.C.; HARA, H. Thymol as a biocide in Japanese rainwater. **Journal of Atmospheric Chemistry**, v.30, n.2, p.301–310, 1998. <https://doi.org/10.1023/A:1006068415125>
- BARRETT, E.; BRODIN, G. The acidity of Scandinavian Precipitation. **Tellus**, v.7, n.2, p.252–257, 1955. <http://dx.doi.org/10.3402/tellusa.v7i2.8780>.
- BOEGER, M.R.T.; WISNIEWSKI, C.; REISSMANN, C.B. Nutrientes foliares de espécies arbóreas de três estádios sucessionais de floresta ombrófila densa no sul do Brasil. **Acta Botanica Brasílica**, v. 19, n.1, p.167–181, 2005. <https://doi.org/10.1590/S0102-33062005000100017>.
- BOUWMAN, A.F.; VAN DER HOEK, K.W. Scenarios of animal waste production and fertilizer use and associated ammonia emission for the developing countries. **Atmospheric Environment**, v.31, n.24, p.4095–4102, 1997. [http://dx.doi.org/10.1016/S1352-2310\(97\)00288-4](http://dx.doi.org/10.1016/S1352-2310(97)00288-4).
- BROWN, I.F.; SILVA-FILHO, E.V.; DE PAULA, F.C.; OVALLE, A.R.C. Measurements of atmospheric deposition at tree canopy level in a subtropical premontane wet forest, Rio de Janeiro, Brazil. **Biotropica**, v. 21, n.1, p 15–19, 1989.
- BURNS, D.A.; AHERNE, J.; GAY, D.A.; LEHMANN, C.M.B. Acid rain and its environmental effects: Recent scientific advances. **Atmospheric Environment**, 2016, v.146, p.1– 4, 2016.
- CAMPOS, V.P.; COSTA, A.C.A.;TAVARES, T.M. Comparação de dois tipos de amostragem de chuva: Deposição total e deposição apenas úmida em área costeira tropical. **Química Nova**, v.21, n.4, p. 418–423, 1998. <http://dx.doi.org/10.1590/S0100-40421998000400008>.
- CARVALHO, C.N.; LEPRUN, J.C. Atmospheric deposition to a rural tropical site—Analysis of the relationship between amount of precipitation and chemical composition. **Biogeochemistry**, v.14, n.2, p.99–112, 1991. <https://doi.org/10.1007/BF00002900>
- CASARTELLI, M.R.; MIRLEAN, N.; PERALBA, M.C.; BARRIONUEVO, S.; GÓMEZ-REY, M.X.; MADEIRA, M. An assessment of the chemical composition of precipitation and throughfall in rural-industrial gradient in wet subtropics (southern Brazil). **Environmental Monitoring Assessment**, v.144, n.1–3, p. 105–116, 2008. <http://dx.doi.org/10.1007/s10661-007-9949-y>.
- COELHO, V.M. B. **Baía de Guanabara: uma história de agressão ambiental**. Rio de Janeiro, 1 ed., Casa da Palavra, 2007.
- CONCEIÇÃO, F.T.; SARDINHA, D.S.; NAVARRO, G.R.B. Composição química das águas fluviais e deposição atmosférica anual na bacia do alto Sorocaba, **Química Nova**, v.34, n.4, p.610–616, 2011.
- CONOVER, W.J. **Practical non-parametric Statistics**. 3 ed., John Wiley & Sons Inc. 1980.
- CORNELL, S.E.; JICKELLS, T.D.; THORNTON, C.A. Urea in rainwater and atmospheric aerosol. **Atmospheric Environment**, v.32, n.11, p.1903–1910, 1998. [http://dx.doi.org/10.1016/S1352-2310\(97\)00487-1](http://dx.doi.org/10.1016/S1352-2310(97)00487-1).
- DE MELLO, W.Z. Precipitation chemistry in the coastal of Metropolitan Region of Rio de Janeiro, Brazil. **Environmental Pollution**, v.114, n.2, p.235–242, 2001. [http://dx.doi.org/10.1016/S0269-7491\(00\)00209-8](http://dx.doi.org/10.1016/S0269-7491(00)00209-8)

- DE MELLO, W.Z.; ALMEIDA, M.D. Rainwater chemistry at the summit and southern flank of the Itatiaia massif, southeastern Brazil. **Environmental Pollution**, v.129,n.1, p.63–68, 2004. <http://dx.doi.org/10.1016/j.envpol.2003.09.026>.
- DE SOUZA, P.A.; DE MELLO, W.Z.; MALDONADO, J.; EVANGELISTA, H. Composição química da chuva e aporte atmosférico na Ilha Grande, RJ. **Química Nova** v.29, n.3, p.471–476, 2006. <https://doi.org/10.1590/S0100-40422006000300013>.
- DE SOUZA, P.A.; DE MELLO, W.Z.; MARIANI, R.L.; SELLA, S.M. Caracterização do material particulado fino e grosso e composição da fração inorgânica solúvel em água em São José dos Campos (SP). **Química Nova**, v.33, n.6, 1247–125, 2010. <https://doi.org/10.1590/S0100-40422010000600005>.
- DE SOUZA, P.A.; DE MELLO, W.Z.; MARIANI, R.L.; SELLA, S.M. Variações temporais do material particulado fino e grosso e íons inorgânicos solúveis em São José dos Campos, SP. **Revista Brasileira de Geofísica**, V.29, n.1, p.71–82, 2011. <https://doi.org/10.1590/S0102-261X2011000100005>.
- DE SOUZA, P.A.; DE MELLO, W.Z.; SILVA, J.J.N.; RODRIGUES, R.A.R.; DA CONCEIÇÃO, M.C.G. Deposições atmosféricas úmida, seca e total de nitrogênio inorgânico dissolvido no estado do Rio de Janeiro. **Revista Virtual de Química**, v.9, n.5, p.2052–2066, 2017. <https://doi.org/10.21577/1984-6835.20170122>.
- DE SOUZA, P.A.; PONETTE-GONZÁLEZ, A.P.; DE MELLO, W.Z.; WEATHERS, K.C.; SANTOS, I.A. Atmospheric organic and inorganic nitrogen inputs to coastal urban and montane Atlantic Forest sites in southeastern Brazil. **Atmospheric Research**, v.160, p.126–137, 2015. <http://dx.doi.org/10.1016/j.atmosres.2015.03.011>.
- DECESARI, S.; FUZZI, S.; FACCHINI, M.C.; MIRCEA, M.; EMBLICO, L.; CAVALLI, F.; MAENHAUT, W.; CHI, X.; SCHKOLNIK, G.; FALKOVICH, A.; RUDICH, Y.; CLAEYS, M.; PASHYNSKA, V.; VAS, G.; KOURTCHEV, I.; VERMEYLEN, R.; HOFFER, A.; ANDREAE, M.O.; TAGLIAVINI, E.; MORETTI, F.; ARTAXO, P. Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds. **Atmospheric Chemistry and Physics**, v.6, p.375–402, 2006. doi:10.5194/acp-6-375-2006.
- DEPARTAMENTO ESTADUAL DE TRÂNSITO (DETRAN), 2001. http://detran.rj.gov.br/_estatisticas.veiculos/02.asp, accessed in 20/02/2020.
- DERECYNSKI, C.P.; OLIVEIRA, J.S.; MACHADO, C.O. Climatologia da precipitação no município do Rio de Janeiro. **Revista Brasileira de Meteorologia**, v.24, n.1, p.24–38, 2009. <http://dx.doi.org/10.1590/S0102-77862009000100003>.
- FIGUERÊDO, D.V. Influence of calcareous soil particulates on acid rain: Belo Horizonte metropolitan region, Brazil. **Ambio**, v. 28, n.6, p.514–518, 1999.
- FILOSO, S.; WILLIAMS, M.R.; MELACK, J.M. Composition and deposition of throughfall in a flooded forest archipelago (Negro River, Brazil). **Biogeochemistry**, v.45, n.2., p.169–195, 1999. <http://dx.doi.org/10.1023/A:1006108618196>.
- FLUES, M.; HAMA, P.; FORNARO, A. Avaliação do nível de vulnerabilidade do solo devido à presença de termelétrica a carvão (Figueira, PR–Brasil). **Química Nova**, v. 26, n.4, p.479–483, 2003. <https://doi.org/10.1590/S0100-40422003000400006> (in Portuguese with English abstract).
- FORNARO, A.; GUTZ, I.G.R. Wet deposition and related atmospheric chemistry in the São Paulo metropolis, Brazil Part 2—contribution of formic and acetic acids. **Atmospheric Environment**, v.37, n.1, p.117–128, 2003. [http://dx.doi.org/10.1016/S1352-2310\(02\)00885-3](http://dx.doi.org/10.1016/S1352-2310(02)00885-3).
- FORNARO, A.; GUTZ, I.G.R. Wet deposition and related atmospheric chemistry in the São Paulo metropolis, Brazil, Part 3: Trends in precipitation chemistry during 1983–2003. **Atmospheric Environment**, v.40, n.30, p.5893–5901, 2006. <https://doi.org/10.1016/j.atmosenv.2005.12.007>.
- FORTI, M.C.; BOUROTTE, C.; CICCIO, V.; ARCOVA, F.C.S.; RANZINI, M. Fluxes of solute in two catchments with contrasting deposition loads in Atlantic Forest (Serra do Mar/SP-Brazil). **Applied Geochemistry**. v.22, n.6, p.1149–1156, 2007. <http://dx.doi.org/10.1016/j.apgeochem.2007.03.006>.
- FUNDAÇÃO GEORio, 2020a. <http://www.sistema-alerta-rio.com.br/dados-meteorologicos/download/dados-pluviometricos/>, accessed in 20/02/2020.
- FUNDAÇÃO GEORio, 2020b. http://portalgeo.rio.rj.gov.br/_pcontrole/content/out/content.asp?gcod=315, accessed in 20/02/2020.
- GALLOWAY, J.N.; KEENE, W.C. Processes controlling the concentrations of SO_4^{2-} , NO_3^- , NH_4^+ ,

- H⁺, HCOOT and CH₃COOT in precipitation on Bermuda. **Tellus B**, v.41, n.4, 427–443, 1989. <http://dx.doi.org/10.3402/tellusb.v41i4.15098>.
- GALLOWAY, J.N.; LIKENS, G. E.; KEENE, W.C.; MILLER, J.M. The composition of precipitation in remote areas of the world. **Journal Geophysical Research**, v.87, n.C11, p.8771–8786, 1982. <https://dx.doi.org/10.1029/JC087iC11p08771>.
- GASTON, C.J.; FURUTANI, H.; GUAZZOTTI, S.A.; COFFEE, K.R.; BATES, T.S.; QUINN, P.K.; ALUWIHARE, L.I.; MITCHELL, B.G.; PRATHER, K.A. Unique ocean-derived particles serve as a proxy for changes in ocean chemistry. **Journal of Geophysical Research**, v.116(D18), n.D18310, p.1–13, 2011. <http://doi.org/10.1029/2010JD015289>.
- GORHAM, E. Acid deposition and its ecological effects: a brief history of research. **Environmental Science and Policy**, v.1, n.3, p.153 – 166, 1998. [https://doi.org/10.1016/S1462-9011\(98\)00025-2](https://doi.org/10.1016/S1462-9011(98)00025-2).
- GRASSHOFF, K.; EHRHARDT, M.; KREMILING, K. **Methods of Sea Water Analysis**. 2 ed., Verlag Chemie, Weinheim., 1983.
- GUEDES, V.P. Estudo do fluxo de gases através do solo de cobertura de aterros de resíduos sólidos urbanos. **Disertação de mestrado**. Universidade Federal do Rio de Janeiro–COPPE, 2007.
- GUIMARÃES, G.P.; DE MELLO, W.Z. Estimativa do fluxo de amônia na interface ar-mar na Baía de Guanabara—estudo preliminar. **Química Nova**, v.29, n.1, p.54–60, 2006. <https://doi.org/10.1590/S0100-40422006000100012>.
- GRENNFELT, P.; ENGLERYD, A.; FORSIUS, M.; HOV, Ø.; RODHE, H.; COWLING, E. Acid rain and air pollution: 50 years of progress in environmental science and policy. **Ambio**, v. 49, n.4, p. 849–864, 2020. <https://doi.org/10.1007/s13280-019-01244-4>
- HADI, D.A.; CAPE, J.N. 1995. Preservation of throughfall samples by chloroform and thymol. **International Journal of Environmental Analytical Chemistry**, v.61, n.2, p.103–116, 1995. <https://doi.org/10.1080/03067319508026241>.
- INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA (IBGE), 1988. Produção da Pecuária municipal em 1988–Região Sudeste. <http://bibliotecaary.ibge.gov.br/biblioteca-catalogo?id=784&view=detalhes>, accessed in February 2020.
- INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA (IBGE), 1998. Produção da Pecuária municipal em 1998–Região Sudeste. <https://bibliotecaary.ibge.gov.br/biblioteca-catalogo?id=784&view=detalhes>, accessed in February 2020.
- INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA (IBGE), 2000. <https://sidra.ibge.gov.br/tabela/2332#resultado>, accessed in February 2020.
- INSTITUTO NACIONAL DE PESQUISA ESPACIAL (INPE), 2020a. <http://clima1.cptec.inpe.br/spi/pt>, accessed in February 2020.
- INSTITUTO NACIONAL DE PESQUISA ESPACIAL (INPE), 2020b. https://queimadas.dgi.inpe.br/queimadas/estatistica_estados, accessed in February 2020.
- INSTITUTO PEREIRA PASSOS (IPP), 2013. Mudanças na ocupação do solo urbano da cidade do Rio de Janeiro entre os anos de 2009, 2010 e 2011. http://www.rio.rj.gov.br/dlstatic/10112/6165511/4162017/mudancas_na_ocupacao_do_uso_do_solo_urbano_28_02_13.pdf, accessed in February 2020.
- KEENE, W.C.; PSZENNY, A.A.P.; GALLOWAY, J.N.; HAWLEY, M.E. Sea—salt corrections and interpretation of constituent ratios in marine precipitation. **Journal Geophysical Research**, v.91, n.D6, p.6647–6658, 1986. <http://dx.doi.org/10.1029/JD091iD06p06647>.
- KLUMPP, A.; DOMINGOS, M.; KLUMP, G. Foliar nutrient contents in tree species of the Atlantic Rain Forest as influenced by air pollution from the industrial complex Cubatão, SE–Brazil. **Water, Air, Soil and Pollution**, v.133, n.1–4, p.315–333, 2002. <https://dx.doi.org/10.1023/A:1012914720934>.
- 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. Chemical composition of rainwater and anthropogenic influences in the Piracicaba River Basin, Southeast Brazil. **Atmospheric Environment**, v.35, n.29, p.4937–4945, 2001. [https://doi.org/10.1016/S1352-2310\(01\)00198-4](https://doi.org/10.1016/S1352-2310(01)00198-4).
- LEAL, T.F.M.; FONTENELE, A.P.G.; PEDROTTI, J.J. Composição iônica majoritária de águas de chuva no centro da cidade de São Paulo. **Química Nova**, v.27, n.6, p.855–861, 2004. <http://dx.doi.org/10.1590/S0100-40422004000600003>.
- LOUREIRO, L.N. Panorâmica sobre as emissões atmosféricas—Estudo de caso: Avaliação do inventário de emissões atmosféricas da Região Metropolitana do Rio de Janeiro para fontes móveis..

Dissertação de mestrado. Universidade Federal do Rio de Janeiro–UFRJ, 2005.

MARIANI, R.L.; DE MELLO, W.Z. $PM_{2.5-10}$, $PM_{2.5}$ and associated water-soluble inorganic species at a coastal urban site in the metropolitan region of Rio de Janeiro. **Atmospheric Environment**, v.41, n.13, p.2887–2892, 2007. <http://dx.doi.org/10.1016/j.atmosenv.2006.12.009>.

MIGLIAVACCA, D.; TEXEIRA, E.C.; PIRES, M.; FACHEL, J. Study of chemical elements in atmospheric precipitation in South Brazil. **Atmospheric Environment**, v.38, n.11, p.1641–1656, 2004. <http://dx.doi.org/10.1016/j.atmosenv.2003.11.040>.

MIGLIAVACCA, D.; TEIXEIRA, E.C.; WIEGAND, F.; MACHADO, A.C.M.; SANCHEZ, J., 2005. Atmospheric precipitation and chemical composition of an urban site, Guaíba hydrographic basin, Brazil. **Atmospheric Environment**, v.39, n.10, p.1829–1844, 2005. <http://dx.doi.org/10.1016/j.atmosenv.2004.12.005>.

MILLERO, F.J. **Chemical Oceanography**. 3 ed., Frank and Taylor, CRC Press. 2006.

MOPER, K.; ZICA, R.G. Free amino acids in marine rains: evidence for oxidation and potential role in nitrogen cycling. **Nature**, v.325, n.6101, p.246–249, 1987.

MORAES, R.M.; DOMINGOS, M. Elementos minerais em folhas de espécies arbóreas de Mata Atlântica e Mata de Restinga, na Ilha do Cardoso, SP. **Revista Brasileira de Botânica**, v. 20, p.133–138, 1997. <https://doi.org/10.1590/S0100-84041997000200004>.

ODÉN, S. The acidity problem e an outline of concepts. **Water, Air, Soil and Pollution**, v.6, n 2-4, p.137–166, 1976.

OLIVEIRA, P.L.; FIGUEIREDO, B.R.; CARDOSO, A.A. Rainwater Major and Trace Element Contents in Southeastern Brazil: an Assessment of a Sugar Cane Region in Dry and Wet Period. **Journal of the Brazilian Chemical Society**, v.23, n.12, p.2258–2265, 2012. <http://dx.doi.org/10.1590/S0103-50532012001200015>.

PAULIQUEVIS, T.; LARA, L.L.; ANTUNES, M.L.; ARTAXO, P. Aerosol and precipitation chemistry measurements in a remote site in Central Amazonia: the role of biogenic contribution. **Atmospheric Chemistry and Physics**, v.12, n.11, p.4987–5015, 2012. <http://dx.doi.org/10.5194/acp-12-4987-2012>.

PIMENTEL, L.C.G.; MORTON, E.; DA SILVA, M.S.; JOURDAN, P. Caracterização do regime de vento em superfície na Região Metropolitana do Rio de Janeiro. **Engenharia Sanitária e Ambiental**, v.19, n.2, p.121–132, 2014. <https://doi.org/10.1590/S1413-41522014000200003>.

PONTES, A.S. Avaliação do impacto das emissões atmosféricas provenientes das atividades portuárias sobre a qualidade do ar na Região Metropolitana do Rio de Janeiro. **Dissertação de mestrado.** Universidade Federal do Rio de Janeiro – UFRJ, 2015.

ROCHA, F.R.; SILVA, J.A.F.; LAGO, C.L.; FORNARO, A.; GUTZ, I.G.R. Wet deposition and related atmospheric chemistry in the São Paulo metropolis, Brazil: Part 1. Major inorganic ions in rainwater as evaluated by capillary electrophoresis with contactless conductivity detection. **Atmospheric Environment**, v.37, n.1, p.105–115, 2003. [https://doi.org/10.1016/S1352-2310\(02\)00722-7](https://doi.org/10.1016/S1352-2310(02)00722-7).

SALTER, M.E.; HAMACHER–BARTH, E.; LECK, C.; WERNER, J.; JOHNSON, C.M.; RIIPINEN, I.; NILSSON, E.D.; ZIEGER, P. Calcium enrichment in sea spray aerosol particles. *Geophysical Research Letter*, v.43, n.15, p.8277–8285, 2016. <https://doi.org/10.1002/2016GL070275>.

SANTOS, M.A.; ILLANES, C.F.; FORNARO, A.; PEDROTTI, J.J., 2007. Acid Rain in Downtown São Paulo City, Brazil. **Water Air Soil and Pollution**, v.7, 85–92, 2007. http://dx.doi.org/10.1007/978-1-4020-5885-1_10.

SEINFELD, J.H.; PANDIS, S.N. **Atmospheric Chemistry and Physics from Air Pollution to Climate Change**. 2 ed.. John Wiley & Sons, Inc, 2006.

SHRESTHA AB; WAKE CP ; DIBB JE. Chemical composition of aerosol and snow in the high Himalaya during the summer monsoon season. **Atmospheric Environment**, v.31, n.17, p. 2815–2826, 1997. [https://doi.org/10.1016/S1352-2310\(97\)00047-2](https://doi.org/10.1016/S1352-2310(97)00047-2).

SILVA, A.C. Tratamento do percolato de aterro sanitário e avaliação da toxicidade do efluente bruto e tratado. **Dissertação de mestrado.** Universidade Federal do Rio de Janeiro- COPPE, 2002.

SILVA–FILHO, E.V. Estudo de chuva ácida e entradas atmosféricas de Na, K, Ca, Mg e Cl na bacia do Alto Rio Cachoeira, Parque Nacional da Tijuca—RJ. **Dissertação de mestrado.** Universidade Federal Fluminense – UFF, Niterói, 1985.

SOBRADO, M.A.; MEDINA, E. General Morphology, Anatomical Structure, and Nutrient Content of Sclerophyllous Leaves of the 'Bana'

Vegetation of Amazonas. **Oecologia**, v.45, n.3, p.341–345, 1980.

n.26, p.4223–4233, 1999.
10.1016/S1352-2310(99)00186-7.

<https://doi.org/>

VASCONCELLOS, P.C.; SOUZA, D.Z.; SANCHEZ-CCOYLLO, O.; BUSTILLOS, J.O.V.; LEE H.; SANTOS, F.C.; NASCIMENTO, K.H.; ARAÚJO, M.P.; SAARNIO, K.; TEINILÄ, K.; HILLAMO, R. Determination of anthropogenic and biogenic compounds on atmospheric aerosol collected in urban, biomass burning and forest areas in São Paulo, Brazil. *Science of the Total Environment*, v.408, n.23, p.5836–5844, 2010.
<https://doi.org/10.1016/j.scitotenv.2010.08.012>.

VET, R.; ARTZ, R.S.; CAROU, S.; SHAW, M.; RO, C-U.; AAS, W.; BAKER, A.; BOWERSOX, V.C.; DENTENER, F.; GALY-LACAUX, .C.; HOU, A.; PIENAAR, J. J.; GILLET, R.; FORTI, M.C.; GROMOV, S.; HARA, H.; KHODZHE, T.; MAHOWALD, N.M.; NICKOVIC, S.; RAO, P.S.P.; REID, N.W. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH and phosphorus. **Atmospheric Environment**, v.93, Special Issue, p.3–100, 2014.
<http://dx.doi.org/10.1016/j.atmosenv.2013.10.060>.

VIEIRA-FILHO, M.S.; LEHMAN, C.; FORNARO, A. Influence of local sources and topography on air quality and rainwater composition in Cubatão and São Paulo, Brazil. **Atmospheric Environment**, v.101, p.200–208, 2015.
<http://dx.doi.org/10.1016/j.atmosenv.2014.11.025>.

VITOUSEK, P.M.; SANFORD, R.L. Nutrient cycling in moist Tropical Forest. **Annual Review of Ecology and Systematics**. v.17, p.137–167., 1986.
<https://doi.org/10.1146/annurev.es.17.110186.001033>

VITOUSEK, P.M.; TURNER, D.R.; KITAYAMA, K. Foliar nutrients during long-term soil development in Hawaiian montane rain forest. **Ecology**, v.76, n.3, p.712–720, 1995. <https://doi.org/10.2307/1939338>.

WILLIAMS, M.R.; FISHER, T.R.; MELACK, J.M. Chemical composition and deposition of rain in the Central Amazon, Brazil. **Atmospheric Environment**, v.31, n.2, p.207–217, 1997.
[https://doi.org/10.1016/1352-2310\(96\)00166-5](https://doi.org/10.1016/1352-2310(96)00166-5).

WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH (WMO/GAW), 2004. Manual for the GAW Precipitation Chemistry Programme. <http://www.dtic.mil/docs/citations/ADA442512>, accessed in february 2020.

ZHUANG, H.; CHAN, C. K.; FANG, M.; WEXLER, A.S. Formation of nitrate and non-sea-salt sulfate on coarse particles. **Atmospheric Environment**, v.33,