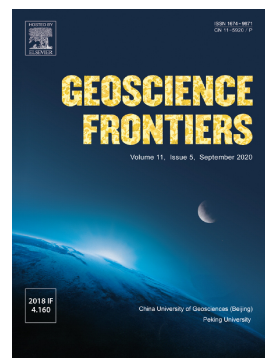


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Geochemical study of submicron particulate matter (PM₁) in a metropolitan area

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Abstract

Air pollution has become a major problem in urban areas due to increasing industrialization and urbanization. In this study ambient concentrations of PM₁ and metal concentrations as well as source contributions were identified and quantified by using Positive Matrix Factorization (PMF) in receptor modeling in the Metropolitan Area of Porto Alegre, Brazil. The PM₁ samples were collected on PTFE filters from December 2012 to December 2014 in two sampling sites. Major ion and trace element concentrations were assessed. The

average concentrations were 12.8 and 15.2 $\mu\text{g}/\text{m}^3$ for Canoas and Sapucaia do Sul sites, respectively. Major ion contributions of PM_{10} were secondary pollutants such as sulfate and nitrate. Trace elements, especially Cu, Pb, Zn, Cd, and Ni also made important contributions which are directly associated with anthropogenic contributions. Our results show significantly higher levels in winter than in summer. Most of the PM_{10} and the analyzed PM species and elements originated from anthropogenic sources, especially road traffic, combustion processes and industrial activities, which are grouped in 7 major contributing sources. A back-trajectory analysis showed that the long-range transport of pollutants was not relevant in relation to the contribution to PM_{10} and metal concentrations. This work highlights the importance of urban planning to reduce human health exposure to traffic and industrial emissions, combined with awareness-raising actions for citizens concerning the impact of indoor sources.

Keywords: PM_{10} , Trace elements, Source apportionment, PMF, Back trajectory.

1. Introduction

Urban air pollution is one of the most serious environmental issues confronting modern civilization in the face of rapid economic development (Fuertes et al., 2020). In 2016, particulate matter (PM) in ambient air was classified as a group 1 contaminant by the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC) (Feng et al., 2016). The actual health effects of PM depend on its chemical composition and the ability of the respiratory tract to remove inhaled PM, which depends in turn on its size (Li et al., 2020). Atmospheric particulate matter (PM) originates from a variety of emission sources, including natural and anthropogenic ones. Moreover, PM may be emitted directly into the atmosphere (primary PM) or formed in the atmosphere from

gaseous precursors (secondary PM) (Pey et al., 2009; Schneider et al., 2015). Among emission sources, heavy industries are considered to be a major anthropogenic trace metal source (Zheng et al., 2010; Zhou et al., 2014; Silva et al., 2020), although traffic emissions can also be considered an important source of PM and metal concentrations in urban atmospheres (Lough et al., 2005; Birmili et al., 2006; Johansson et al., 2009). Particles emitted from combustion process can be formed through transfer of inherent mineral matter into PM with minor phase changes (mostly coarse particles in the range of 1 to 10 μm PM_{1-10}), with the exception of diesel soot, with a mode at around 0.04–0.06 μm , and through nucleation and condensation of gaseous precursors and agglomeration of nanoparticles (in this case, yielding ultrafine and fine particles) (Ninomiya et al., 2004; Yoo et al., 2005; Saarnio et al., 2014; Oliveira et al., 2021). However, modern municipal waste incinerators have extremely low nanoparticle emissions (Buonanno et al., 2009; Ragazzi et al., 2013).

Atmospheric PM is one of the most important pollutants of the atmosphere and has highly variable undergoes a high variability concerning levels and composition (Nazir et al., 2011). Different components of PM may have diverse health impacts and, although increased PM-mass concentration is associated to increased mortality and morbidity, it is still unclear which specific components should be abated to diminish health effects from ambient aerosols (WHO, 2013). The traditional geochemical methods used in hazardous elements determinations are relatively complex, time-consuming and expensive, requiring more cost-efficient approaches are needed (Li et al., 2020). In recent years, machine learning models have been applied to predict the concentrations of airborne-pollutants such as SO_x , NO_x , O_3 , CO , $\text{PM}_{2.5}$, airborne heavy metals, and atmospheric nitrogen as well as the air quality index, because the necessary input variables are more easily accessed, in contrast to numerical forecast models. However, only few studies have focused on the

potential use of easily obtained atmospheric pollutants and meteorological factors to characterize atmospheric hazardous elements statistically (Leng et al., 2017).

Chemical composition of PM is particularly important for environmental assessment of specific source contributions to ambient air (Almeida et al., 2006). There is a wide range of known sources contributing to the increase of metal levels, such as Na, Ca, K, Al, Fe, As, Se, Ti and heavy metals in the finer PM fractions (Sanderson et al., 2014). Concentrations of metals with lower boiling point (As, Cd, Zn) were found to decrease with particle size, whereas those with higher boiling points (Co, Cr, Fe, Sb, Sc, Sm, Th, Eu, Yb) to increase with particle size. The more volatile elements emitted in gaseous form at high temperatures nucleate or condense during cooling (Hebble, 2000; Sanderson et al., 2014), whereas less volatile elements remain in the solid phase (Buonanno et al., 2011).

Particles with different aerodynamic diameters have different impacts on human health because fine particles may penetrate more deeply into the respiratory system. Fine particles contain higher concentrations of toxic metals, such as Pb, Cd, and Ni (Kauppinen and Pakkanen, 1990; Lin et al., 2005; Yoo et al., 2005; Tao et al., 2012; Cheng et al., 2014). Studies identifying trace elements to fingerprint specific emission sources to particulate matter (based on receptor source profiles) based on air quality data are relatively scarce due to the fact that (1) it is difficult to establish a direct connection between markers and specific emission sources for some elements; and (ii) tracers are generally not unique and source profiles may change over time (Querol et al., 2007 as an example). Some of these studies focus on road traffic emissions, whereas others present tracers of industrial sources, mostly from combustion processes, smelters, and other high temperature processes. Nevertheless, only few data are available on specific tracer elements for specific industrial processes. Adults have been the main targets of personal exposure assessment;

nevertheless, children have distinct time-activity patterns and are more vulnerable to the harmful effects of air pollutants. Children have higher breathing rates, since they are generally more physically active, they inhale a higher volume of air per body weight and their defense mechanisms are still evolving. Moreover, PM_{10} personal measurements are scarce in the literature and to the authors' knowledge, personal exposure to sized-fractioned $PM_{2.5}$ among children has not yet been assessed in detail.

Receptor modeling is one of the most commonly tools used to identify and quantify the contribution of individual emission sources to ambient levels of atmospheric particulate matter. It helps to achieve this purpose by measuring the concentration of pollutants at the sampling site (Hopke, 1991). One type of receptor model is the multivariate model, which was recently improved in a significant manner due to a new approach called Positive Matrix Factorization (PMF), developed by Paatero and others (Paatero and Tapper, 1994; Paatero, 1997), and to the least-squares approach. PMF is an advanced source apportionment method which successfully assesses particle source contributions and is applied in many different places around the world (Aldabe et al., 2011).

As a consequence of the growing interest of the scientific community in submicron particulate matter and of the lack of PM_{10} data (Caggiano et al., 2010), especially in Latin America, this study focuses on a temporally extended evaluation on this fraction to obtain statistically significant data from the Metropolitan Area of Porto Alegre, Rio Grande do Sul, Brazil. The study included the following aspects: (1) a chemical characterization of PM_{10} samples, (2) source apportionment analysis of source contributions, and (3) a cross-correlation analysis of major and trace elements, and calculation of the enrichment factors to support source attributions. The results of this study represent an important contribution to the knowledge of submicron particles measured at ground level and evaluate the impact

of these particles on environment and human health in the study area. The results obtained may be useful for programs to reduce air pollution and can motivate future studies on metal distribution, source contribution and enrichment factor on the clean atmospheric background.

2. Material and methods

2.1. Study area

The Metropolitan Area of Porto Alegre (MAPA), located in southern Brazil, is the most urbanized area of the state of Rio Grande do Sul. This region is characterized by different types of industries, including some stationary sources such as the Alberto Pasqualini Refinery (REFAP), steel mills which do not use coke, III Petrochemical Industrial Complex, coal-fired power plants, and a cement grinding mill (Fig. 1). Besides, it is estimated that there is a significant contribution of mobile sources due to the large number of vehicles in circulation in the region (Teixeira et al., 2008, 2010; Agudelo-Castañeda et al., 2014). The gasoline-powered vehicles use a mixture of gasoline and 20% of ethanol, and the diesel-powered vehicles usually contain 500 ppm of sulfur and 5% of biodiesel is added (Mattuzzi et al., 2012; PETROBRAS, 2012). Even if the diesel fleet in the region is less than 7%, the environmental impact in the air caused by this source is elevated and responsible for most particulate matter and NO_x emissions (Teixeira et al., 2012).

The two sampling sites evaluated in this study (Sapucaia do Sul and Canoas) are located to the north of Porto Alegre, as shown in Fig. 1. The Sapucaia do Sul sampling site has a greater industrial (oil refinery and steel mills) and vehicular influence than Canoas, and it is near a highway where there is heavy vehicle traffic of light and heavy fleet, with daily traffic congestion. However, in spite of Canoas site being located alongside the same

highway and being opposite to Sapucaia do Sul, the prevailing winds are downstream. The traffic in Canoas is also influenced by daily traffic congestion, as well as the Canoas air base and industries (oil refinery).

2.2. Sampling and analysis

Sampling of atmospheric PM₁ followed the criteria established by the USEPA (1994), using a sequential automatic particle sampler model PM162M of the Environment S.A.. PM₁ sampler used the EN 12341 method (LECES, nº RC. 9826) and included a set of two holders that act as support for the filters. Samples on PTFE filters of 47 mm diameter for a continuous period of 72 hours with a flow rate of 1.0 m³/h were collected. In order to evaluate different seasonal conditions, from December 2012 to December 2014, 38 samples of PM₁ for Sapucaia do Sul and 40 samples for Canoas were selected.

PM mass concentrations were determined by standard gravimetric procedures. Thereafter, half of each filter was acid digested (HF:HNO₃:HClO₄) for the determination of major elements (Al, Ca, Fe, K, Na, Mg, S, Ti, P) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, rare earths, Pb, Bi, Th, U) by Inductively Coupled Plasma Atomic Emission and Mass Spectrometry (ICP-AES and ICP-MS). Another quarter of each filter was water leached to determine soluble ion concentrations by ion chromatography (SO₄²⁻, NO₃⁻ and Cl⁻) and ion selective electrode (NH₄⁺). More analytical details can be found in Querol et al. (2001).

2.3. Data analysis

2.3.1. Enrichment Factors

Enrichment Factors (EF) were calculated to identify the contribution of anthropogenic sources on the levels of a specific element in PM₁ airborne particles. This information is very useful to identify the anthropogenic origin of the different elements, not

only at the urban scale, but also at a regional extent. In previous studies performed on atmospheric PM, several elements have been suggested as reference elements of the natural crust (for instance, Al, Ti, and Fe) (Moreno et al., 2013). In this study, Ti was chosen as the reference element. To obtain such factors, it is necessary to compare the concentration of the element in a sample to its concentration in the Upper Continental Crust (UCC), calculated by Equation (1):

$$EF_{Ti}(X_i) = (X_i/Ti)_{PM} / (X_i/Ti)_{Crust} \quad (1)$$

where, $(X_i/Ti)_{Crust}$ is the average ratio of the element of interests (X) and crustal representative element (Ti) (Mason, 1966), and $(X_i/Ti)_{PM}$ is the same ratio in particulate matter.

The degree of enrichment of trace metals with respect to the Earth's crust can be ranked in various levels: an EF close to 1 will suggest a natural origin for a certain element, whereas higher values will indicate to be a more probable anthropogenic source. However, despite a low EF be an indicative of its "crustal" origin, this cannot exclude the involvement of anthropogenic processes, such as resuspension of rock-forming mineral dust caused by agriculture, construction works or traffic. Several authors indicate that a significant non-crustal source is assumed to be predominant when $EF > 10$, natural sources when $EF < 1$, and mixed sources when $1 < EF < 10$ (Wu et al., 2009; Witt et al., 2010; Niu et al., 2015).

2.3.2. Source apportionment

A Positive Matrix Factorization (PMF) model was applied to the chemical dataset (78 samples) obtained through the chemical analysis to investigate the temporal variability of the main PM_{10} sources. PMF is a multivariate factor analysis tool that decomposes the data matrix into two matrices: factor contributions and factor profiles (Paatero and Tapper,

1994; Paatero, 1997) with a residual matrix (Vestenius et al., 2011). The fundamental principle of source/receptor relationships in receptor models is that mass conservation can be assumed, and a mass balance analysis can be used to identify and apportion sources of airborne particulate matter in the atmosphere (Hopke, 2003), as equation(2) :

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{jk} + \sigma_{ij} \quad i = 1, 2, \dots, m \quad j = 1, 2, \dots, n \quad (2)$$

where x_{ij} is the j^{th} species concentration measured in the i^{th} sample, g_{ik} is the contribution of the k^{th} source to the i^{th} sample, f_{jk} is the concentration of the j^{th} species in the k^{th} source and σ_{ij} is the residual associated with the j^{th} species concentration measured in the i^{th} sample. The task of PMF is to minimize the sum of the squares of the residuals weighted with the estimated uncertainties. The uncertainties were estimated according to the following equations (3) and (4) :

$$\sigma_i = \sigma_i^a + 0.05 * x_i \quad \text{if } x_i > DL_i \quad (3)$$

$$\sigma_i = \frac{3}{2} * DL_i \quad \text{if } x_i < DL_i \quad (4)$$

where x_i is the concentration of the i species, σ_i^a is the analytical error calculated for the i species and DL_i is the detection limits calculated for each species calculated following the three-sigma criterion. Chemical species were selected based on the signal to noise ratio, the percentage of values above detection limits and on the database size requirements. Based on these criteria, only 25 species were selected as strong species.

In this study the US-EPA PMF model version 5.0 was used. This receptor model is described in more detail in other published studies (Amato et al., 2010; Minguillón et al., 2012; Teixeira et al., 2013; Agudelo-Castañeda and Teixeira, 2014).

2.3.3. Back trajectory analysis

In order to interpret the variation of PM_{10} levels over time and the possible contribution of long-range transport, the origin of air masses reaching the study area was investigated by means of meteorological back trajectories. The Hysplit model (Draxler and Rolph, 2003; Stein et al., 2015) was used to calculate daily back-trajectories, ending at 12:00 UTC for 5 days at 100 m and 1000 m above ground level. These heights were chosen as they are within the boundary layer where most interactions affecting aerosols occur and they represent mid to high layers of the boundary layer, respectively. Height different air mass scenarios were considered for this study according to the cardinal and collateral points of the initial position of each trajectory. To determine the pollutant sources, all air mass back trajectories were clustered into eight types that were manually identified by visual analysis. The proportions of air masses associated with each track and the corresponding concentrations of PM_{10} and chemical elements associated to each receptor model factor were calculated.

3. Results and discussion

3.1. PM_{10} levels and elemental concentrations

Table 1 shows the PM_{10} average concentration levels obtained in the two sampling sites. The average concentrations were 12.8 ± 8.1 and $15.2 \pm 10.3 \mu\text{g}/\text{m}^3$ for Canoas and Sapucaia do Sul sites, respectively. Higher PM_{10} average concentration level in Sapucaia do Sul than in Canoas was observed. As stated above, Sapucaia do Sul site has a stronger vehicular influence by dense traffic of passenger cars, but also of light and heavy-duty vehicles, frequent traffic congestion and slow vehicle speed. This site has also the industrial influence (oil refinery and steel mills that do not use coke) upstream from the prevailing winds, as reported in other studies (Teixeira et al., 2012, 2013; Agudelo-Castañeda and Teixeira, 2014). Compared to other studies, PM_{10} average concentrations display similar

values to other cities, except for Wuhan (China) (Cheng et al., 2014) where the concentrations were close to 10 times higher than those observed in the present study. These higher PM₁ average concentrations, mainly in China, are a result of being a highly polluted area impacted by intense emission of particle sources such as traffic and coal combustion.

Average elemental concentrations in PM₁ measured at Canoas and Sapucaia do Sul sites compared to other studies are also reported in Table 1. Major components of PM₁ are SO₄²⁻ and NO₃⁻, followed by NH₄⁺ and Cl⁻, and some crustal elements. Moreover, crustal elements and major ions do not show much variation when compared to other studies, with the exception of Ca, for which high levels were obtained in the present study, together with Tito Scalo (Italy) and Tiang Hong (China). Tito Scalo (Italy) was the site that presented the highest level of Ca (1.0 µg/m³), probably due to larger emissions of fine mineral dust particles (Caggiano et al., 2010).

The SO₄²⁻ and NO₃⁻ concentrations in Canoas and Sapucaia do Sul sites were found to be lower than Broechem-antwerp (Belgium), Tito Scalo (Italy), Barcelona (Spain) and especially Wuhan (China) (22.0 µg/m³) (see references in Table 1). The latter site shows significant differences in relation to other sites, influenced by major pollution sources as coal combustions (SO₂) and vehicles (NO₃⁻). Some studies related the NO₃⁻/SO₄²⁻ ratio to different anthropogenic sources (Cheng et al., 2014). The NO₃⁻/SO₄²⁻ ratios of Canoas and Sapucaia do Sul were 1.2 and 0.8, respectively. For Canoas, the ratio suggested higher vehicular influence (>1.0), and for Sapucaia do Sul, stationary sources (<1.0) as dominant sources. However, the influence of vehicle exhausts in Sapucaia do Sul site should not be neglected due to the rapid increase in numbers of motor vehicles, confirmed by other studies (Teixeira et al., 2008; Agudelo-Castañeda and Teixeira, 2014).

Trace element concentrations were compared with those reported from other cities around the world. PM_{10} shows enriched levels of Cu, Zn, Mn and Pb for Canoas and Sapucaia do Sul, although different in comparison with other cities. Concentrations of Zn differs from mostly all the cities, although levels were higher than Brisbane (Australia), Tito Scalo (Italy), Helsinki (Finland) and similar to Barcelona (Spain) and Broechem (Belgium) (see references for these sites in Table 1). The Cu mean concentration for Canoas (19 ng/m^3) is different from most of the other countries, with higher values except for Iran (Tehran) and Australia (New South Wales and Whyalla). For Sapucaia do Sul, Cu mean concentration (10 ng/m^3) is similar to Frankfurt (Germany) and Barcelona (Spain), and higher than the other studies, except for the values reported from Iran (Tehran) and Australia (New South Wales and Whyalla) which show higher values than the results obtained in this study. The Pb levels are also low as compared to those of other countries, except for Iran (see references in Table 1). The Ti and Sn show similar or higher levels, except for Iran. The Sb content shows higher concentrations than all the compared countries, as shown in Table 1.

In this study, the Cu, Sn, Sb and Zn, may be emitted from road traffic and mainly, from break wear (Furuta et al., 2005; Gugamsetty et al., 2012; Hassanvand et al., 2015). The Cu and Zn commonly occur as submicron particles (Sanderson et al., 2014), as observed in our study. For both sites, Zn was found the most abundant trace element (33 ng/m^3 for Canoas and 59 ng/m^3 for Sapucaia do Sul). Sapucaia do Sul shows higher concentrations because of the presence of steel mills, smelters, and more vehicular traffic, that characterize the study area. However, Zn concentration (59 ng/m^3) in Sapucaia do Sul was smaller than in Tehran/Iran (Hassanvand et al., 2015). Moreover, variable amounts of Pb, Fe, Cu, Zn, Ni and Cd, in the sampling sites, can be observed due to contribution of

both sources, from industrial processes and from traffic (Vecchi et al. 2004; Hassanvand et al., 2015). Correlations between elements are shown in Table 2 and these findings are discussed in detailed later.

As explained above, the elements analysed in this study are associated with submicron particles, mainly in the fraction PM_{10} . This not only results in large areas that are available for reaction with fluids within the human body, but also allows these to be transported over distances of hundreds of kilometers. Although the studies shown in Table 1 were carried out at different periods and have used different experimental procedures (sampling techniques and methodologies - analytic techniques), there is an overall correlation, especially with regard to the type of source and common element.

3.2. Enrichment Factors (EFs)

Fig. 2 shows the mean EFs of PM_{10} samples for Canoas and Sapucaia do Sul sites. For both sites, less than only 1 EF was observed for Mg and Sr, showing that their compositions were very close to that of the upper continental crust indicating a natural origin. Other elements such as Al, Ca, Fe, K, Na, V, Mn, Ni, Rb and Ba presented EFs between 1 and 10, indicating the contribution of both natural and anthropogenic sources.

The $EF > 10$ was observed for K and Rb (Sapucaia do Sul site) and Cr (both sites), which indicates some anthropogenic contributions. However, the highest EF, i.e., $EF > 100$ and in some case $EF \gg 100$ for both sites, were observed for Cu, Zn, As, Cd, Sn, Sb and Pb, indicating very high anthropogenic contributions. These elements are usually derived from road traffic and industrial emissions, as will be discussed below in the source apportionment analysis. Other major anthropogenic sources in the study area are the combustion of petroleum products, non-ferrous metal production and coal combustion. The

enrichment of these elements in the particles affects the air quality of the study region and results in high anthropogenic emissions and low renovation of the air masses at the regional scale which leads to an elevated proportion of low dispersive conditions.

3.3. Source apportionment

PMF was performed based on the assembled dataset of PM₁ samples from both Canoas and Sapucaia do Sul. Samples of the two sites were examined together after a previous analysis that indicated a similar source contribution in both sites. Fig. 3 shows the source profiles whose columns and square represent the mass contribution of species to the factor ($\mu\text{g}/\text{m}^3$) and the percentage of species in the factor, respectively. Seven factors were identified and are discussed below.

Factor 1 was characterized by high contributions of NO_3^- (89%) and NH_4^+ (60%) and was assigned as secondary nitrate (Fig. 3). These contributions correspond to secondary pollutants and result from the transformation of their precursors NO_x and NH_3 , respectively, and are probably related to emissions from road traffic, high temperature industrial processes, power generation and biomass burning (Drechsler et al., 2006; Cheng et al., 2014). As indicated in Fig. 4, Factor 1 represents 35% of the average contribution in the PM₁ samples in an annual basis, with lower contributions being observed during the summer, what can be attributed to the ammonium nitrate (NH_4NO_3) thermal instability (Querol et al., 2001; Mariani and Mello, 2007; Cusack et al., 2013a,b). For summer, the mean concentration observed was $0.13 \mu\text{g}/\text{m}^3$, while for winter the mean concentration was $3.14 \mu\text{g}/\text{m}^3$. This can be seen in Fig. 4 where the contribution to the mass increases to 50% in winter and decreases to only 4% in summer. Significant positive correlation (Table 2) of NH_4^+ with secondary NO_3^- was observed in winter ($\rho = 0.81$). However, these compounds

do not show any correlation during summer, which can be explained by their volatilization in the atmosphere in warmer conditions (Parker et al., 2008).

Factor 2 represents 4% of the average contribution to the PM₁ samples (Fig. 4). This factor presents higher contribution of Al and Mg, 90% and 78%, respectively (Fig. 3). These elements in general are defined to be of crustal origin (Vecchi et al., 2004; Park and Kim, 2005; Perez et al., 2008; Caggiano et al., 2010; Sánchez de la Campa et al., 2010; Crilley et al., 2014). The low concentrations of metals associated with crustal mineral, average of 0.18 µg/m³ (Fig. 4), can be explained as they are generally accumulated in coarser particles (Pakkanen et al., 2003; Perez et al., 2008; Buczynska et al., 2014; Crilley et al., 2014). Factor 2 does not show a clear seasonal variation. Its average contribution of concentration was 0.15 µg/m³ (5%) and 0.20 µg/m³ (3%) for summer and winter, respectively (Fig. 4). In addition, significant positive correlations (Table 2) were observed between Al and Mg in summer and winter ($\rho = 0.72$ and 0.83 , respectively), thus not revealing seasonal variation.

Factor 3 was characterized by high Cl⁻ (85%) (Fig. 3), the origin of which can be attributed to a coal-fired power station, located near the sampling site. Contribution of Cl⁻ from coal-fired power station source has been identified by other studies (He et al., 2001; Duan et al., 2004; Wang et al., 2005; Cheng et al., 2014). In addition, Cl⁻ in the atmosphere can also be associated with some fugitive emissions from waste or garbage burning close to the sampling sites, and from industrial activities in the area, such as paper manufacturing companies. Factor 3 contributed with 0.70 µg/m³ (15%) of the average contributions in an annual basis, with seasonal variation: 0.69 µg/m³ (11%) for winter, and 0.72 µg/m³ (23%) for summer. Low Na levels associated with this factor, at about 2% of the total Na

concentration, suggest that there is no marine contribution to Cl⁻ levels observed in the PM₁ samples.

Factor 4 was related to the influence of metallurgical industry, with predominance of Fe, Cr and Mn concentrations. Significant correlation was observed between Fe-Mn for winter ($\rho = 0.93$), and Fe-Cr for summer ($\rho = 0.46$). Generally, metals are better correlated in winter, as can be seen in Table 2. This is probably related to the metallurgical facilities in the study area, and these contributions were higher in winter due to the lower dispersive conditions. Correlation among the metals for summer may be due to enhanced soil resuspension and the favorable dispersion conditions, making it difficult to clearly identify the different sources (Minguillón et al., 2012). As reported above, the metals may be associated with mineral material, suggesting the presence of metals in soil resuspension. Various authors (Moreno et al., 2010, 2011) have reported that Cr influence in the atmosphere is attributed mostly to industrial metallurgical emissions which were also verified in relation to the contributions of Fe and Mn. In the microscopy analysis presented above, the presence of Fe, Cr and Mn was observed, thus, highlighting the contribution of this source. Factor 4 is related to only 2% of the average concentrations observed in the PM₁ samples, i.e. $0.29 \mu\text{g}/\text{m}^3$ (Fig. 4). No significant seasonal variation in the metal concentrations was observed, with average contributions of $0.11 \mu\text{g}/\text{m}^3$ (3%) for summer, and $0.07 \mu\text{g}/\text{m}^3$ (1%) for winter.

Factor 5 of the source apportionment analysis indicated the association of several anthropogenic metals, such as As, Rb, Sn, Pb, Cd, Zn, Mn, Cr, Cu and K, with the PM₁ samples. Potassium in the fine PM fraction is usually associated with biomass combustion (Vecchi et al., 2004; Wang et al., 2005; Spindler et al., 2010; Buczynska et al., 2014; Cheng et al., 2014), and the two study sites are influenced by emissions from this activity. In this

group of metals there are also anthropogenic metal tracers related to municipal garbage incineration, smelters, and oil refining processes. These processes in the study area were evidenced by the presence of As, Cd, Pb, and Zn. The presence of these metals has been reported by several studies with similar sources (Schauer et al., 2006; Wåhlin et al., 2006; Perez et al., 2008; Amato et al., 2011; Moreno et al., 2011; Minguillón et al., 2012; Niu et al., 2015). Furthermore, as previously indicated, non-exhaust traffic sources as brakes (Cu, Sn, and Zn) and tires (Cd, Cu, and Pb) (Sanderson et al., 2014) also contributed significantly to this factor. However, metallurgical emissions of Zn, Pb, and Mn associated with other emissions listed above, favor the idea of a mixture of atmospheric pollutants and the difficulty of identifying individual sources (Morales et al., 2011). Indeed, this was observed in this study and, therefore, considered that the association of some metals can be emitted by specific sources mixed with a factor in the atmosphere or by common sources of emissions. Some metals may appear in different factors, or metals may be a characteristic of a factor with more than one emission source. Significant correlations were observed between As/Cd, Zn/As, Zn/Cd, Cr/Ni, Cr/Zn, Mn/Zn, Mn/Ni, Mn/Cu, and Pb/Cd for winter, whereas some correlations between these elements do not show much difference for summer. Metal correlations are in line with the seasonal variation with an average concentration of $0.37 \mu\text{g}/\text{m}^3$ (12%) for summer, and $0.86 \mu\text{g}/\text{m}^3$ (14%) for winter (Fig. 4), thus revealing a clear seasonal variation.

Factor 6 is related mainly to the contributions of Ca, Cr, Ni, and V. This factor corresponds to 11.4% of the average contributions to the PM_{10} samples and corresponds to cement industry, construction and oil combustion sources. Ca can be probably linked to specific anthropogenic activities, such as construction works, cement factories and building material production plants (Munir and Shaheen, 2008; Perez et al., 2008; Amato et al.,

2009; Caggiano et al., 2010; Widory et al., 2010; Crilley et al., 2014). Ni and V can be associated with oil combustion (Arhami et al., 2009; Moreno et al., 2010; Buczynska et al., 2014; Crilley et al., 2014) and these metals are typical tracers of this source (Pandolfi et al., 2011; Cusack et al., 2013b). The study area is mainly influenced by oil combustion that is used in refineries and steel industry. As reported by some authors (Moreno et al., 2011; Mohiuddin et al., 2014), much of this combustion-derived atmospheric V and Ni were predominantly associated with the finest PM size fraction and is therefore capable of travelling long distances. Significant correlations were observed for Ca with V, Cr, and Ni, and for Cr/Ni for winter, and between Ca/V and V/Cr for summer. Factor 6 showed seasonal variation, with average concentrations of $0.52 \mu\text{g}/\text{m}^3$ (17%) for summer, and $0.40 \mu\text{g}/\text{m}^3$ (7%) for winter (Fig. 4).

Factor 7 was identified due to the contribution of SO_4^{2-} and NH_4^+ , given the relevance of these compounds in the chemical profile (37% and 86%, respectively) (Fig. 3). High contributions of this factor to the concentrations of Sb, Pb, Cd, Rb, Ti, Zn, K, Cu (between 10 and 30% of their concentration) were obtained, and most of these are typical tracers of road traffic (Querol et al., 2002; Lin et al., 2005; Pey et al., 2010; Amato et al., 2011; Moreno et al., 2011; Niu et al., 2015). For winter and summer, sulfate concentrations were 1.21 and $1.26 \mu\text{g}/\text{m}^3$, respectively, while ammonium was 1.01 and $0.28 \mu\text{g}/\text{m}^3$, respectively. The winter/summer sulfate ratios (0.96) indicated a relatively stable seasonal pattern, with slightly higher summer levels possibly because of enhanced photochemistry associated with more intense solar radiation (Cusack et al., 2012). Ammonium showed higher concentration for winter (winter/summer ratio of 3.5). Among the constituents of Factor 7 a significantly higher correlation was obtained in winter compared to summer (Table 2). As reported in Factor 5, some metals may appear in different factors as non-

exhaust traffic sources, such as Cu, Sb, Zn and Cd, Cu, Pb, and Cu (Sörme et al., 2001; Kupiainen and Pirjola, 2011; Wiseman et al., 2013; Buczynska et al., 2014; Crilley et al., 2014; Wiseman and Zereini, 2014; Hassavand et al., 2015). Also, these elements and compounds can be characterized by anthropogenic activities from industrial sources, traffic and coal combustion. This factor was associated with a mixture of anthropogenic sources as its chemical profile is dominated by secondary ammonium sulfate, probably from SO₂ emissions from coal-fired power plants, smelters and oil refining, but was also associated with contributions of tracers of different sources, probably mixed during the atmospheric transport. Factor 7 showed seasonal variation with 0.87 $\mu\text{g}/\text{m}^3$ (14%) for winter and 1.12 $\mu\text{g}/\text{m}^3$ (36%) for summer.

3.4. Back trajectory analysis

Table 3 shows the average concentrations of PM₁, the contributions of each factor of the source apportionment obtained from PMF and the sum of metals for both back trajectory heights. As can be seen, in both cases when air masses from the north of the study area reach the studied sites, the PM₁ concentrations become higher. However, after carrying out a comparison between the means using the non-parametric Mann-Whitney test, it was observed that the mean differences were not statistically significant. No statistically significant differences were also observed between the mean concentrations of the PMF factors and the sum of metal. This is an indication that both PM₁ and metal concentrations observed in this study correspond mainly to contributions from regional-local sources, as identified by the source apportionment.

In addition, the sensitivity of PM concentrations to the airflows decreased with increasing arrival-height (Table 3). This result may be due to the fact that polluted air masses at high altitudes have on average a lower impact at the surface PM. Airflows at

higher altitudes are on average characterized by larger path lengths and, as a consequence, they are prone to being more affected by the atmospheric physical and chemical processes occurring during the transport and, hence, are less dependent on source properties (Perrone et al., 2013).

In summary, the complex spatial and temporal relationship of the elements measured in this study revealed no spatial pattern with regard to the origin of the air masses, therefore studies with more sophisticated techniques are necessary to advance the understanding of the identification of long-range transport of aerosol sources. This case-crossover work considered the short-term effects of size-specific particles on emergency department visits among Brazilian metropolitan populations. We identified clear evidence that exposures to ambient PM₁ elevated risks for emergency department visits. Besides, PM₁-emergency department visits associations may vary by age groups and season. Our findings may have some clinical and public health implications in guiding the public and patients to take active actions against air PM₁ pollution, so as to reduce associated health risks. Prior time-series and case-crossover studies have investigated short-term AAP effects on EDVs for various causes, including cardiovascular and respiratory diseases (Metzger et al., 2004; Peel et al., 2005; Stieb et al., 2009; Fan et al., 2016; Szyszkowicz et al., 2018). The toxic effects on human cardiorespiratory systems could possibly be interpreted by several biological changes in response to damage from PM, such as increased oxidative stress, inflammation, and vasoconstriction (Zhang et al., 2020).

4. Conclusion

Hazardous elements concentrations associated with particulate matter <1 µm (PM₁) revealed strong anthropogenic influence in the study area, located in southern Brazil. The average concentrations of PM₁ of this urban and industrialized area corresponded to levels

similar to those reported for several European countries, but much lower than those found in China. Major contributions of PM_{10} were secondary pollutants sulfate (SO_4^{2-}) and nitrate (NO_3^-). Trace elements, especially Cu, Pb, Zn, Cd, and Ni, also made important contributions by being directly associated with anthropogenic contributions. Among these, as verified by PMF, the major sources correspond to secondary nitrate and sulfate, industrial emissions, especially metallurgical, cement and oil refining processes, in addition to coal, biomass and oil combustion, as well as traffic fuel burning and non-exhaust sources. The crustal contribution was less than 4%, as it is generally present in coarser size mode. The analysis for detecting potential long-range transport contributions showed no significant influence on the PM_{10} as for metal concentrations, which are attributed mostly to contributions from regional-local sources, as identified by the source apportionment. However, it was observed that the association of some metals with atmospheric particles can be due to emissions from a specific source or from different sources. Some hazardous elements may appear in different factors, or metals may be a characteristic of a factor with more than one emission source. Nevertheless, the PMF model was found to be an efficient tool for identifying the main sources responsible for trace elements. The absence of marker species in the input data sets, such as organic tracers, may be one of the problems of the inefficacy of the model to separate sources.

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Figure captions

Fig. 1. Location of the sampling sites at Canoas and Sapucaia do Sul in Brazil.

Fig. 2. Mean EF for PM₁ samples in Canoas and Sapucaia do Sul.

Fig. 3. Source profiles identified for PM₁ samples. The mass of each species apportioned to the factor (blue bar, left axis) and the percentage of each species apportioned to each factor (red square, right axis) are shown.

Fig. 4. Pie charts shows average contribution of each source ($\mu\text{g}/\text{m}^3$) to PM₁ during different seasons obtained by PMF.

Table captions

Table 1

Comparison of mean PM₁ levels and composition of this study with those from different areas reported around the world.

Table 2

Spearman's correlation (ρ) matrix for major and trace components in PM₁. Correlations in red correspond to summer and in black to winter.

Table 3

Proportion of air masses associated air mass origin sectors and the corresponding concentrations of PM₁, PMF factors and sum of the evaluated elements ($\mu\text{g}/\text{m}^3$).

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Table 1

	Canoa ^s	Sapucaia ^a	Brochem/Belgium ^b	Brisbane/Australia ^c	Tehran/Iran ^d	Brno/Czech Republic ^e	New South Wales and Whyalla/Australia ^f	Salento/Italy ^g	Frankfurt am Main/Germany ^h	Tito Scaio/Italy ⁱ	Milan/Italy ^j	Hel sinki/Finland ^k	Wuhan/China ^l	Barcelona/Spain ^m			
µg/m ³	Mean	Mean	Even t da y	Non even t da y		Summer	Winter			Winter	Summer		Winter	Summer			
PM ₁	12.7	15.2	36.7	14.8	11.0	7.0-32.0	11.6	13.0	2.3-10.3	8.00	41.0	16.4	11.0	11.7	12.3	19.0	
Al	0.13	0.15			0.002	0.03-0.07			0.07	0.11	0.02	0.01	0.02				
Ca	0.12	0.14			0.03				0.03	1.00	0.02	0.02	0.02	0.14	0.30		
Fe	0.09	0.13			0.02	0.13-0.17		0.001-1.27	0.06	0.10	0.09	0.04	0.06				
K	0.21	0.33	0.32	0.17	0.01				0.14	0.10	0.26	0.08	0.02	1.39	1.34		
Mg	0.01	0.02						0.005		0.00		0.01	0.05	0.05	0.05		
Na	0.11	0.15			ND			0.03		0.10		0.03	0.30	1.33	0.33		
SO ₄ ²⁻	1.10	1.41	5.80	1.70			1.01	1.27	2.30			1.29				2.90	
NO ₃ ⁻	1.36	1.16	11.3	3.10			0.08	2.46	0.23			0.06	1.62	21.3	1.70		
Cl ⁻	0.79	0.58			0.02			0.03			0.29	0.04	0.01	20.7	21.6		
NH ₄ ⁺	0.72	0.57	4.20	1.20			0.40	1.14	0.75			0.58	1.72	1.76	1.10		
ng/m ³																	
Ti	4	5			2	12-15		ND-3.7		5	6	7	4	1	10	12	2
V	0.6	0.8	7	3	0.6	ND-3		0.6-1	3	1		5	4	8		6	
Cr	2	3	1	N	3	2-3		ND-4	4	4	38	2	1			1	

	D													
Mn	5	8	6	4	4	20-23	0.6-32	1	3	3	9	4	2	4
Ni	0.7	0.7	5	3	0.9	4-5	0.8-4	3	2	6	4	2	4	3
Cu	19	10	8	7	3	14-20	ND-25	2	11	4	4	3	2	12
Zn	33	59	63	30	6	84-161	3-146			6	66	32	7	48
As	0.5	1	4	2		4			0.6		2	1	0.4	0.6
Rb	0.8	1											0.1	0.2
Sr	0.3	0.4	1	ND	10	1							0.1	0.9
Cd	0.3	0.4			5.5	0.3		0.1		4			0.1	0.3
Sn	3	4				12-20								2
Sb	4	7							0.5				0.4	0.9
Ba	1	4				10-15		4					1	9
Pb	9	11	31	17	10	55-71		4	5	12	35	15	2	17
Region	urban	urban + industrial	urban	urban	urban	urban	urban	industrial	urban	urban	industrial	urban	urban	urban

a - This Study; b - Buczyńska et al. (2014); c - Crilley et al. (2014); d - Hassarvand et al. (2015); e - Mikuska et al. (2011); f - Mohiuddin et al. (2014); g - Perrone et al. (2013); h - Wiseman and Zereini (2014); i - Caggiano et al. (2010); j - Vecchi et al. (2004); k - Pakkanen et al. (2003); l - Cheng et al. (2014); m - Perez et al. (2002)
 ND - non detected

Table 2

Fe	K	Mg	Na	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Ti	V	Cr	Mn	Ni	Cu	Zn	As	Rb	Sr	Cd	Sn	Sb
0.33	0.23	0.72**	0.42*	0.38*	-0.20	0.08	-0.06	0.33	0.12	0.01	0.25	0.13	0.30	0.17	0.45**	0.21	0.56**	0.22	0.47**	0.21
-0.02	0.17	0.01	0.43*	0.36*	-0.03	-0.11	-0.14	-0.51**	0.12**	0.376*	-0.21	0.33	-0.34	0.00	0.29	-0.01	0.05	0.13	-0.22	-0.32
1.00	0.37*	0.23	0.19	0.24	-0.35*	-0.25	-0.01	0.20	0.15	0.46**	0.65**	0.31	0.34	0.46**	0.34	0.37*	0.33	0.09	0.28	0.50**
0.64**	1.00	0.27	0.44**	0.66**	-0.02	-0.14	0.31	0.19	0.19	0.19	0.26	0.45**	0.42*	0.42*	0.61**	0.92**	0.53**	0.64**	0.11	0.56**
0.07	-0.09	1.00	0.45**	0.42*	-0.21	0.14	-0.11	0.35	0.19	0.25	0.11	0.16	0.04	0.12	0.48**	0.21	0.70**	0.19	0.28	-0.03
0.41*	0.53**	0.45**	1.00	0.72**	0.03	-0.08	-0.02	-0.20	0.38*	0.41*	0.06	0.46**	0.24	0.24	0.42*	0.39*	0.44*	0.47**	0.15	0.10
0.61**	0.35*	-0.11	0.18	1.00	0.15	-0.10	0.46**	-0.09	0.54**	0.49**	0.26	0.63**	0.22	0.45**	0.59**	0.64**	0.50**	0.63**	0.25	0.28
0.29	0.12	-0.02	0.01	0.13	1.00	0.02	0.05	-0.19	0.13	-0.09	-0.24	0.20	-0.07	-0.24	-0.03	0.06	-0.22	0.30	-0.02	0.00
0.13	0.20	0.14	0.07	0.28	0.24	1.00	-0.09	0.04	0.07	0.04	-0.01	-0.08	0.04	-0.04	0.15	-0.10	0.12	0.16	-0.07	0.05
0.15	-0.01	-0.16	-0.20	0.25	0.81**	0.44**	1.00	0.05	0.04	0.00	0.09	0.47**	0.11	0.30	0.13	0.40*	0.12	0.30	0.09	0.45**
0.63**	0.29	0.16	0.22	0.58**	0.20	0.31	0.21	1.00	-0.36*	-0.17	0.12	-0.09	0.20	0.06	0.11	0.22	0.48**	-0.11	0.18	0.22
0.02	0.00	0.62**	0.22	-0.07	-0.13	-0.17	-0.25	-0.16	1.00	0.67**	0.04	0.50**	-0.18	0.20	0.51**	0.12	0.23	0.29	0.02	-0.11
0.33*	0.26	0.32	0.54**	0.12	-0.04	-0.31	-0.24	-0.02	0.47**	1.00	0.22	0.41*	-0.02	0.46**	0.34*	0.18	0.23	0.17	0.13	0.04
0.93**	0.68**	0.10	0.47**	0.56**	0.25	0.17	0.11	0.55**	0.06	0.34*	1.00	0.27	0.54**	0.66**	0.18	0.35*	0.29	0.29	0.43*	0.46**
0.37*	0.22	0.40*	0.55**	0.09	-0.03	-0.27	-0.23	0.13	0.48**	0.89**	0.38*	1.00	0.25	0.44**	0.32	0.46**	0.27	0.46**	0.18	0.22
0.32	0.38*	0.27	0.35*	0.12	0.08	0.02	0.02	0.24	0.25	0.34*	0.35*	0.37*	1.00	0.55**	0.11	0.45**	0.36*	0.46**	0.34	0.65**
0.78**	0.73**	0.08	0.49**	0.41*	0.16	-0.11	-0.05	0.26	0.26	0.52**	0.85**	0.44**	0.35*	1.00	0.33	0.47**	0.38*	0.52**	0.31	0.41*

0.62**	0.89**	0.01	0.51**	0.34*	0.15	0.13	-0.01	0.23	0.29	0.42*	0.66**	0.40*	0.46**	0.77**	1.00	0.59**	0.58**	0.64**	-0.01	0.34	0
0.65**	0.98**	-0.13	0.50**	0.39*	0.15	0.18	0.02	0.31	0.00	0.22	0.70**	0.20	0.40*	0.72**	0.89**	1.00	0.45**	0.72**	0.15	0.63**	0
0.56**	0.28	0.51**	0.47**	0.41*	0.13	0.11	0.09	0.52**	0.32	0.35*	0.49**	0.38*	0.45**	0.45**	0.38*	0.24	1.00	0.40*	0.32	0.28	0
0.52**	0.74**	0.05	0.52**	0.49**	0.03	0.11	-0.03	0.30	0.21	0.31	0.57**	0.24	0.58**	0.66**	0.78**	0.77**	0.36*	1.00	0.17	0.44**	0
0.46**	0.53**	0.10	0.43**	0.10	0.08	0.17	-0.08	0.39*	0.01	0.06	0.51**	0.17	0.38*	0.35*	0.49**	0.59**	0.14	0.48**	1.00	0.05	0
0.38*	0.59**	0.13	0.39*	0.18	0.20	0.18	0.07	0.16	0.11	0.17	0.43**	0.19	0.81**	0.42**	0.59**	0.63**	0.25	0.61**	0.47**	1.00	0
0.68**	0.41*	0.39*	0.40*	0.54**	0.10	0.18	0.06	0.67**	0.28	0.32	0.67**	0.33*	0.49**	0.62**	0.44**	0.42**	0.63**	0.51**	0.37*	0.40*	1
0.52**	0.73**	0.05	0.46**	0.29	0.14	0.06	0.04	0.28	0.12	0.29	0.58**	0.27	0.78**	0.66**	0.74**	0.77**	0.34*	0.82**	0.55**	0.83**	0
0.07	0.31	0.01	0.33	0.03	-0.19	-0.01	-0.16	0.07	-0.01	-0.01	0.07	-0.01	0.39*	0.15	0.26	0.33*	0.11	0.36*	0.21	0.40*	0

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

Table 3

Trajectory height	Air mass (proportion)	PM ₁	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Sum of metals
100 m agl	N (4%)	41.3	0.02	0.20	0.06	0.06	0.70	0.34	0.78	3.07
	NE (11%)	12.1	0.87	0.13	0.83	0.13	0.79	0.28	1.82	4.73
	E (4%)	9.36	2.66	0.06	0.81	0.04	1.04	0.42	0.51	5.32
	SE (11%)	8.68	1.77	0.15	0.76	0.16	0.35	0.52	0.89	4.56
	S (18%)	9.93	1.52	0.20	0.62	0.12	0.51	0.58	1.28	4.82
	SW (41%)	14.9	2.05	0.20	0.63	0.06	0.59	0.44	0.70	4.71
	W (0%)									
1000 m agl	NW (8%)	14.9	1.98	0.17	0.79	0.06	0.93	0.58	1.15	5.49
	N (10%)	16.9	2.07	0.10	0.79	0.06	0.53	0.38	0.85	4.68
	NE (10%)	10.6	1.26	0.15	0.90	0.09	0.69	0.30	1.62	4.99
	E (0%)									
	SE (7%)	11.4	3.18	0.10	0.67	0.03	0.61	0.35	1.00	5.83
	S (4%)	9.38	0.00	0.10	0.44	0.18	0.17	0.32	1.51	2.46
	SW (40%)	13.2	2.04	0.25	0.70	0.10	0.48	0.56	0.79	5.05
W (5%)	15.6	0.56	0.11	0.86	0.07	1.05	0.31	0.75	3.66	

NW (23%)	16.1	1.18	0.16	0.59	0.08	0.88	0.50	1.09	4.47
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

HIGHLIGHTS

- Determination of species and elements concentrations in PM₁.
- Mean levels of PM₁ and analyzed species and elements were higher in winter.
- Seven major contributing sources or mixed sources were identified.
- Significant anthropogenic contributions were observed.
- Long range transport of pollutants was not relevant to PM₁.

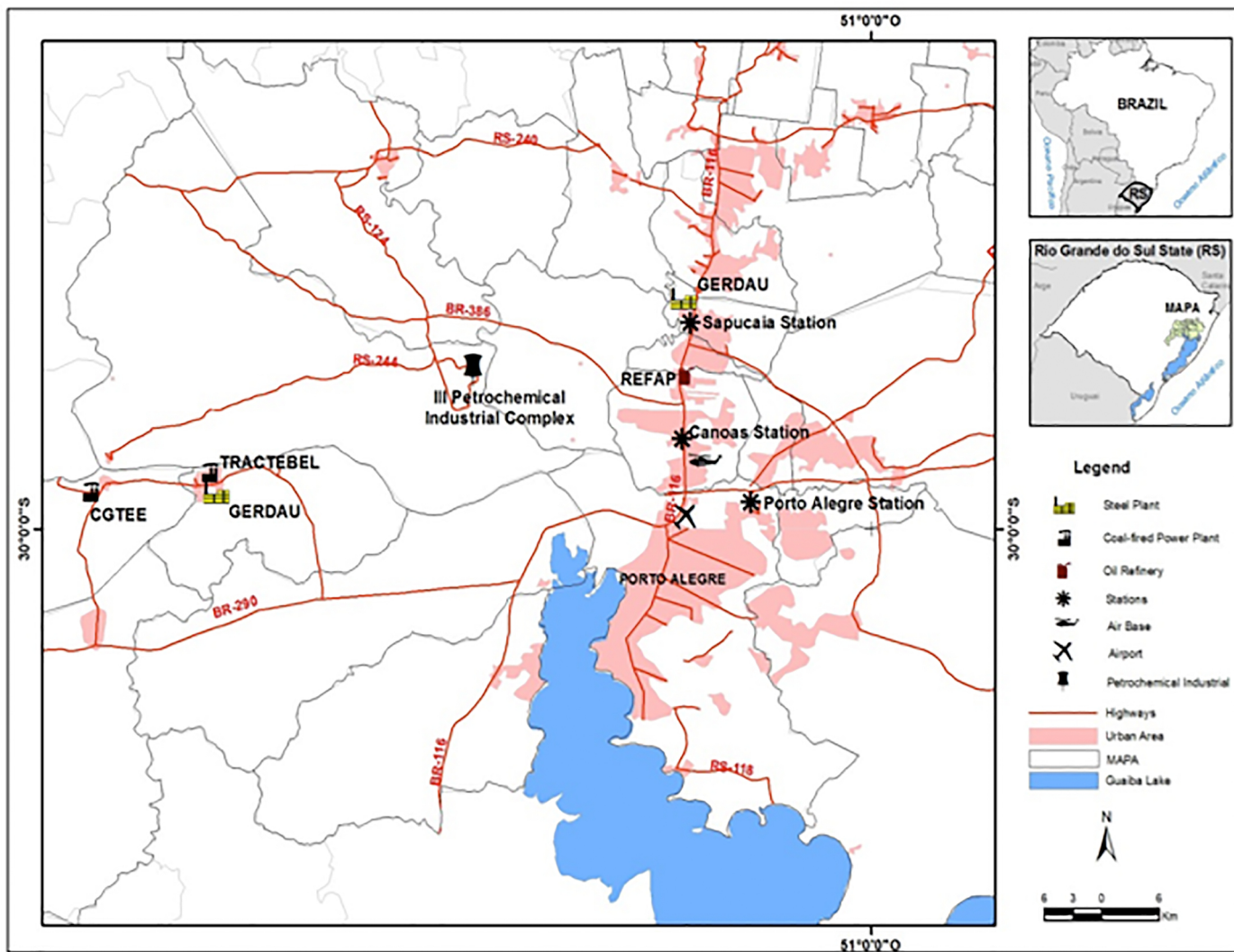


Figure 1

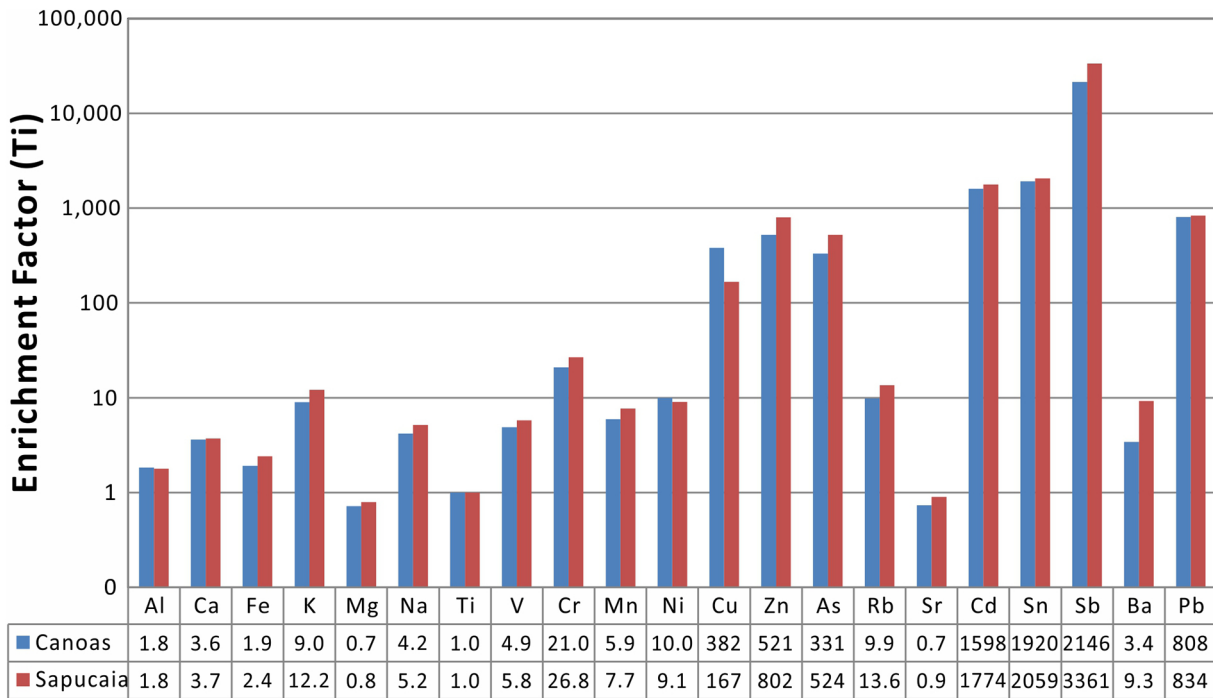


Figure 2

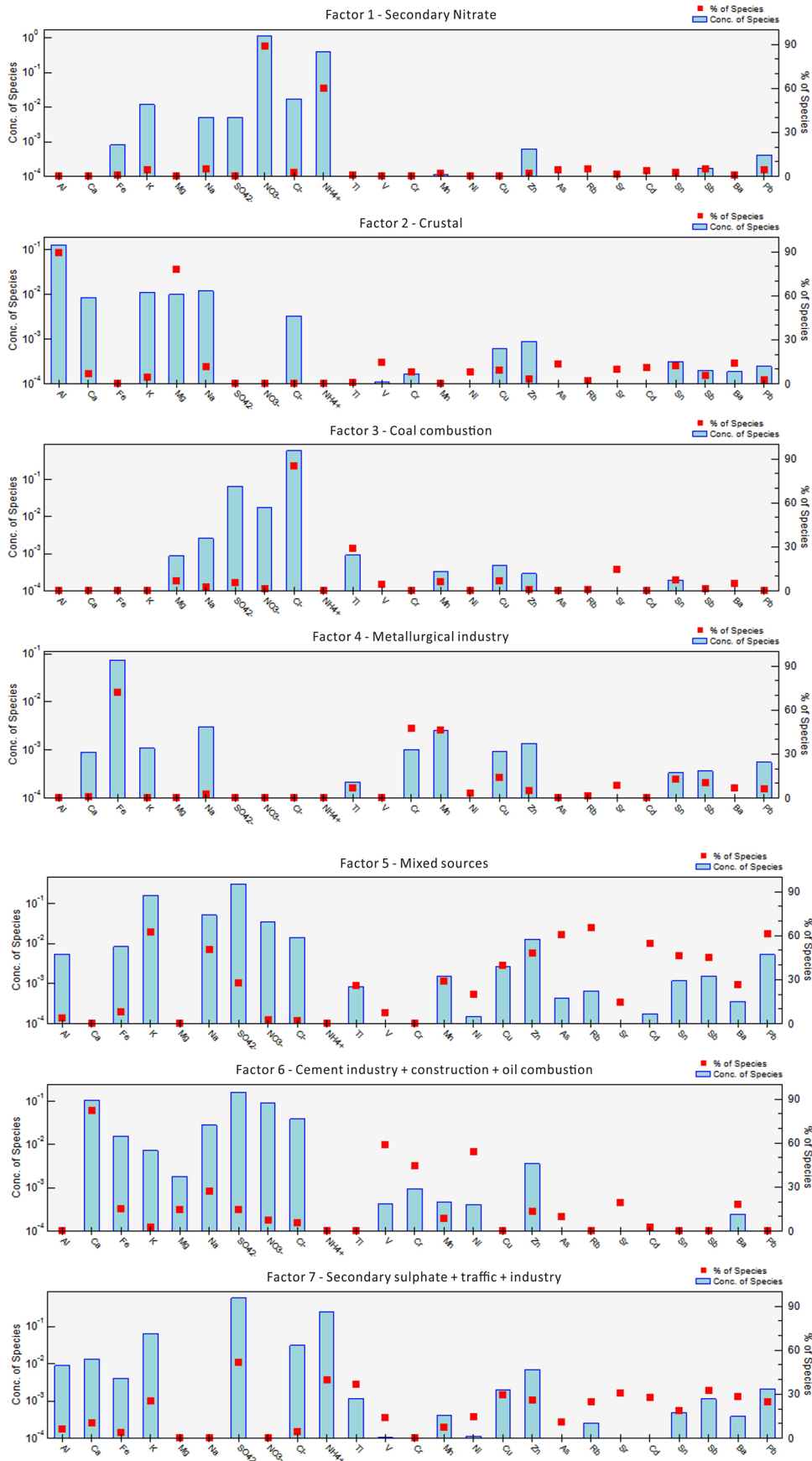
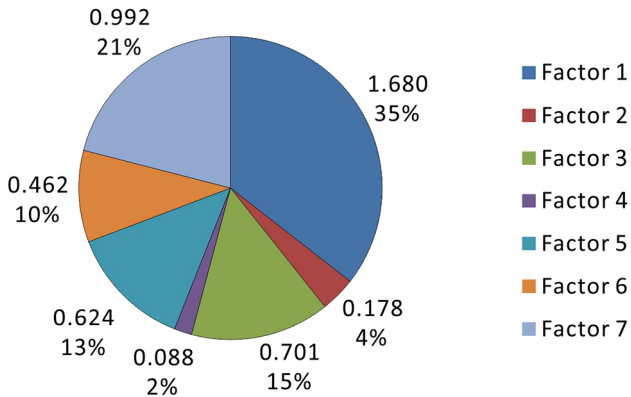
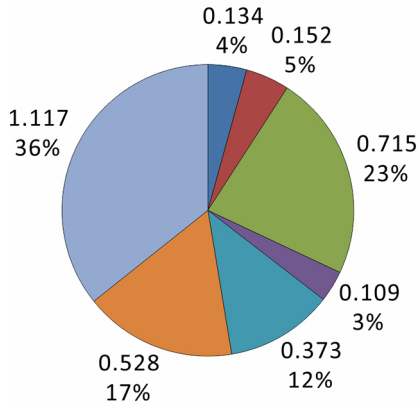


Figure 3

Annual



Summer



Winter

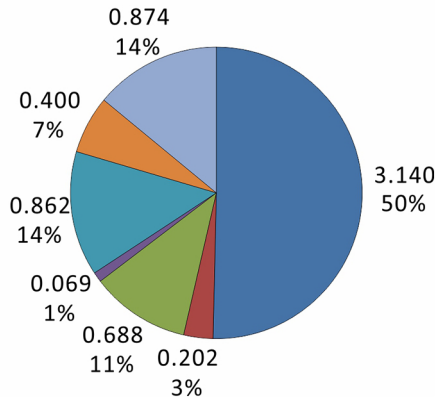


Figure 4