



Characterization of wet precipitation by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in the metropolitan area of Porto Alegre, Brazil

Daniela Montanari Migliavacca^{a,b}, Elba Calesso Teixeira^{b,*}, Fernanda Gervasoni^c, Rommulo Vieira Conceição^c, Maria Teresa Raya Rodriguez^a

^a Instituto de Biociências, Programa de Pós-Graduação em Ecologia, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91509-900 Porto Alegre, RS, Brazil

^b Fundação Estadual de Proteção Ambiental Henrique Luis Roessler, RS, Rua Carlos Chagas 55/802, 90030-020 Porto Alegre, RS, Brazil

^c Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91509-900 Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:

Received 16 December 2008

Received in revised form 27 May 2009

Accepted 28 May 2009

Available online 6 June 2009

Keywords:

Precipitation wet

X-ray diffraction

Energy dispersive system

Cluster analysis

ABSTRACT

The purpose of this study is to assess the composition of wet precipitation in three sites of the metropolitan area of Porto Alegre. Besides the variables usually considered, such as pH, conductivity, major ions (Cl^- , NO_3^- , F^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , NH_4^+ and Ca^{2+}) and metallic elements (Cd, Co, Cr, Cu, Fe, Mn and Ni), the suspended matter was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), with energy dispersive system (EDS), for better identification of possible anthropogenic material in this wet precipitation. Results showed an alkaline pH in the samples analyzed and higher concentrations for Na^+ , Cl^- and SO_4^{2-} . The acidification and neutralization potential between anions ($\text{SO}_4^{2-} + \text{NO}_3^-$) and cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{NH}_4^+$) showed a good correlation (0.922). The metallic elements with highest values were Zn, Fe and Mn. Results of XRD identified the presence of some minerals such as quartz, feldspar, mica, clay, carbonates and sulfates. In samples analyzed with SEM, we detected pyroxene, biotite, amphibole and oxides. Cluster analysis (CA) was applied to the data matrix to identify potential pollution sources of metals (natural or anthropogenic) and the association with minerals found in the analysis of SEM.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In the major urban centers, and especially in the metropolitan areas, pollution is more significant due to a higher concentration of industries and a greater flux of people and vehicles. Therefore, the atmosphere is the most affected medium. The inherent characteristics of air masses, water-soluble gases, droplets forming clouds and suspended particles are reflected during rainfall in the chemical composition of rainwater [1,2]. The precipitation shows interactions between the natural and anthropogenic processes during its formation, indicating variations in a time and space scale [3].

Rainwater contamination by atmospheric pollutants is growing, not only local but also in a global scale [4]. Therefore, researchers have shown great interest in the chemistry of atmospheric precipitation in recent decades [4–9].

The chemical composition of rainfall is mainly the result of the atmospheric condition, i.e., by the type and amount of natural or anthropogenic pollutants it contains. On the other hand, the chemical composition also depends on the type of precipitation (rainfall, sleet or snow), wind direction, and the height of the cloud layer. The displacement of air masses influences transport, dispersion and

dilution of primary and secondary pollutants to adjacent areas and even to areas far from the sources of emission. The atmospheric precipitation is a main process of removal and transport of atmospheric pollutants such contaminating the rainwater can affect ecosystems, such as rivers, lakes and soil.

The major pollutants transported by this mechanism include sulfur, nitrogen and carbon compounds, usually associated with the atmospheric particulate matter, either in form of aerosols or wet and dry precipitation. Other pollutants, such as industrial gaseous, by products from the incomplete burning of fossil fuels, and typical industrial emissions (CO_2 , NH_3 , H_2SO_4 , sulfur and nitrogen oxides, heavy metals, and metal oxides) can also be found in industrial areas. These chemical substances may dissolve in the precipitation and then quickly incorporate in elementary cycles. This may produce permanent changes in the geochemical processes of the affected ecosystems [10].

Acid rain may be one of the consequences of the dissolution of substances in the precipitation, when the SO_x molecule present in the atmosphere gets in contact with water and changes into acid (H_2SO_4). Acid rain may cause direct and indirect effects on human health, due to transport mechanisms and chemical reactions occurring in the composition of the species present in rainfall. Emissions of alkaline substances such as ammonium and carbonates significantly influence rainfall acidity, neutralizing its acid fraction, especially HNO_3 and H_2SO_4 [11,12].

* Corresponding author. Tel.: +55 5132251588; fax: +55 5132124151.

E-mail address: gerpro.pesquisa@fepam.rs.gov.br (E.C. Teixeira).

In contrast to Europe and the USA, emissions of atmospheric pollutants in Asia are increasing significantly due to population and thriving economy increase, which speed up energy production and consumption. In India, rainfall and aerosols are considered alkaline, due to the small contribution of secondary aerosols (SO_4^{2-} and NO_3^-) from anthropogenic sources and the primary contribution of aerosols from the Earth's crust (Ca, K and Mg) [12–18].

In South Brazil, the problem is not different from that of other countries. Especially in the metropolitan area of Porto Alegre (MAPA), which concentrates a large number of industries (steel plant, coal-fired power plants, oil refineries, cement plants, paper pulp plant, and tanneries) in a major urban agglomeration, since approximately 37% of population of the state of Rio Grande do Sul lives in this area. Furthermore, the MAPA concentrates a high vehicle flow, as for example the lower branch of the BR-116 highway, where the flow is of approximately 100 thousand vehicles/day, releasing a high amount of vehicle pollution into the atmosphere. Consequently, the amount of pollutants emitted into the atmosphere is higher than the tolerated limit, which would cause no effects on the population.

Thus, the knowledge on the chemical composition of rainfall may provide information about the status prevailing in the atmospheric environment of a specific area.

The purpose of the present study is to assess and understand the chemistry of the atmospheric precipitation in the MAPA and detect the action of potential pollutants, through the analysis of suspended particulate matter in the atmosphere by the techniques

of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Sampled at three strategic sites in the MAPA, i.e., in Porto Alegre, Canoas and Sapucaia do Sul.

2. Materials and methods

2.1. Study site

The area of study comprises the cities of Porto Alegre ($29^\circ 58'S-51^\circ 06'W$), Canoas ($29^\circ 55'S-51^\circ 10'W$) and Sapucaia do Sul ($29^\circ 49'S-51^\circ 10'W$), located in the metropolitan area of Porto Alegre (Fig. 1 and Table 1). The MAPA is located in the mid-eastern region of the state. To the South, it is limited by the Patos Lagoon; to the East, there is the Coastal Plain and the Atlantic Ocean (at the distance of 80–100 km); to the North, there is the Serra Geral mountain range characterized by an upland area that gently descends to the South and more abruptly to the East; and to the West, there is the Peripheral Depression, with many coal mines. Therefore, to the South of the MAPA, altitudes may reach below 20 m and to the north, over 300 m. Spatially, the industrial region of the MAPA extends from the city of Guaíba, to the southeast of Porto Alegre, to the north, passing by the capital, reaching Canoas, Esteio and Sapucaia do Sul, and the shoe and leather industrial area of the Rio dos Sinos. North of the MAPA is the periphery of the region and the more important road represented by the BR-116 highway. [19]

The MAPA is the most densely populated area of the state, concentrating 37% of its population in 31 cities. It includes 10 of the

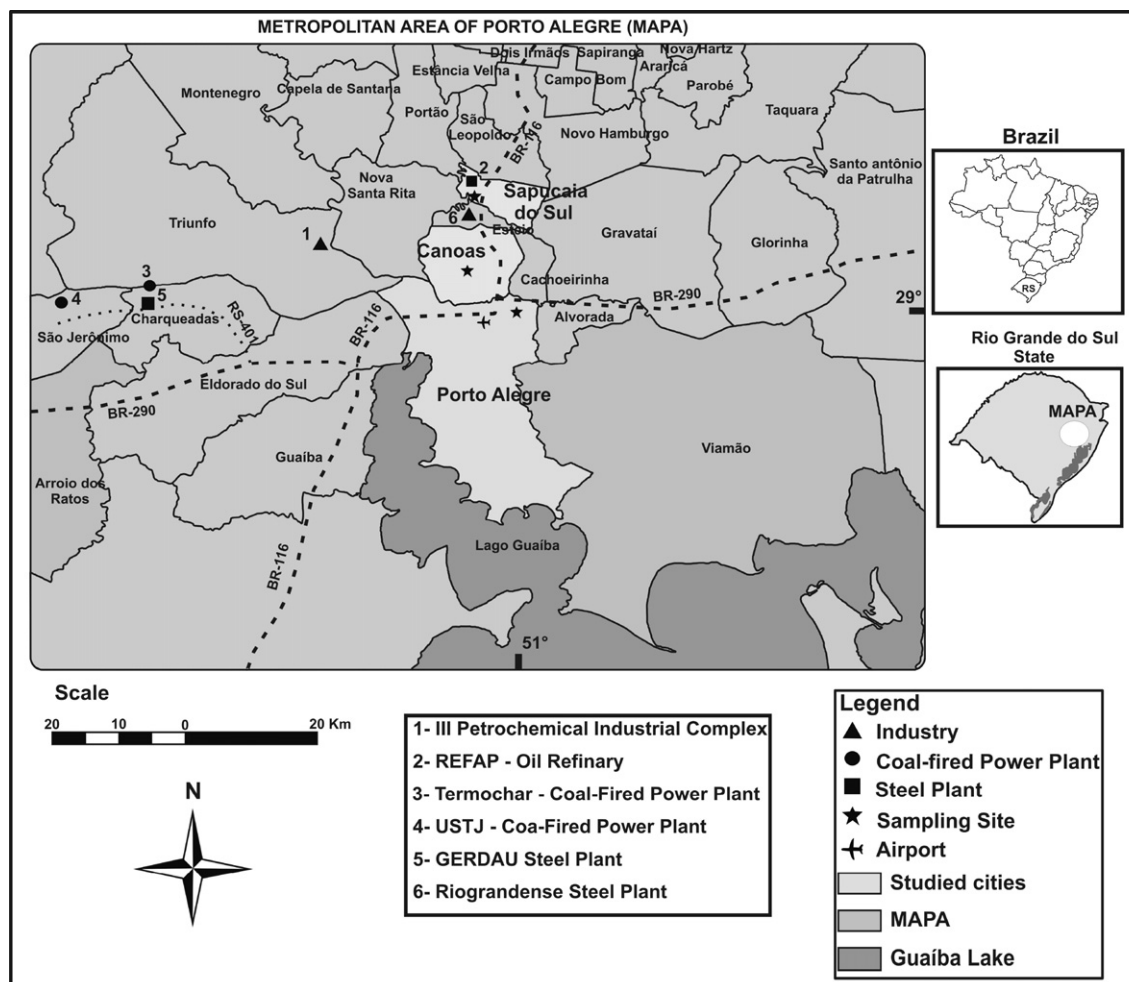


Fig. 1. Location of the sites studied in MAPA.

Table 1
Location of the sampling sites in the metropolitan area of Porto Alegre (MAPA).

City	Sampling sites	Geographic coordinates X (latitude)/Y (longitude)	Comments
Porto Alegre	Porto Alegre/FIERGS	29° 58' 39" S/51° 06' 48" W	Located north of Porto Alegre, away from major industrial sources such as steel plant, oil refinery and cement plant in the region studied.
Canoas	Canoas	29° 55' 19" S/51° 10' 41" W	Located in the city center, near the BR-116 highway, direct influence of vehicular emissions.
Sapucaia do Sul	Sapucaia	29° 49' 14" S/51° 10' 15" W	Located near the BR-116 highway activities and industries such as steel plant, oil refinery and cement plant in the region studied.

17 cities of the Rio Grande do Sul state whose the population is higher than 100 thousand inhabitants. The demographic density of the region is 445.17 inhabitants km⁻² [20].

The geology in the MAPA has two lithological boundaries, represented by the Precambrian granite-gneiss basement and Gondwanan sedimentary cover of Paleozoic and Mesozoic (Paraná Basin province) and Cenozoic (Coastal Plain) ages [21].

The granite-gneiss basement that outcrops in Porto Alegre is the Ponta Grossa and Chácara das Pedras gneisses and by the Viamão, Porto Alegre and Itapuã intrusive suites, represented basically by granodiorites, monzogranites, sienogranites and alkali-feldspar granites [22]. Granites are formed by potassic feldspar, plagioclase, quartz, biotite, hornblende and accessory minerals such as apatite, zircon, allanite, titanite and opaque minerals. Gneisses of the region show the same composition.

The Canoas region is characterized by an interface between the Paraná and the Coastal provinces, where fluvial sediments deposited during the Triassic (Sanga do Cabral formation) and alluvial sediments of the Quaternary [21] outcrop. Under surface, the outcrops of the area are the Rio do Rasto, Estrada Nova and Sanga do Cabral formations, stratigraphically overlaid. The Estrada Nova formation is composed of massive mudstones, shale and gray siltstones, with intercalations of lenses and calciferous concretions. The Rio do Rasto formation is characterized by shale and mudstones, intercalated with fine sandstones, characterizing a fluvial-deltaic environment. The Sanga do Cabral formation is characterized by fine to very fine sandstones, reddish siltstones and argillites, belonging to a fluvial/fluvial-aeolian environment.

The geology of Sapucaia do Sul is represented by sedimentary rocks belonging, from the bottom to the top, to the Rio do Rasto and Sanga do Cabral formations. Differently from Canoas, it also appears the Botucatu and Serra Geral formations. The Botucatu formation shows fine to medium aeolian sandstones, usually bimodal, quartzitic and friable [23]. The volcanic rocks of the Serra Geral formation have a predominantly basaltic composition intercalated by intertrappean sandstones and a superior set of acid flows formed by aphyric rhyodacites and rhyolites.

The MAPA has diversified features in terms of anthropogenic sources, geographical and climatic situation. The presence of mobile and stationary sources, such as oil and petrochemical industries, steel plant, leather tanneries, paper industry, coal-fired power stations, and a high population density cause an environmental imbalance in the area of study. Following are the major industries in the MAPA: oil refinery (Alberto Pasqualini—REFAP S.A.), paper industry (Aracruz Celulose Group), steel plant (Riograndense and Gerdau Aços Especiais Piratini), III Petrochemical Complex and the Gravataí Automotive Complex.

Most notably among the mobile sources are the vehicle emissions. Between 1997 and 2002, the vehicle fleet showed an average increase on 5% per year. Based on this growth rate, the fleet in 2010 will reach approximately 5 million vehicles. About 79% of the fleet uses gasoline as fuel, 9% use diesel oil, and 8% alcohol.

2.2. Sampling site

The location of the sites for installing the wet precipitation samplers was defined as [24]. The proximity of some anthropogenic sources, such as the BR-116 highway, the Alberto Pasqualini oil refinery (REFAP S.A.), the Riograndense steel plant, and the Votorantin cement plant, was also taken into account.

The samples of wet precipitation were collected during the rain event in three selected sites in MAPA, Porto Alegre, Canoas and Sapucaia. The rain events selected for chemical and mineralogical analysis of the wet precipitation and suspended particulate matter, respectively, occurred between July 2005 and March 2006. The wet precipitation sampler was installed at a height of 1.5 m from the ground level and free of obstacles [25]. The collecting and storage flasks were first washed with an Extran Neutral solution (Merck) and then several times with deionized water Type I (Milli-Q, Millipore), having been stored in this water for at least 24 h. After this, the water conductivity was measured and it did not exceed 2 $\mu\text{S cm}^{-1}$ [26].

The pH measures were performed *in situ* in the wet/dry precipitation sampler (W/D sampler-Micros). The equipment collects separately the wet and dry precipitations. It has a movable lid, usually positioned in the container of wet precipitation. At the beginning of each precipitation event, approximately 0.6 mm of rain, the rain sensor opens the lid of the rain container. When there is no rain, the lid retreats back into the container of wet precipitation. The W/D sampler has instant pH analysis in wet precipitation, storing these data every 2 min in a 64-kB data acquisition system. The pH sensor is calibrated with Merck pH standard solution (pH 4.0 and 7.0) every 15 days.

2.3. Chemical analysis

After collecting, the samples were sent to the laboratory, for volume measuring. Two subsequent sample aliquots were filtered through a 0.22 μm membrane filter (Millipore), one aliquot was preserved in chloroform and was used for determining major ions, while the other aliquot, preserved in suprapur HNO₃ (Merck) with pH <2.0, was used for determining metallic elements. Both were stored at 4 °C for further chemical analyses.

The major ions were determined by ion chromatography (Dionex DX 500, with electric conductivity detector). Dionex AS4A-SC and CS12A columns were used in the analysis of anions (Cl⁻, NO₃⁻, SO₄²⁻ and F⁻) and cations (Na⁺, Ca²⁺, Mg²⁺, K⁺ and NH₄⁺), respectively. Detection limits for the ion chromatography were 0.01–0.05 mg l⁻¹ [27].

In order to certify the quality of the analyses done by Ion Chromatograph for the present study, rainwater standard reference materials (CRM 408 and CRM 409) were also analyzed (Community Bureau of Reference). The reference material consists of artificial rainwater with relatively low electrolyte levels stored in sealed quartz flasks of approximately 100 ml. The reproducibility of the data obtained in six replicates was satisfactory and showed a coefficient of variation of 2%. The accuracy of anions and cations was

Table 2Average, maximum and minimum concentrations values of major ions in the samples of atmospheric precipitation ($\mu\text{equiv. l}^{-1}$) for the three sites studied.

	Canoas		Porto Alegre		Sapucaia	
	<i>n</i>	\bar{X} (min.–max.)	<i>n</i>	\bar{X} (min.–max.)	<i>n</i>	\bar{X} (min.–max.)
F ⁻	8	2.39 (0.33–8.60)	8	2.60 (0.00–6.50)	9	2.36 (0.00–6.73)
Cl ⁻	8	20.8 (0.00–77.2)	8	10.6 (1.33–21.1)	9	18.5 (0.00–54.6)
NO ₃ ⁻	8	2.31 (0.89–3.89)	8	3.55 (0.96–7.42)	9	3.02 (0.95–4.66)
SO ₄ ²⁻	8	14.2 (3.37–25.5)	8	17.3 (3.56–36.0)	9	26.4 (6.52–61.3)
Na ⁺	8	20.6 (8.33–58.7)	8	13.7 (6.15–24.0)	9	20.1 (8.44–44.7)
NH ₄ ⁺	8	29.8 (9.77–66.3)	8	50.9 (13.5–119)	9	42.7 (21.6–75.7)
K ⁺	8	3.87 (1.96–5.01)	8	5.44 (2.61–8.34)	9	5.27 (2.94–7.12)
Mg ²⁺	8	6.78 (3.98–16.5)	8	5.99 (3.52–9.32)	9	16.2 (4.77–46.1)
Ca ²⁺	8	9.59 (5.78–12.8)	8	12.9 (7.07–22.7)	9	38.4 (10.8–133)
\sum_{anions}	8	39.7 (4.60–99.3)	8	34.1 (10.2–70.9)	9	50.2 (7.88–96.3)
\sum_{cations}	8	71.7 (39.4–114)	8	55.5 (17.8–112)	9	123 (58.2–248)

n = number of cases. \bar{X} = average.

largely satisfactory, being higher than 95% for all studied ions (Cl⁻, NO₃⁻, SO₄²⁻, F⁻, Na⁺, Ca²⁺, Mg²⁺, K⁺ and NH₄⁺).

The analysis of the metallic elements Co, Cr, Cu, Fe, Mn, Ni, Zn, Pb and Sr was performed by inductively coupled plasma (ICP–Jobin Yvon, 38 S) coupled to an ultrasonic nebulizer using the PE-PURE atomic spectroscopy standard as certified standard. The volume of injected sample three replicates were made for each sample. The reproducibility was about 3%. Detection limits were 0.5–3.0 $\mu\text{g l}^{-1}$.

2.4. X-ray diffraction analyses and scanning electron microscopy (SEM)

The qualitative analysis of the suspended matter of the wet precipitation was performed by X-ray diffraction and scanning electron microscopy (SEM), performed at the X-ray Diffraction Laboratory of the Institute of Geosciences, and at the Electron Microscopy Laboratory, respectively, to identify potential anthropogenic sources contained in this suspended matter. Twelve samples that presented higher mass of suspended matter (range between 65 and 261 μg) were selected.

The diffractometry analysis with a SIEMENS D5000 diffractometer with θ – θ goniometer directly on the membrane containing the suspended matter. A diffraction analysis of a membrane without the presence of suspended matter, and whose result was used as a blank for comparison purposes, was also performed. Radiation is K α in copper tube at 40 kV and 25 mA. Measurements were made at an exposing interval of 2θ 2–60°, at a pitch of 2θ 0.05° with an

exposing time of 5 s per pitch. With some samples, different intervals and speeds were used in order to obtain a better diffractometry, which however did not occur [28].

Minerals identification was troublesome due to the many mineral phases present in the suspended matter, which makes the interpretation of each of them in the diffractometer difficult; also due to the small percentage of each of the phases (in principle, diffractometry identifies mineral phases greater than 5% of the sample). These analyses were performed from approximately one fourth of the membrane, which was placed on a sample holder of plane glass.

Scanning electron microscopy (SEM) was performed using a JEOL–JSM 5800 coupled with the energy dispersive system (EDS), which provides the qualitative and semiquantitative composition of the samples. Two samples were previously metalized with carbon, and three samples with gold. The acceleration voltage of the instrument ranged from 0.3 to 30 kV, with an image point resolution of 3.5 nm, with the magnification ranging between 18 \times and 300.000 \times and a 5-axis motorized goniometric stage [29].

2.5. Deposition rate

The deposition rate was determined for metallic elements in samples from wet precipitation, and was calculated using the following equation:

$$D = \frac{[i] \cdot V}{A} \quad (01)$$

where *D* is the deposition rate in $\mu\text{g m}^{-2}$, [*i*] the concentration of the metallic element in $\mu\text{g l}^{-1}$, *V* the volume of the collected sample in liters and *A* the area of the funnel in m^2 .

In order to determine the wet precipitation contribution to the environment, the deposition rates for the metallic elements ($\mu\text{g m}^{-2}$) were calculated. Since the deposition rate takes the volume of precipitation of each event into account, it allows a direct comparison between the studied sites.

2.6. Cluster analysis

The hierarchical cluster analysis using Ward's method, calculated by the similarity of the Euclidean distance between variables, was applied to the set of chemical data on wet precipitation. The objective was to verify potential associations formed between the groups (clusters) and the source of the chemical composition of the wet precipitation in the region studied. The variables were standardized by means (*z*-scores) for further application of cluster analysis.

Ward's method is suitable for quantitative variables, which compares measuring either the distance or the similarity between

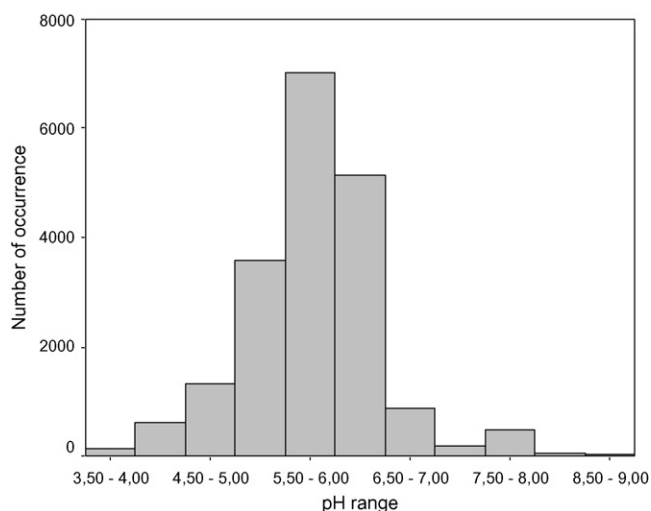


Fig. 2. Histogram in the frequency of pH in the wet precipitation in the region studied.

Table 3
Pearson's correlation matrix for samples wet precipitation from tree sites studied.

	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1.00	0.102	0.490	0.308	-0.024	0.519	0.376	-0.022	0.036
Cl ⁻		1.00	0.142	0.439	0.915	0.134	0.084	0.450	0.192
NO ₃ ⁻			1.00	0.705	-0.016	0.948	0.660	0.225	0.274
SO ₄ ²⁻				1.00	0.346	0.623	0.605	0.786	0.787
Na ⁺					1.00	-0.019	0.143	0.494	0.235
NH ₄ ⁺						1.00	0.647	0.103	0.130
K ⁺							1.00	0.334	0.403
Mg ²⁺								1.00	0.947
Ca ²⁺									1.00

Values in bold $p > 0.01$.

objects to be clustered, and is also based on the principle of analysis of variance [30].

3. Results and discussion

3.1. Chemical composition of the precipitation

Table 2 shows the average, range values (minimum and maximum) for major ions concentration and the sum of cations and anions for samples of wet precipitation. The magnitude of major ions in wet precipitation followed the order: $\text{NH}_4^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Na}^+ > \text{Cl}^- > \text{Mg}^{2+} > \text{K}^+ > \text{NO}_3^- > \text{F}^-$. Among all ions, SO_4^{2-} showed the largest contribution (28%), followed by Cl^- (24%) and Na^+ (20%), and other ions with a relatively moderate contribution. The major ions concentrations showed a high variation for the events, with coefficient of variation between 10 and 67%, indicating greater variation in levels of ionic composition of wet precipitation in the studied region.

The difference between the sum of anions and cations was approximately 43%, that is, approximately $50 \mu\text{equiv. l}^{-1}$ of cations excess [31,32]. On the other hand, the sum of excess cations has been observed in other studies ranging from 29 to $197 \mu\text{equiv. l}^{-1}$, indicating that organic anions (formiate and acetate), in spite of not having been analyzed, are probably present in the atmospheric precipitation of that area [9,16,17]. The main source of organic acids in the atmosphere is related to oxidation of hydrocarbons emitted by vegetation or by industrial sources [33].

Fig. 2 shows the pH histogram for samples analyzed in the W/D sampler, where the average value for the studied events was 5.76, very close to the pH reference level of 5.65 in acid precipitation [1].

The events ranged from 3.81 to 8.73, with Canoas and Sapucaia do Sul presenting pH values of less than 5.65 in only 30% of events studied. The average pH values were slightly alkaline in Sapucaia do Sul (6.20), which may be related to the neutralization of atmospheric precipitation in the region studied. These values might indicate that alkaline species, such as NH_3 and carbonates, might neutralize the rainwater of the area under study. The average values of pH recorded in Canoas and Porto Alegre were 5.72 and 5.30, respectively, with acid values being reported in approximately 80% of the studied events for Porto Alegre.

Alkaline pH has already been registered elsewhere, as in India and Turkey (Central Anatolia), where only 5% of the events studied showed acidic pH of less than 5.65 [16,17,33]. In the region studied, Migliavacca et al. [9] recorded an alkaline (average value 5.75 ± 0.48) pH for 76% of the events of wet precipitation analyzed.

The neutralization process of wet precipitation can be confirmed by the significant correlation ($r < 0.6$) between anions SO_4^{2-} and NO_3^- and cations Ca^{2+} , Mg^{2+} and K^+ , as shown in Table 3.

Fig. 3 shows the analysis of linear regression applied to the set of variables with acidification ($\text{SO}_4^{2-} + \text{NO}_3^-$) and neutralization potential ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{NH}_4^+ + \text{K}^+$) for samples of wet precipitation of the region studied, with a good correlation coefficient of 0.922.

A good correlation was found between Ca^{2+} and SO_4^{2-} ($r = 0.787$), Mg^{2+} and SO_4^{2-} ($r = 0.786$), and NH_4^+ and NO_3^- ($r = 0.948$), as shown in Table 3. These correlations indicate the importance of these ions in the neutralization and acidification processes in the samples studied. Similar data were also reported by Kaya and Tuncel [34] and Alastuery et al. [35].

The presence of a significant correlation for ions NH_4^+ and NO_3^- ($r = 0.948$) and NH_4^+ and SO_4^{2-} ($r = 0.605$) (Table 2) may indicate the occurrence of the forms NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ in the atmosphere, but usually ammonia is in the atmosphere. This significant correlation, mainly of NH_4^+ and NO_3^- , may suggest the influence of agricultural activities [33]. It also shows a good correlation to Na and Cl ($r = 0.915$), indicating the presence of marine aerosol, also recorded in several studies [36,33].

Usually, a potential for acidification in precipitation is due to the presence of H_2SO_4 , HNO_3 and organic acids [34]. These acidic species are neutralized by the presence of NH_3 and CaCO_3 , and the pH of precipitation depends on the relative abundance of these acids and bases and the reactions to neutralize them. The contribution of H_2SO_4 and HNO_3 in the events assessed was over 91%, and H_2SO_4 was responsible for 83%.

Figs. 4 and 5 show the boxplot with the average concentrations of major ions in the three sites studied. The ions with the most significant concentrations were NH_4^+ , SO_4^{2-} , Cl^- and Na^+ , the last two with similar distribution in the three sites studied, indicating origin of natural precipitation. The SO_4^{2-} may derive from anthropogenic activities, sewage treatment plants, traffic of vehicles and industrial activities [37]. The contribution of NH_4^+ is due to human and animal waste and fertilizer use in agriculture [38,16].

Chloride ions present in rainwater, when correlated with Na^+ is linked to the contribution of aerosols from sea salts [36,37]. However, it may originate from anthropogenic sources, such as coal combustion, the burning of polyvinyl chloride in incinerators, and paper manufacturing. However, it was found in approximately 28%

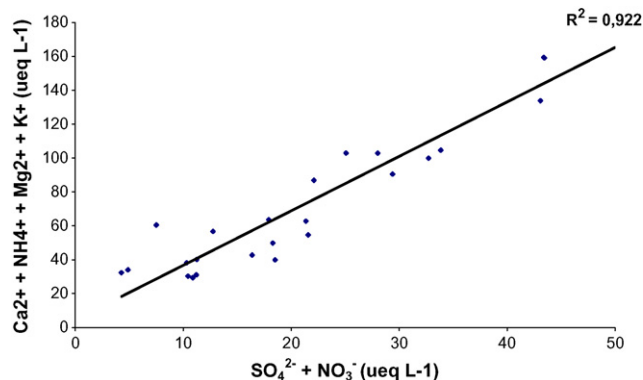


Fig. 3. Relation between ($\text{SO}_4^{2-} + \text{NO}_3^-$) and ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{NH}_4^+$) in samples wet precipitations of the tree sites studied.

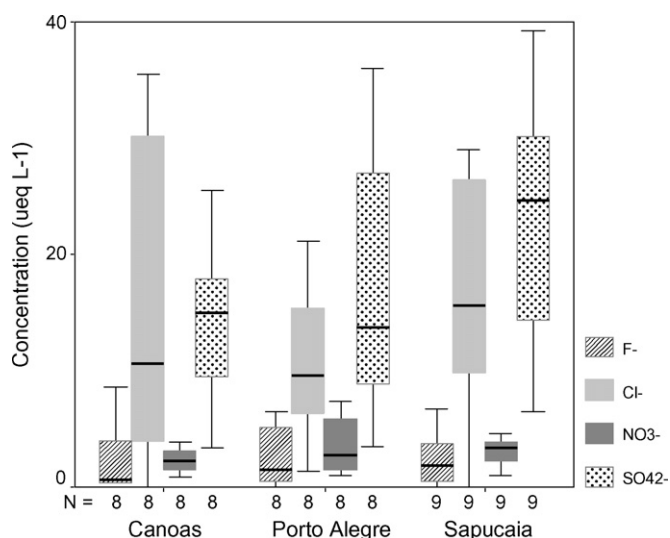


Fig. 4. Boxplot, average concentration of anions, $\mu\text{equiv. l}^{-1}$, in the studied region in the period from July 2005 to March 2006.

of the studied events, suggesting that Cl^- originates from industrial activities in the area. When the relation amongst the analyzed ions and Na^+ is higher than the seawater ratio, it indicates that the marine contribution is negligible, for values of ratio Cl^-/Na^+ above 1.17 indicate anthropogenic origin [39].

Sanusi et al. [37] report that the concentrations of Cl^- , NO_3^- and SO_4^{2-} found in urban areas are usually higher than in rural areas, indicating an anthropogenic origin of these ions more associated with large urban centers.

Ions SO_4^{2-} and NO_3^- , usually more found in precipitation have a variable contribution to the acidity of rainwater. It is estimated that 60–70% of the contribution to samples of acid precipitation is due to H_2SO_4 and 30–40% to HNO_3 [36,40]. However, the contribution of H_2SO_4 to the atmospheric acidity of precipitation has been significantly less than that of HNO_3 . This is directly related to the control of sources and the reduction of sulfur content in oil derivatives, as opposed to less restrictive regulations in controlling NO_x emissions, particularly in the USA and Europe [41,42].

A study reported by Luca et al. [43] in the early 1990s in the MAPA showed a $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio of 17.2. Migliavacca et al. [9] in 2004 showed a decrease of about 50% in this ratio, 8.70. In the present

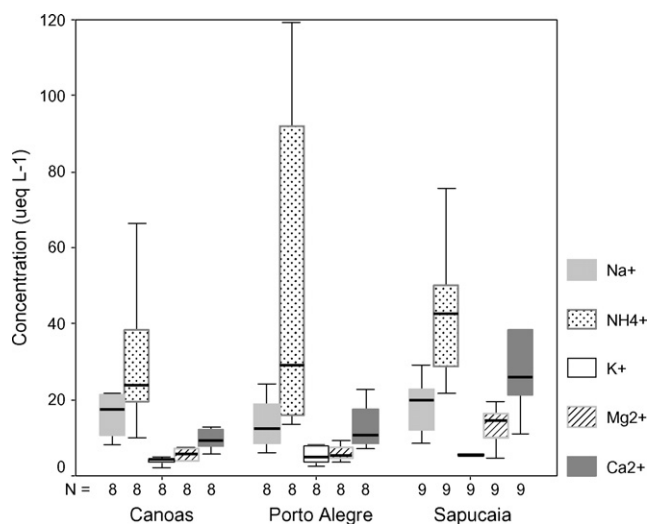


Fig. 5. Boxplot, average concentration of cations, $\mu\text{equiv. l}^{-1}$, in the studied region in the period from July 2005 to March 2006.

study, the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio showed an average of 6.72, with a decrease of approximately 22% in less than three years. This might be related to the use of low-sulfur diesel oil in the buses of the urban transport system in the MAPA from 1996 on, and by encouraging the use of renewable fuels such as alcohol and vehicular natural gas in smaller cars.

The NH_4^+ present in the atmosphere might originate from several sources, including the volatilization of animal residues, human excrements, natural loss by plants, biomass burning and industrial processes, such as the use or the production of fertilizers and emissions from the combustion of fossil fuels. These industrial processes, responsible for only 1% of the ammonia sources in the atmosphere, generate the high NH_4^+ concentrations found in atmospheric precipitation [44,45]. When fertilizers containing $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 are applied to the soil, part of these compounds may convert into NH_3 , which, in its turn, may escape into the atmosphere and take part in the neutralization of rain acidity. Furthermore, part of these fertilizers may become airborne by wind action and form $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 aerosols, which can be incorporated into rain droplets. This mechanism introduced into rain droplets can also explain the ions SO_4^{2-} and NO_3^- [16,34,36].

3.2. Deposition of the metallic elements

Table 4 shows the average concentration of metallic elements ($\mu\text{g l}^{-1}$) in the sites studied. Mn and Zn showed a higher average in Sapucaia do Sul, while Fe was higher in Porto Alegre. The other concentrations of metallic elements such as Co and Cr showed averages less than $1 \mu\text{g l}^{-1}$, while Ni, Pb and Sr had similar average concentrations in the three sites studied. Zn showed higher concentration during the study period, evidencing high emission of Zn from anthropogenic sources, mainly in Sapucaia do Sul, located near a steel plant [46].

The solubility of anthropogenic elements is consistent with several studies Al-Momani et al. [36] and Chester et al. [47], where mostly Zn is classified as more soluble as compared to other elements such as Ni, Cr, Cu and Pb. The moderate or high solubility of some elements may be related to some factors, including rain pH and the type of particle with which these elements are associated in the atmosphere.

Fig. 6 shows the average deposition rate of the metallic elements studied. Fe, Mn and Zn showed the highest deposition rates, followed to a lesser extent by Cu, Pb and Sr. Elements such as Cd, Pb and Zn, and to a lesser extent Cu and Ni, originating from anthropogenic sources and scavenging in wet precipitation, are mainly in the dissolved form, especially at a $\text{pH} < 5$ [47]. Spoke and Jickels [48] suggested that the anthropogenic elements such as Cu, Pb and Zn are controlled by the process adsorption/desorption.

Wet precipitation can be considered an important process for removing elements associated with fine particles. Elements that show enrichment on the surface of the particles are predomi-

Table 4

Average concentration of metallic elements ($\mu\text{g l}^{-1}$) in wet precipitation for the period from July 2005 to March 2006.

	Canoas $\bar{X} \pm \alpha$	Porto Alegre $\bar{X} \pm \alpha$	Sapucaia $\bar{X} \pm \alpha$
Co	0.161 ± 0.0842	0.191 ± 0.0839	0.189 ± 0.110
Cr	0.436 ± 0.284	0.502 ± 0.414	0.455 ± 0.261
Cu	1.19 ± 0.503	1.31 ± 0.605	1.30 ± 0.771
Fe	6.78 ± 6.56	11.3 ± 15.2	6.37 ± 3.79
Mn	3.63 ± 1.63	4.13 ± 1.83	14.7 ± 9.25
Ni	0.776 ± 0.464	1.17 ± 0.826	0.669 ± 0.255
Zn	22.9 ± 13.1	23.1 ± 9.21	38.0 ± 19.6
Pb	1.85 ± 2.56	0.876 ± 0.528	0.760 ± 0.373
Sr	0.795 ± 0.213	0.956 ± 0.555	1.36 ± 0.405

\bar{X} = average concentration in $\mu\text{g l}^{-1}$; α , standard deviation.

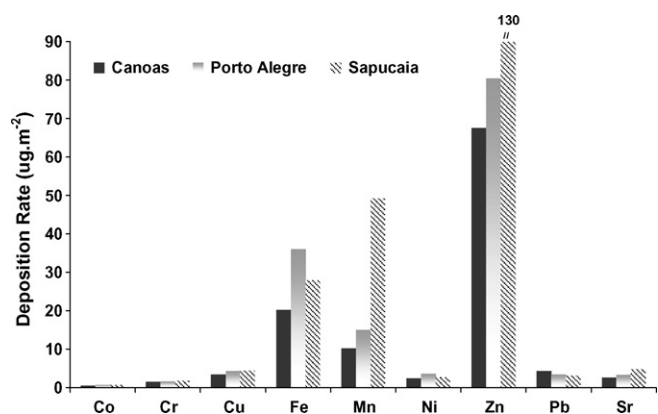


Fig. 6. Deposition rate ($\mu\text{g}\cdot\text{m}^{-2}$) to metallic elements in wet precipitation samples in Canoas, Porto Alegre e Sapucaia.

nantly of anthropogenic origin. Wet precipitation removes from the atmosphere about 80% of Pb, Cd, Cu, Ni and Zn, while dust precipitation removes about 40% of Fe and Al [49]. Therefore, we can relate the high rates of deposition for Fe, Mn and Zn from anthropogenic sources in the region, as evidence of anthropogenic origin are considered highly soluble in precipitation when compared to those from emissions from the surface of the Earth's crust [50].

In the present study, the deposition rates of Fe and Mn amounted to approximately 82% of the total deposition at the three sites studied, reinforcing the anthropic influence, especially the high vehicle flow and the great concentration of industrial emission sources in the state of Rio Grande do Sul. Sapucaia do Sul station had the highest deposition rate for Zn and Mn; however, this might be associated with the steel mill located near the sampling location.

The high deposition rate for Mn may be related to the speciation of this element in wet precipitation. Studies reported that the Mn present in water from rain and snow is in the soluble form of this element, Mn^{2+} [51].

Elements associated with aerosols collected in urban areas tend to have higher solubility than aerosols of natural origin, collected in rural areas. This difference is related to larger components of the Earth's crust (Al, Fe, Si, O, C, etc.), because of present low reactivity and solubility in water of variable rainfall [52,53]. The metallic elements of anthropogenic origin tend to have high solubility in most conditions [52]. Experimental studies have shown a strong relationship between the solubility of certain metallic elements with the pH of wet precipitation. For example, Fe in higher concentration in urban aerosols showed solubilization in high pH. This can be attributed to organic complexation, one of the ways by which these metals may be kept in solution at high pH. These studies corroborate the results presented herein, where the samples studied showed an alkaline pH and a higher deposition rate for Fe and Mn (Fig. 6).

Iron may be scavenged in the liquid phase of precipitation, especially by particles of natural and/or anthropogenic origin. The forms in which it occurs in the atmosphere are manifold, and its compounds may be associated with atmospheric particles in a concentration and a solubility that varies due to pH, redox potential and the presence of chemical compounds, which may act as complexing or precipitating agents.

Weschler et al. [54] observed that depending on the pH Fe can occur in the form of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$, $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ and $[\text{Fe}(\text{SO}_3)(\text{H}_2\text{O})_4]^+$ droplets in the air. Moreover, these authors reported that about 80% of the total Fe content is in form of oxides, while 10% are present in the ionic form Fe(III) and 10% as Fe(II).

Table 5
Mineralogy present suspended particulate matter by X-ray diffraction in MAPA.

Month/year	Porto Alegre			Canoas			Sapucaia do Sul						
	August/05	December/05	January/06	February/06	March/06	July/05	December/05	January/06	August/05	September/05	January/06	February/06	
Mineralogy	Quartz k-Feldspar Plagioclase Kaolinite	Quartz k-Feldspar Plagioclase Kaolinite Smectite Mica Sulfate	Quartz k-Feldspar Plagioclase	Quartz k-Feldspar Plagioclase Kaolinite Smectite Mica Pyrite	Quartz	Quartz Plagioclase Kaolinite Mica Gypsum Carbonate	Quartz k-Feldspar Plagioclase Kaolinite Smectite Mica	Quartz k-Feldspar Plagioclase Kaolinite Smectite Mica	Quartz Plagioclase Kaolinite Carbonate Zeolite Phosphate	Quartz Plagioclase Kaolinite Clorita	Quartz k-Feldspar Plagioclase Kaolinite Smectite Mica Gypsum	Quartz k-Feldspar Plagioclase Smectite Zeolite	Quartz k-Feldspar Plagioclase

3.3. Mineral composition

Twelve samples of the 25 studied events have been selected to assess the presence of minerals in the suspended particulate matter of the wet precipitation collected at the three sampling sites (Canoas, Porto Alegre and Sapucaia do Sul).

Table 5 shows that the minerals present in the suspended particulate matter obtained at these three sites are mostly quartz, K-feldspar and plagioclase. Clay minerals such as kaolinite, smectite and illite, and micas such as muscovite, also show up frequently. The potential sources of these minerals may be natural sources, such as soil resuspension.

Fig. 7 shows the X-ray diffraction to the three sites studied, Porto Alegre, Canoas and Sapucaia do Sul for some months analyzed, the results showed small variability of minerals.

In December 2005 and February and March 2006, sulfur appears in the particulate matter in Porto Alegre, probably as sulfate and sulfide (pyrite – FeS_2). Pyrite may originate from the coalmines and coal-fired power plants located to the west of the MAPA. The

sulfates and sulfides found may also originate from the oil refinery in Canoas. These data compared with the average analysis of ion SO_4^{2-} (Table 3) may explain its high concentration in Porto Alegre and Sapucaia do Sul, due to its dissolution in wet precipitation. Sulfate measured by X-ray diffractometry did not present a very clear diffractogram due to amorphous material present in the membrane with suspended particulate matter in the samples of wet precipitation.

Gypsum (calcium sulfate – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was observed in Canoas in July 2005, and in Sapucaia do Sul in September 2005. It is known that gypsum is part of the manufacturing process of cement and, therefore, it may be related to the cement plant located in Sapucaia do Sul.

Calcium carbonate (calcite – CaCO_3) and calcium phosphate (apatite – $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$) occurred only in Canoas. Zeolite was also identified in samples from Canoas and Sapucaia do Sul, while only Sapucaia do Sul showed chlorite ($\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2\text{Mg}_3(\text{OH})_6$). Both minerals are related to volcanic rocks of the Serra Geral.

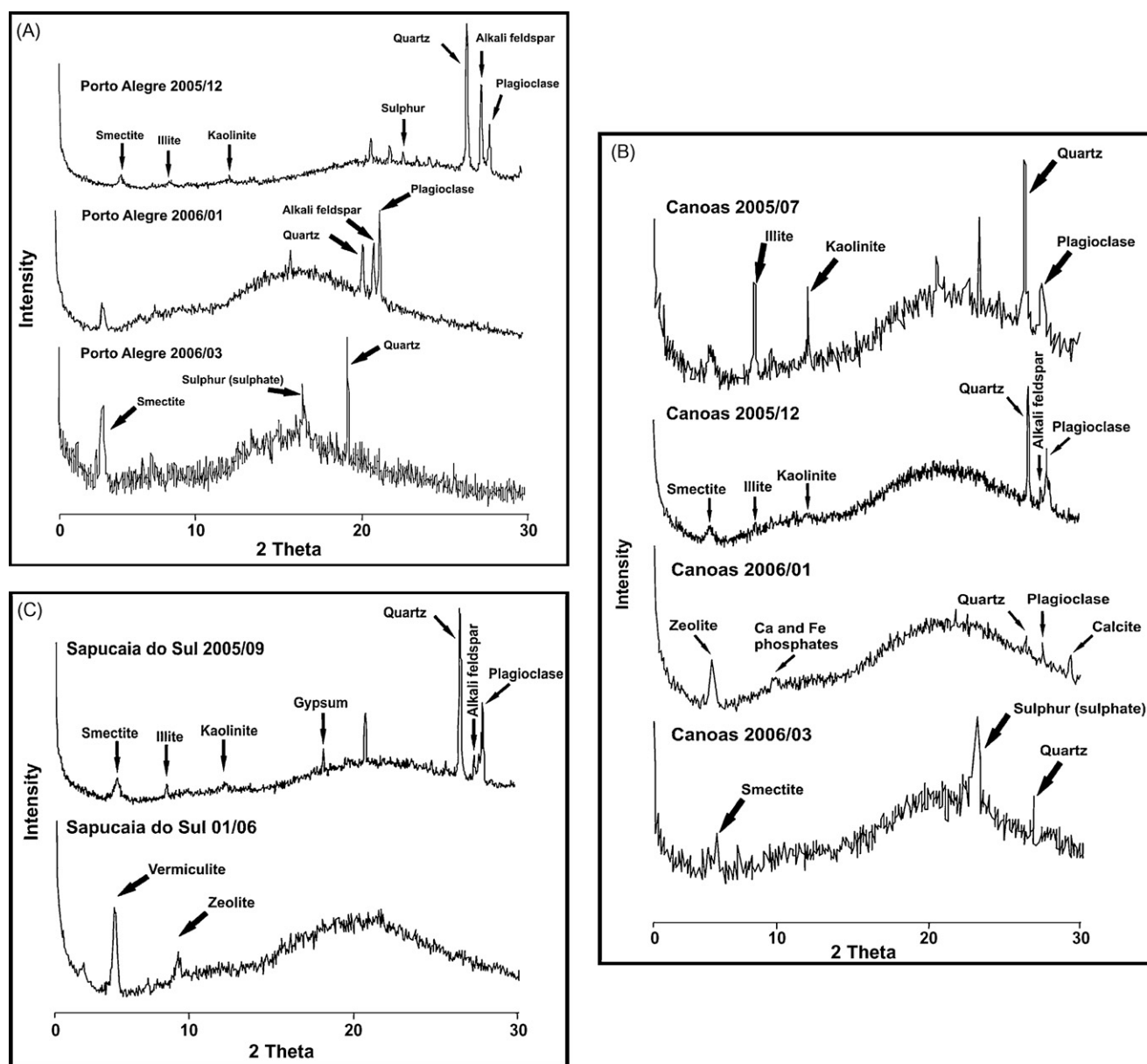
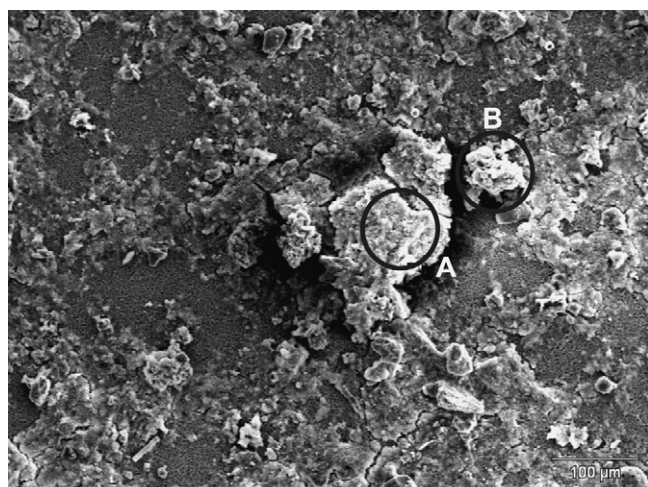


Fig. 7. (A) The suspended particulate matter by X-ray diffraction in Porto Alegre. (B) The suspended particulate matter by X-ray diffraction in Canoas. (C) The suspended particulate matter by X-ray diffraction in Sapucaia do Sul.



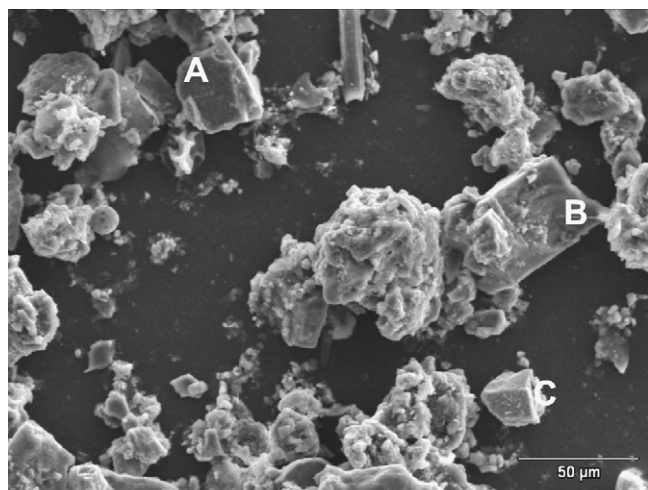
Porto Alegre 2006/03

Fig. 8. Characterization of the suspended particulate matter by SEM in Porto Alegre, March/2006. (A) Iron and manganese oxides; (B) iron and manganese oxides and zinc oxide.

Ca^{2+} and SO_4^{2-} concentrations in samples of wet precipitation were higher in Porto Alegre and Sapucaia do Sul (Table 2). The dissolution of minerals such as calcite (CaCO_3), chlorite ($\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2\text{Mg}_3(\text{OH})_6$) and gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) may be related to these high concentrations, thus confirming the contribution of minerals present in the rocks and soil of the area and the contribution of the cement plant located near the Sapucaia do Sul sampling site.

EDS analysis using the scanning electron microscopy (SEM) detected the same minerals such as quartz, plagioclase, K-feldspar, chlorite and muscovite, thus not differing from X-ray diffractometry. However, oxides such as hematite (iron oxide – Fe_2O_3), ilmenite (titanium oxide – FeTiO_2), iron and manganese oxides, zinc oxides, iron compounds, aluminum and silica (Figs. 8 and 9) were observed. Pyroxenes of the augite type, micas of the biotite and amphibole (hornblende) types were also present, and this may be related to the basalts of the Serra Geral and the granites of Porto Alegre.

SEM results, when compared to major ions analyses and deposition rates, indicate the interaction of minerals and oxides present in the atmosphere with wet precipitation. Average concentrations



Porto Alegre 2005/12

Fig. 9. Characterization of the suspended particulate matter by SEM in Porto Alegre, December/2005. (A) Quartz; (B) plagioclásio; (C) ilmenite.

of cations Ca^{2+} , Na^+ and Mg^{2+} may be related to the presence of minerals from soil dust and marine aerosols enriched in these elements. Ca^{2+} values in Porto Alegre and Canoas may be related to the pyroxene identified by the SEM; this mineral has high CaO values in its composition. The average deposition rate of Mg^{2+} found in Sapucaia do Sul may be related to chlorite, which has a high rate of magnesium. This mineral comes from the alteration of ferromagnesian rocks and it may be easily found in the atmosphere due to resuspension. The geology of Porto Alegre is formed mainly by granites, with high potassium in their composition. The average cationic value of K^+ in the area of Porto Alegre may be related to the alteration of these rocks and to wind suspension of minerals rich in K, such as alkali feldspar.

Analyses with SEM may also explain the high deposition rate of metallic minerals in the areas of study. The high deposition rates of Fe and Mn may refer to the various iron and manganese oxides identified in the SEM (Fig. 8), especially in Porto Alegre. It is known that Mn is an important element for the production of steel and, together with iron, it is melted to generate a metallic alloy crucial for the automobile and construction industries. In the MAPA, we find steel plant (Gerdau Riograndense and Gerdau Aços Especiais Piratini) and the Gravataí Automotive Complex, which most certainly use this metallic alloy.

The high Zn deposition rates agree with the element detected in the SEM. Zinc is largely used in steel and iron galvanization, as protection against corrosion. The high deposition rates are in all likelihood due to zinc oxides released by the steel plant.

The solubilization of Mn, Fe and Al in aerosols from natural sources reveal that 90% of Fe and Al were in the aluminum silicate phase and approximately 70 and 20% of Mn in the aluminum silicate and oxide/carbonate phase, respectively. On the other hand, in urban aerosols of anthropogenic origin, >10% of Fe and Al were identified in the oxide/carbonate phases and approximately 20% of Mn [55].

SEM has also detected a compound formed by Al_2O_3 , SiO_2 and Fe_2O_3 . It is known that bauxite is a heterogeneous material deriving essentially from the composition of aluminum hydroxide, iron and silica. Bauxite is used as raw material for producing alumina. Thereafter, most alumina is used as raw material in the production of metallic aluminum and ceramics. Bauxite is also commercially used as abrasive and cement. The element detected in the SEM probably originates from the various steel plant that use bauxite as abrasive and from the cement plant located in the MAPA, which uses bauxite in their production process.

3.4. Cluster analysis

Cluster analysis (CA) was applied to the data from wet precipitation chemicals in order to relate cluster groups to the homogeneity of the variables studied. The results of CA for the variables are shown in Fig. 10 as dendrogram, resulting in four groups, heterogeneous amongst them, but with homogeneous variables within the group. The first group contains the major ions (NO_3^- , NH_4^+ , K^+ and F^-), the second group comprises the metallic elements (Cr, Ni and Fe), the third group includes ions Na^+ and Cl^- , and the fourth and final group clusters the variables Mg^{2+} , Ca^{2+} , SO_4^{2-} , Mn, Zn, Sr and Cu.

In the first group (cluster 1), NO_3^- , NH_4^+ , K^+ and F^- are related, being the first two ions of anthropogenic origin. These ions can be considered more soluble, because their presence was not evident in the fraction of suspended particulate matter from wet precipitation. The presence of NH_4NO_3 in the atmosphere is primarily related to processes of acidification and neutralization of wet precipitation and often to the major forms of ammonia in the atmosphere.

The second cluster (cluster 2) is correlated with a lower deposition rate of metallic elements (Ni and Cr), except that Fe showed an average deposition rate of $28 \mu\text{g m}^{-2}$, while the other elements did

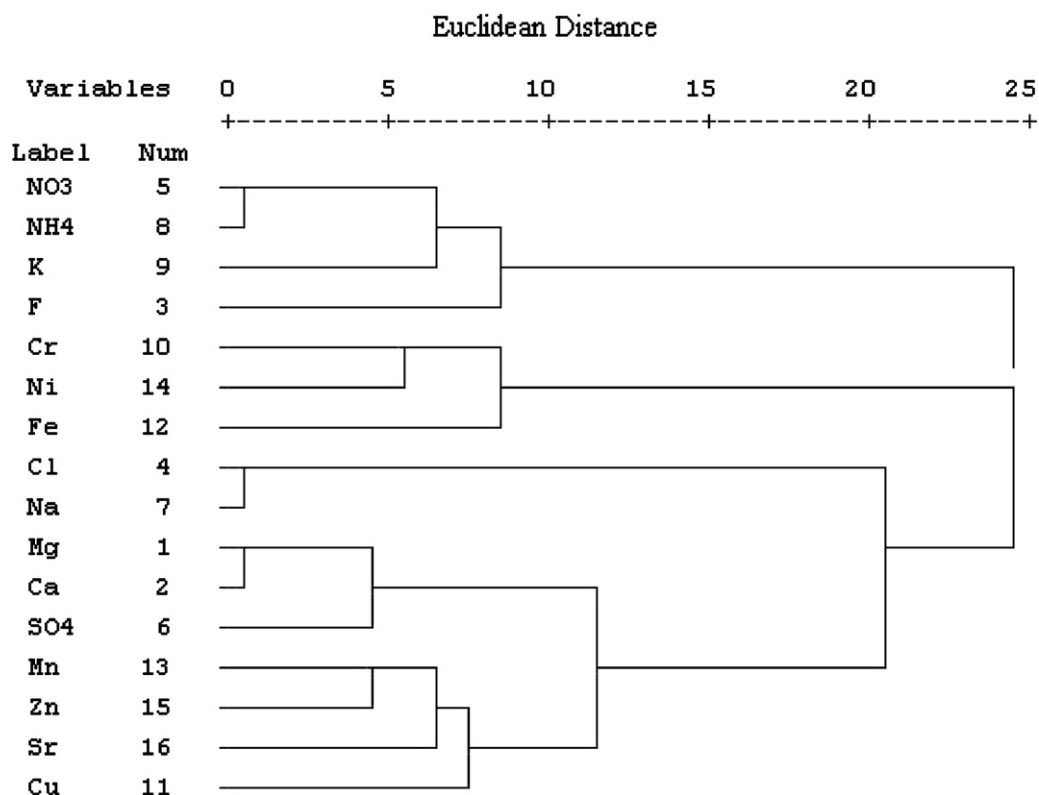


Fig. 10. Dendrogram resulting from the Ward's method of hierarchical cluster analysis for the wet precipitations samples in tree sites studied.

not exceed $3 \mu\text{g m}^{-2}$. The high Fe deposition rates indicate the presence of oxides containing Fe in its composition, such as hematite, ilmenite, pyrite and iron oxide itself, which was identified in the analysis by SEM (Fig. 8).

Due to the strong correlation between ions Na^+ and Cl^- , they grouped in a single cluster (cluster 3), thus corroborating their marine origin.

In the fourth and last cluster (cluster 4), ions and elements of anthropogenic origin, mainly Ca^{2+} , SO_4^{2-} and Zn, were identified and show a significant average concentration in the chemical composition of wet precipitation (Tables 1 and 3). Ions Ca^{2+} and SO_4^{2-} are associated with the presence of such minerals as calcite and gypsum, found in rocks and soil of the region. Minerals present in the Earth's crust can strongly impact the formation of hydrometeors, especially in ice crystals and rain droplets, due to wet removal processes of particulate matter and may be one of the key processes of removal by drops nucleation and by Brownian diffusion.

Finally, the presence of these elements in different clusters formed by cluster analysis is consistent with the minerals and oxides found in the SEM analysis. The removal of these minerals and oxides is most likely related to procedures for aerosol removal by rainfall, and they can be classified as the most important, as they may act as a cloud or ice condensation nucleus and gas dissolution in drops of clouds.

4. Conclusions

Preliminary results indicate a slightly alkaline pH (average of 5.76) at the monitored sites of the MAPA. High concentrations of SO_4^{2-} , and in a lesser extent of NH_4^+ , indicate the presence of anthropogenic sources associated with vehicle flow and industrial activities. However, Na^+ , Cl^- , Mg^{2+} and Ca^{2+} come from natural sources, where the first three indicate the influence of sea breeze, and Ca^{2+} and Mg^{2+} come from the soil of origin.

The suspended particulate matter in the rainwater samples presents a great range of minerals as seen in the X-ray diffraction and scanning electron microscopy with SDS. It can be noted that the chemical composition of the suspended particulate matter is manifold due to the varying geology in the area of study and the source of atmospheric suspended matter. Most of times, it is classified in the group of silicates and oxides. The highest deposition rates were observed for elements Fe, Zn and Mn, which were also found in form of oxides in the suspended particulate matter of wet precipitation. Potential sources of the minerals groups found are primarily linked to natural sources such as soil resuspension and to anthropogenic sources such as cement plants, coal-fired power stations, steel plant and petrochemical industries.

Through the four clusters formed in the CA, we were able to identify the chemical homogeneity of the variables in each cluster, characterizing the origin of each cluster formed: cluster 1, anthropogenic origin (NO_3^- , NH_4^+); cluster 2, metallic elements (anthropogenic origin); cluster 3, marine origin (Na^+ and Cl^-), and, finally, cluster 4, with the largest number of variables (Mg^{2+} , Ca^{2+} , SO_4^{2-} , Mn, Zn, Sr and Cu), of which the most important are Ca^{2+} , SO_4^{2-} and Zn, basically of anthropogenic contribution.

Acknowledgments

To the CNPq and FAPERGS for financial support. To the Sampling Service and Laboratory of Chemistry of FEPAM and the Laboratories of the Institute of Geosciences of (UFGRS) for their contribution to the study.

References

- [1] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, J. Wiley & Sons, New York, 1998.
- [2] B.J. Finlayson-Pitts, J.N. Pitts, Chemistry of the Upper and Lower Atmosphere, Academic Press, New York, 2000.

- [3] P.A. Souza, W.Z. Mello, J. Maldonado, H. Evangelista, Composição química da chuva e aporte atmosférico na Ilha Grande, RJ, *Quim. Nova* 29 (2006) 471–476.
- [4] J.N. Galloway, R.J. Charlson, M.O. Andreae, H. Rhode, M.S. Marston, The Biogeochemical Cycling of Sulphur and Nitrogen in the Remote Atmosphere (NATO ASI Series), Reidel, Dordrecht, 1984.
- [5] G.P. Ayres, R.W. Gillet, P.W. Selleck, S.T. Bentley, Rainwater composition and acid deposition in the vicinity of the fossil fuel-fired plants in southern Australia, *Water Air Soil Pollut.* 85 (1995) 2313–2318.
- [6] J.S. Galpin, C.R. Turner, Trends in composition of rain quality data from South African interior, *S. Afr. J. Sci.* 95 (1999) 225–228.
- [7] B.K. Lee, S.H. Hong, D.S. Lee, Chemical composition the precipitation and wet deposition of major ions on the Korean peninsula, *Atmos. Environ.* 34 (2000) 563–575.
- [8] W. Marquardt, E. Bruggemann, A. Renate, H. Herrmann, D. Moller, Trends of pollution in rain over East Germany caused by changing emissions, *Tellus B53* (5) (2001) 529–545.
- [9] D. Migliavacca, E.C. Teixeira, F. Wiegand, A.C.M. Machado, J. Sanchez, Atmospheric precipitation and chemical composition of an urban site, Guaíba hydrographic basin, Brazil, *Atmos. Environ.* 39 (2005) 1829–1844.
- [10] Ż. Polkowska, A. Astel, B. Walna, S. Małek, K. Mędrzycka, T. Górecki, J. Siepak, J. Namieśnik, Chemometric analysis of rainwater and throughfall at several sites in Poland, *Atmos. Environ.* 39 (2005) 837–855.
- [11] M. Placet, D.B. Streets, First interim assessment, National acid precipitation assessment programme, Jackson Place, NW, Washington, DC, 1987.
- [12] L.T. Khemani, G.A. Momin, P.S. Naik, P.S. Prakasa Rao, R. Kumar, B.V. Ramana Murthy, Impact of alkaline particulates on pH of rainwater in India, *Water Air Soil Pollut.* 24 (1985) 365–376.
- [13] T.N. Mahadevan, B.S. Negi, V. Meenakshy, Measurements of elemental composition of aerosol matter and precipitation from a remote continental site in India, *Atmos. Environ.* 23 (1989) 869–874.
- [14] M.S. Naik, G.A. Moin, A.G. Pillai, P.D. Safai, P.S.P. Rao, L.T. Khemani, Precipitation chemistry at Singhad a hillstation in India, *Water Air Soil Pollut.* 85 (1995) 2161–2166.
- [15] U.C. Kulshrestha, M.J. Monika, R. Sekar, G.S.R. Sastry, M. Vairamani, Chemical characteristics of rainwater at an urban site of South Central India, *Atmos. Environ.* 37 (2003), 3019–30 26.
- [16] A. Saxena, U.C. Kulshrestha, N. Kumar, K.M. Kumari, S.S. Srivastava, *Atmos. Environ.* 30 (1996) 3405–3412.
- [17] G.S. Satsangi, A. Lakhani, P. Khare, S.P. Sing, K.M. Kumari, S.S. Srivastava, Composition of rain water at a semi-arid rural site in India, *Atmos. Environ.* 32 (21) (1998) 3783–3793.
- [18] S. Balachandran, P.S. Khillare, Occurrence of acid rain over Delhi, *Environ. Monit. Assess.* 71 (2001) 165–176.
- [19] FEPAM, Relatório de Qualidade do ar no Estado do Rio Grande do Sul 2001/2002, Série Relatórios/Secretaria Estadual do Meio Ambiente, Porto Alegre, 2003.
- [20] IBGE, Instituto Brasileiro de Geografia e Estatística, <http://www.ibge.gov.br/home.htm>.
- [21] R. Midugno, Comportamento Geoquímico dos Metais Associados com Hidrocarbonetos de Petróleo na área da Refinaria Alberto Pasqualini S/A, Canoas, RS, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre, 2003.
- [22] L.D. Oliveira, E. Koester, E. Soliani, Geoquímica das rochas graníticas pós-transcorrentes da região de Porto Alegre e Viamão, RS, *Geochimica, Brasil* 15 (1/2) (2001) 65–92.
- [23] M. Franzen, Análise da Contaminação por Nutrientes, Elementos Maiores e Elementos-traço nas águas e Sedimentos do Arroio Sapucaia, RS, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre, 2001.
- [24] ASTM, Standard guide for choosing locations and sampling methods to monitor atmospheric deposition at non-urban locations: D 5111-99, West Conshohocken, PA, v.11.03 (2006) 440–448.
- [25] D. Migliavacca, E.C. Teixeira, M. Pires, J. Fachel, Study of chemical elements in atmospheric precipitation in South Brazil, *Atmos. Environ.* 38 (11) (2004) 1641–1656.
- [26] ASTM, Standard guide for preparation of material used for the collection and preservation of atmospheric wet deposition: D 5012-01, West Conshohocken, PA, v.11.03 (2008) 387–391.
- [27] S. Barrionuevo, R.S.H. Nascimento, A.C.M. Machado, M. Pires, Caracterização Química da Precipitação Atmosférica por Cromatografia iônica, FINEP/PADCT/CIAMB/FABERGS/FEPAM, Estudos ambientais em Candiota: carvão e seus impactos, Porto Alegre, 2004, pp. 193–200.
- [28] T.C. Alves, Caracterização Geoquímica de um Perfil de Alteração em Rochas Graníticas no Parque Estadual de Itapuã/RS, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre, 2004.
- [29] L.C. Duarte, P.L. Juchem, G.M. Pulz, T.M.B. Martini, N. Chodur, A. Liccardo, A.C. Fischer, R.B. Acauan, Aplicações de microscopia eletrônica de varredura (MEV) e sistema de energia dispersiva (EDS) no estudo de gemas: exemplos brasileiros, *Pesquisas* 30 (2) (2003) 3–15.
- [30] Ş. Tokaloğlu, Ş. Kartal, Multivariate analysis of the data and speciation of heavy metals in street dust samples from the organized industrial district in Kayseri (Turkey), *Atmos. Environ.* 40 (2006) 2797–2805.
- [31] V.P. Campos, A.C. Costa, T.M. Tavares, Comparação de dois tipos de amostragem de chuva: deposição total e deposição apenas úmida em área costeira tropical, *Quim. Nova* 21 (1998) 418–423.
- [32] R. Mosello, M. Bianchi, H. Geiss, A. Marchetto, G. Serrini, G. Lanza Serrini, G.A. Tartari, H. Muntau, Acid rain analysis, Project AQUACON – MED BAS, Luxembourg, 1997, 47 pp.
- [33] C.P. Mouli, V.S. Mohan, S.J. Reddy, Rainwater chemistry at a regional representative urban site: influence of terrestrial sources on ionic composition, *Atmos. Environ.* 39 (2005) 999–1008.
- [34] G. Kaya, G. Tunçel, Trace element and major ion composition of wet and dry deposition in Ankara, Turkey, *Atmos. Environ.* 31 (1997) 3985–3998.
- [35] A. Alastuery, X. Querol, C.R. Aura Chaves, A. Carratala, A. Lopez-Soler, Bulk deposition in rural area located around a large coal-fired power station, Northeast Spain, *Environ. Pollut.* 106 (1999) 359–367.
- [36] I.F. Al-Momani, O.Y. Ataman, A.M. Anwari, S. Tunçel, C. Köse, G. Tunçel, Chemical composition of precipitation near an industrial area at Izmir, Turkey, *Atmos. Environ.* 29 (1995) 1131–1143.
- [37] A. Sanusi, H. Wortham, M. Millet, P. Mirabel, Chemical composition of rainwater in eastern France, *Atmos. Environ.* 30 (1996) 59–71.
- [38] L.B.L.S. Lara, P. Artaxo, L.A. Martinelli, R.L. Victoria, P.B. Camargo, A. Krusche, G.P. Ayers, E.S.B. Ferraz, M.V. Ballester, *Atmos. Environ.* 35 (2001) 4937–4975.
- [39] W.C. Keene, A.A.P. Pszenny, J.N. Galloway, M.E. Hawley, Sea-salt corrections and interpretation of constituent ratios in marine precipitation, *J. Geophys. Res.* 91 (1986) 6647–6658.
- [40] B. Tuncer, B. Bayar, C. Yesilyurt, G. Tunçel, Ionic composition of precipitation at the Central Anatolia (Turkey), *Atmos. Environ.* 35 (2001) 5989–6002.
- [41] E.R. Byron, R.P. Axler, C.R. Goldman, Increased precipitation acidity in the central Sierra Nevada, *Atmos. Environ.* 21 (1991) 271–275.
- [42] H.A. Khawaja, L. Husain, Chemical characterization of acid precipitation in Albany, New York, *Atmos. Environ.* 24A (1990) 1869–1882.
- [43] S.J. Luca, L.B. Milano, C.N. Ide, Rain and urban storm water quality, *Water Sci. Technol.* 23 (1991) 133–140.
- [44] C. Ugucione, E.P. Felix, G.O. Rocha, A.A. Cardoso, Daytime and nighttime removal processes of atmospheric NO₂ and NH₃ in Araraquara's region, SP, *Eclat. Quim.* 27 (2002) 1–9.
- [45] M. Flues, P. Hama, M.J.L. Lemes, E.S.K. Dantas, A. Fornaro, Evaluation of the rainwater acidity of a rural region due to a coal-fired power plant in Brazil, *Atmos. Environ.* 36 (2002) 2397–2404.
- [46] F.G. Carvalho, A. Jablonski, E.C. Teixeira, Estudo das partículas totais em suspensão e metais associados em áreas urbanas, *Quim. Nova* 23 (5) (2000) 1–4.
- [47] R. Chester, K.J. Murphy, F.J. Lin, A.S. Berry, G.F. Bradshaw, P.A. Corcoran, Factors controlling the solubilities of trace elements from non-marine aerosols deposited to the sea surface by the dry deposition mode, *Mar. Chem.* 42 (1993) 107–126.
- [48] L.J. Spokes, T.J. Jickels, Speciation of metals in the atmosphere, in: A.M. Ure, C.M. Davidson (Eds.), *Chemical Speciation in the Environment*, Chapman & Hall, 1995.
- [49] R.A. Duce, N.W. Tindale, The atmospheric transport of iron and its deposition in the ocean, *Limnol. Oceanogr.* 36 (1991) 1715–1726.
- [50] T.E. Graedel, C.J. Weschler, M.L. Mandich, Influence of transition metal complexes on atmospheric acidity, *Nature* 315 (1985) 240–242.
- [51] A.M. Ure, C.M. Davidson, *Chemical Speciation in the Environment*, Second ed., Blackwell Science, 2002.
- [52] T.D. Jickells, T.D. Davies, E.C. Teixeira, M. Tranter, S. Landsberger, K. Jarvis, P. Abrahams, Trace elements in snow samples from the Scottish Highlands: sources and dissolved/particulate distributions, *Atmos. Environ.* 26A (1992) 393–401.
- [53] R. Losno, G. Bergametti, P. Carlier, G. Mouvier, Major ions in marine rainwater with attention to sources of alkaline and acidic species, *Atmos. Environ.* 25A (1991) 763–770.
- [54] C.J. Weschler, M.L. Mandich, T.E. Graedel, Speciation, photosensitivity and reactions of transition metal ions atmospheric droplets, *J. Geophys. Res.* 91 (1986) 5189–5204.
- [55] M. Pires, Meio Ambiente e Carvão, FINEP/PADCT-GTM/CAPES/PUCRS/UFSM/FEPAM, Porto Alegre, 2002.