Concentrations of $PM_{2.5-10}$ and $PM_{2.5}$ and metallic elements around the Schmidt Stream area, in the Sinos River Basin, southern Brazil

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Abstract

This research aimed to evaluate the air quality, by determining the concentrations of $PM_{2.5-10}$, $PM_{2.5}$ and the metallic elements Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn and Hg in the leaf part of ryegrass (*Lolium multiflorum*) in an area close to Schmidt Stream, at the lower section of Sinos River Basin (SRB), in a research campaign of six months, from October 2013 to March 2014. The particles collected in the PM sampling were analyzed by Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray Spectrometry (EDS), in order to study their morphology and chemical composition. The mean concentration of $PM_{2.5-10}$ was 9.1 μg m^{-3}, with a range of 2.2 μg m^{-3} to 15.4 μg m^{-3} and the mean concentration of $PM_{2.5}$was 4.7 μg m^{-3}, with a range of 1.9 μg m^{-3} to 8.2 μg m^{-3}. Concentrations of metallic elements, especially Pb, Cr and Zn, were classified as Class 4 (very high pollution levels), according to the classification proposed by Klumpp et al. (2004). Chemical and morphological analysis of PM revealed the presence of particles of biological origin, soot (Cr, Fe, Ni, Zn, Cd, Hg and Pb), salts (KCl) and soil resuspension (Al and Si). The integrated study methodology, employing environmental variables, such as PM and ryegrass, can be of help in the preparation of wide-ranging environmental diagnoses, in addition providing information needed to develop precautionary measures designed to minimize the effects of atmospheric pollution that takes into consideration the environment's supportive capacity and environmental quality.

Keywords: air pollution, particulate matter, biomonitoring, *lolium multiflorum*, mev/eds.

Concentrações de $MP_{2,5-10}$ e $MP_{2,5}$ e elementos metálicos junto à área do Arroio Schmidt, na bacia do Rio dos Sinos, sul do Brasil

Resumo

O objetivo desta pesquisa foi avaliar a qualidade do ar, por meio da determinação das concentrações do $MP_{2,5-10}$, $MP_{2,5}$ e dos elementos metálicos Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn e Hg na folha do azevém (*Lolium multiflorum*) em uma área próxima ao Arroio Schmidt, no trecho inferior da Bacia do Rio dos Sinos (BRS), em uma campanha de seis meses de pesquisa, de outubro de 2013 a março de 2014. As partículas coletadas na amostragem do MP foram analisadas por Microscopia Eletrônica de Varredura (MEV), combinada com Espectrometria de Energia Dispersiva de Raios X (EDS), a fim de estudar sua morfologia e composição química. As concentrações médias de $MP_{2,5-}$10 e $MP_{2,5}$ foram de 9,1 μg m^{-3} e 4,7 μg m^{-3}, respectivamente. As concentrações médias dos elementos metálicos Pb, Cr e Zn na parte foliar do azevém foram de 13,58 mg kg^{-1}, 5,26 mg kg^{-1} e 88,80 mg kg^{-1}, respectivamente, caracterizando a área como Classe 4 (nível muito elevado de poluição), conforme classificação proposta por Klumpp et al. (2004). A caracterização química e morfológica das partículas coletadas revelou a presença de fuligem (Cr, Fe, Ni, Zn, Cd, Hg e Pb), materiais biológicos, cristais salinos (KCl) e partículas ressuspensas de poeira do solo (Al e Si). Estudos integrados empregando variáveis ambientais como o MP e o biomonitoramento com azevém podem auxiliar na elaboração de diagnósticos ambientais robustos, além de fornecer informações para o desenvolvimento de medidas de precaução que considerem a capacidade de suporte do meio ambiente e que visem à minimização dos efeitos prejudiciais da poluição atmosférica.

Palavras-chave: poluição atmosférica, material particulado, biomonitoramento, *lolium multiflorum*, mev/eds.

1. Introduction

The Sinos River Basin (SRB) is often the subject of reports in the mass media and in scientific researches (Spilki and Tundisi, 2010; Blume et al., 2010; Costa and Schulz, 2010) because of environmental degradation scenarios in which it is inserted, mostly related to the low levels of water quality (Blume et al., 2010), mainly in the lower section of the basin, where the Schmidt Stream is found. This situation is alarming, since the Sinos River is the main source of public water supply in the region. Among the main factors causing the degradation of this area are the processes of urbanization and industrialization, which are responsible for the Sinos River to be listed as one of the most polluted in Brazil (Spilki and Tundisi, 2010).

Integrated assessment of degraded areas has become a widely-used tool capable of providing the systemic overview of environmental conditions which are indispensable to the decision-making processes involved in promoting recovery of degraded environments or preservation of environments that have not yet suffered significant environmental impacts. In such scenarios, air quality assessments are being conducted using both conventional and complementary techniques, such as bioindicators or bioaccumulators, which make it possible to conduct detailed assessments of environmental quality (Klumpp et al., 1994; Guimarães et al., 2000; Costa and Droste, 2012).

The effects of air pollution over the health of living beings can be observed in short, medium and long term and are related to the exposure time, chemical composition and concentration of the pollutant. The symptoms reported on the health of humans range from breathing problems, reduction on the transport of gases between blood and lungs, headaches, nausea, cancer, coma and even death (Goto, 2007; Alcalá et al., 2008; Gomes, 2010).

Particulate Matter (PM) is one of the most strinking elements of atmospheric pollution. The term particulate matter is used generically to refer to air pollution caused by aerosols in urban and non-urban environments and can be defined as a complex mixture of solid and liquid particles in suspension, with composition and aerodynamic diameter related to its emission sources (Seinfeld and Pandis, 2006; Kampa and Castanas, 2008). The majority of environmental studies investigating PM analyze its inhalable fraction (particles with aerodynamic diameters smaller than 10 μm – PM_{10}). This fraction can be further subdivided into coarse ($PM_{2.5-10}$) and the fine fractions ($PM_{2.5}$). Many researchers have undertaken studies of PM designed to identify its chemical composition (Espinosa et al., 2001; Allen et al., 2001; Dallarosa et al., 2008; Hieu and Lee, 2010; Wimolwattanapun et al., 2011) and its morphological properties (Micic et al., 2003; Liu et al., 2005; Adamo et al., 2008; Witt, et al., 2010; Rosasco et al., 2011; Chithra and Shiva Nagendra, 2013). Such researches have being made to understand the behavior of these pollutants and their relationships with meteorological conditions and also their links with harmful impacts to health, such as respiratory and cardiovascular diseases (Schwartz et al., 1996; Borja-Arbuto et al., 1998; Neas et al., 1999; Laden et al., 2006; Bourotte et al., 2007; Lepeule et al., 2012).

Conventional systems for atmospheric monitoring very often demand considerable expenditure on implementation, operation and maintenance. In addition, to conventional monitoring, biomonitoring is a complementary methodology that is effective for assessing chemical elements at low environmental concentrations, which are not always covered in the parameters defined by legislation. Biomonitoring is a method in which the presence of pollutants in a given area is demonstrated using living organisms that respond to stresses to which they are exposed by modifying their lifecycles or by accumulating pollutants (Buss et al., 2003). The technique, therefore, provides important supplementary information, since by using bioindicators it is possible to detect the effects of atmospheric pollutants on living organisms and the responses exhibited by those organisms (Junek, 2009). Plant bioindicators can be used to evaluate the impacts of atmospheric pollution by physiological, biochemical and morphological responses or by quantifying accumulation of specific substances (Klumpp et al., 2004; Migliavacca, 2009). The effects observed on plants cannot be directly extrapolated to human populations, but the results of those experiments are of relevance, once the organisms are highly sensitive, even at low contamination levels. Therefore, it is an acceptable hypothesis that if a toxic substance causes detectable damage to a plant species, it may possibly have effects on another species (Guimarães et al., 2000).

This research aimed to evaluate the air quality, by determining the concentrations of $PM_{2.5-10}$, $PM_{2.5}$ and the metallic elements Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn and Hg in the leaf part of ryegrass (*Lolium multiflorum*) in an area close to Schmidt Stream, in the lower section of SRB, in a research campaign of six months (October 2013 to March 2014). The particles collected in the PM sampling were analyzed by Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray Spectrometry (EDS), in order to study their morphology and chemical composition.

2. Material and Methods

2.1. Study area

The SRB is located in the Northeast of Brazil's southernmost state, Rio Grande do Sul, between the 29th and 30th parallels South, covering an area of 3,820 km^2, which corresponds to 1.5% of the total area of Rio Grande do Sul state. It has a population of approximately 975,000 inhabitants, 91% of whom live in urban areas, with 9% of the population in rural zones. The SRB belongs to the phytogeographic region classified as Semideciduous Seasonal Forest, which nowadays only exists on the slopes of the Serra Geral. The climate is subtropical, with four well-defined seasons (Costa and Schulz, 2010). The region is located in a lithological area characterized by the Botucatu Formation and by basaltic formations in the hillsides (Streck et al., 2008). It is bordered to the East by the Serra Geral, to

the West and the North by the Caí basin and to the South by the Gravataí basin and can be subdivided into upper, middle and lower sections (FEPAM, 2009).

Campo Bom is a town located in the lower section of the Sinos River Basin. The basin is densely urbanized and has a high concentration of industries, therefore, is impacted by water withdrawal for domestic and industrial uses, by domestic and industrial sewage, and by extremely high volumes of domestic garbage (FEPAM, 2009).

The main watercourse in Campo Bom is Schmidt Stream, located at 29°39'15.11"S 51° 04'37.37" W and 29° 41'29.78" S 51°02'41.06" W with an extension of approximately 7 km. Along its course, this creek is responsible for irrigating several areas (a residential area and a mixed residential, commercial and industrial zone) before reaching the Sinos River.

Previous studies (Benvenuti et al., 2013) have shown that the characteristic riparian vegetation is only properly preserved near the Schmidt Stream's headsprings, although physical, chemical, microbiological and visual analysis have found organic contamination, low concentrations of dissolved oxygen, strong odor, solid waste on the banks, sites with foaming, and high concentration of total and thermotolerant coliforms throughout the length of the creek. The organic matter content originates from the semi-deciduous vegetation and many other natural and anthropic sources. Locals report signs of contamination of the Schmidt Stream by industrial and domestic sewage, which may increase the concentrations of organic load and many other pollutants in the watercourse.

The sampling point is located approximately 0.25 km from the RS 010 highway (an important access route to the town of Campo Bom), 1 km from the Schmidt Stream and 1.3 km from the Sinos River, in a semi-urban area, with the following geographical coordinates: –29° 40'39.48"S and –51° 2'25.43"W (Figure 1).

2.2. PM sampling procedures

The PM collections were conducted according to the protocol for atmospheric PM sampling published by Brazil's National Institute for Space Research (INPE, 2012). Samples were collected monthly for 24-hour periods from October 2013 to March 2014, totaling 6 months of sampling. The device used to sample $PM_{2.5\text{-}10}$ and $PM_{2.5}$was similar to the Gent sampler (Maenhaut et al., 1993), which consists of a set of two sequential filters and a support, connected to a vacuum pump with a flow rate of 16 to18 L min^{-1}. The top filter is responsible for collecting the $PM_{2.5\text{-}10}$ and the bottom filter is responsible for collecting the $PM_{2.5}$. The pump flow rate was measured at the start and end of

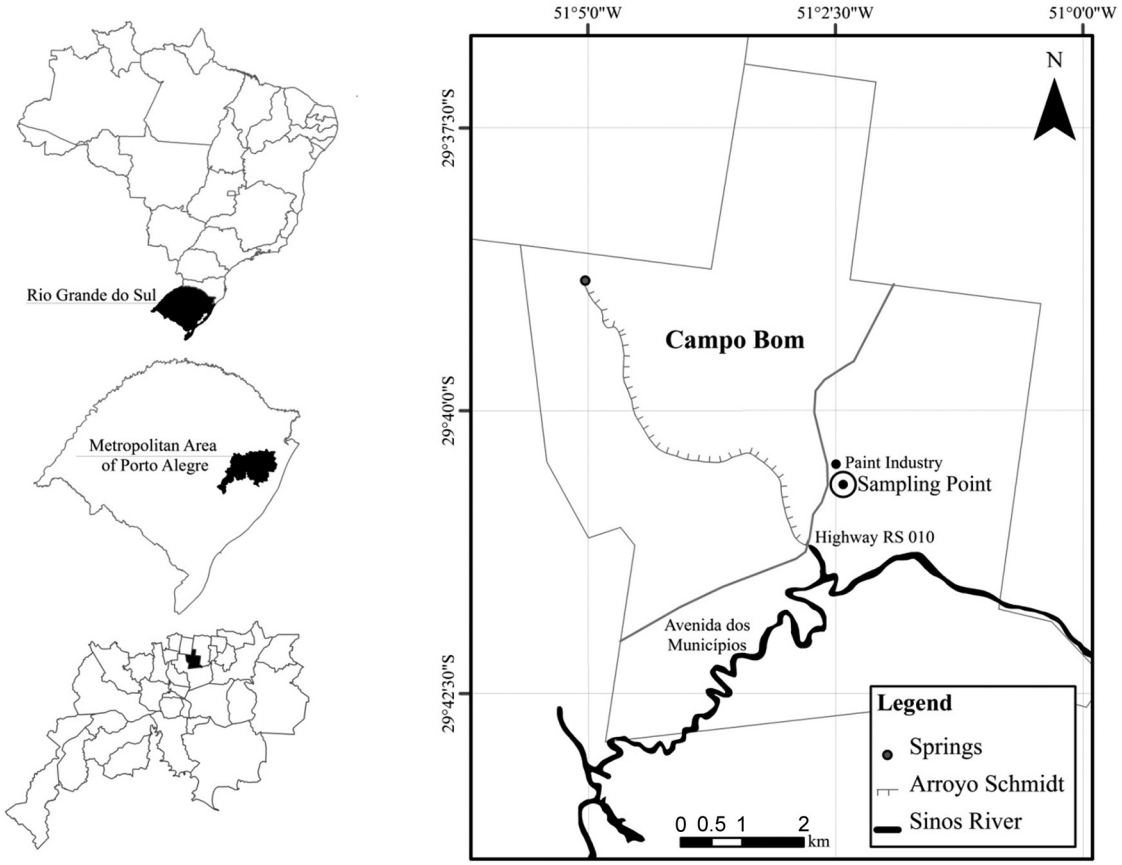

Figure 1. Map of Brazil, Rio Grande do Sul and the SRB and a large scale map showing the sampling point.

each sampling period using a rotameter (4T, Omel) and taking the mean of the two measurements for calculations.

Polycarbonate filters (Millipore®, Isopore Membrane Filter) with 10 µm and 2 µm pore size were used for the collection of $PM_{2.5-10}$ and $PM_{2.5}$, respectively (Liu et al., 2005), both with 47 mm diameter. Polycarbonate filters have a smooth surface with a vitreous appearance, making them ideal for analysis of atmospheric pollutants using electronic microscopy.

2.2.1. Gravimetric analysis

The mass of $PM_{2.5-10}$ and $PM_{2.5}$ was determined by gravimetric analysis. Filters were weighed before and after sampling to obtain the mass of PM collected and then these results were divided by the total volume of air sampled, to obtain the mass concentration of PM in µg m^{-3}. All the filters used for sampling were stored in a desiccators for a minimum of 72 hours in a controlled environment (25 ± 5 °C and relative humidity de 30 – 40%) before weighing (Wimolwattanapun et al., 2011).

2.3. Biomonitoring

2.3.1. Cultivation and exposure

Lolium multiflorum (ryegrass) was cultivated in plastic pots containing standard Carolina Soil substrate. The bottom of each pot was perforated to allow three pieces of string to be inserted, which were left in contact with water in order to ensure that the substrate was humid and the grass hydrated. Approximately 0.3 g of *Lolium multiflorum* seed were sown into 300 g of substrate. After a 2-week growing period, the pots containing *Lolium multiflorum* were exposed, in triplicate, in a structure 1.5 m above ground level in a 5 L plastic box. An expanded polystyrene board designed to fit the pots of ryegrass was fitted into the top of the box. The box was filled with potable water and a plastic pot was placed in the expanded polystyrene board with the strings hanging into the water.

After thirty days, the pots containing the ryegrass were collected and replaced by other ones, which were exposed for the same length of time. The leaf part of the plants was analyzed after collection.

2.3.2. Preparation of samples of bioindicator and standard substrate

The ryegrass leaves were washed with ultrapure water with resistivity of 18 MΩ cm^{-1} (Purelab Classic, ELGA), placed into paper bags and dried in a circulation chamber (MA035, MARCONI) for 72 hours at 70 °C. They were then ground in a porcelain mortar using a pestle. Portions of around 0.25 g of the samples were weighed out in duplicate and then digested in a micro-wave digester (MARS 6, CEM) with 5 mL of nitric acid and 2 mL of water for 10 minutes at 200 °C. The extracts obtained were volumized in 25 mL volumetric flasks and the concentrations of Al, Ba, Cd, Cu, Pb, Cr, Fe, Mn, Ni and Zn were determined in triplicate by flame atomic absorption spectrophotometry (SpectrAA 110, VARIAN), while Hg was assayed using a fluorescence technique (Mercur, Analytik Jena).

The same metals assayed in the ryegrass leaves were also measured in the substrate used to grow the ryegrass, in both pseudo-total and bioavailable forms, in order to demonstrate that the concentrations of metals observed were the result of deposition on leaves (primary route of entry) and not of absorption through the roots (secondary route of entry).

2.4. Morphological analysis of particles and identification of principal elements by SEM/EDS

Morphological analysis of particles were conducted as follow: approximately ¼ of each filter was removed with a scalpel and fixed to a support with double-sided carbon tape and then the samples were gold coated in a sputter coater (Desk V, Denton Vaccum). The particles collected were analyzed by Scanning Electron Microscopy – SEM (JSM-6510LV, JEOL) to obtain the images and Energy Dispersive X-ray Spectroscopy – EDS (Ultra Dray, Thermo Scientific) to identify the major elements present in the samples (Micic et al., 2003; Liu et al., 2005; Adamo et al., 2008; Witt et al., 2010; Rosasco et al., 2011; Chithra and Shiva Nagendra, 2013). All the images were acquired from the samples using a heated tungsten filament as electron source, with an acceleration potential in the range of 10 kV, with resolutions varying from 3,000 to 15,000 times magnification. The EDS analysis were conducted in order to obtain the chemical composition and element mapping of the particles. The identification of the samples was conducted with reference to the atlas of tropospheric aerosols published by Micic et al. (2003).

2.5. Meteorological data

Meteorological data of temperature, relative air humidity and rainfall were provided by the Brazilian meteorology service (INMET - *Instituto Nacional de Meteorologia*), responsible for the 8th meteorology district of Porto Alegre. The rainfall variable was ignored for PM analysis because all samples were collected on sunny days, in order to assess air quality under the most severe conditions. For biomonitoring analysis, rainfall during exposures was taken into consideration because the rain can wash away atmospheric pollutants, changing the concentrations of certain elements in the air (Klumpp et al., 2004; Migliavacca, 2009).

Table 1 shows prevailing climatic conditions of air temperature, relative humidity and the wind speed during PM sampling collection. Mean air temperature was 23.8 °C and mean relative humidity was 72.3%. The mean wind speed was 2.2 m s^{-1}.

3. Results

3.1. Particulate matter

Figure 2 shows the concentration of $PM_{2.5-10}$, $PM_{2.5}$ and the cut line standard for $PM_{2.5}$ (24 hours = 35 µg m^{-3}), in accordance with the United States Environmental Protection Agency (EPA) (EPA, 2014). Throughout the fieldwork period, $PM_{2.5-10}$ concentration was greater than or equal to $PM_{2.5}$ concentration. $PM_{2.5-10}$ mean concentration was

Table 1. Meteorological conditions during PM sampling collection.

Sample	Collection dates	Temperature of air (°C)	Relative humidity (%)	Mean wind velocity (m s^{-1})
I	2013/10/15	19.9	73.0	1.6
II	2013/11/24	24.2	66.9	1.7
III	2013/12/20	24.6	73.6	2.6
IV	2014/01/27	29.7	67.0	1.3
V	2014/02/28	21.2	77.4	1.7
VI	2014/03/26	23.2	75.9	2.2

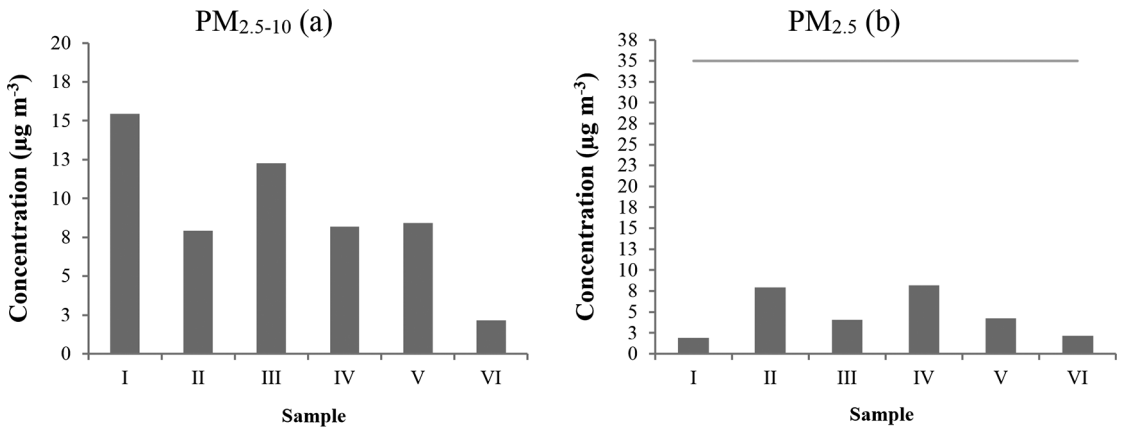

Figure 2. Concentration of $PM_{2.5-10}$ (a), $PM_{2.5}$ and the cut line standard for $PM_{2.5}$ (b).

9.1 µg m^{-3}, ranging from 2.2 µg m^{-3} to 15.4 µg m^{-3}, with a standard deviation of 4.5 µg m^{-3}. The highest $PM_{2.5-10}$ concentration occurred during sample I, coinciding with the lowest temperature during the entire research (19.9 °C). $PM_{2.5}$ mean concentration was 4.7 µg m^{-3}, ranging from 1.9 µg m^{-3} to 8.2 µg m^{-3}, with a standard deviation of 2.7 µg m^{-3}. $PM_{2.5}$ highest concentration occurred during sample II, reaching 7.9 µg m^{-3}. All concentrations of $PM_{2.5}$ were below the cutoffs set out in the EPA air quality standards.

3.2. Biomonitoring

Table 2 lists the period of exposure of the ryegrass with its respective rainfall data. Mean rainfall during ryegrass exposure (199.8 mm) remained within the normal historical limits of Campo Bom, according to INMET (2014). The period with greatest intensity of rain was during exposure II, while the lowest rainfall period was recorded during exposure III.

Table 3 lists the arithmetic mean (n=3), maximum and minimum metal concentrations in the leaves of *Lolium multiflorum*. Metals with the highest mean concentrations were Al, Fe, Mn, and Ba, with results above 100 mg kg^{-1}, calculated on a dry basis.

Table 4 lists the mean concentrations of the metals analyzed, compared to a classification into pollution categories proposed by Klumpp et al. (2004). The reference values used to construct the classification table were obtained from samples collected in several different European cities during monitoring conducted in 2000 and 2001.

Table 2. Ryegrass exposure periods and mean rainfall (mm).

Biomonitoring		
Exposure	**Dates**	**Rainfall (mm)**
I	2013/10/02 to 2013/11/01	153.8
II	2013/11/01 to 2013/12/01	336.2
III	2013/12/17 to 2014/01/16	107.8
IV	2014/01/16 to 2014/02/14	203.4
V	2014/02/14 to 2014/03/17	220.0
VI	2014/03/17 to 2014/04/15	177.6

3.3. SEM/EDS

The analysis of PM collection filters by SEM/EDS (Figure 3) showed the presence of particles of biological origin, soot particles, particles with cubic shape, characteristic of salts, and particles characteristic of soil resuspension and of possible anthropic sources of emissions. A total of 59 particles were analyzed using SEM/EDS, 30 of $PM_{2.5-10}$ and 29 of $PM_{2.5}$. The EDS analysis revealed the presence of the researched metals in many of the particles analyzed.

4. Discussion

4.1. Particulate matter

It was observed that there was no relationship between PM concentration and meteorological data during the studied period. As shown in Figure 3, the concentrations

Table 3. Concentration* of metals in the leaves of *Lolium multiflorum*.

Metal	Exposure						X (max-min)
	I	II	III	IV	V	VI	
Al	489.19	259.29	772.60	421.34	233.43	401.71	429.59 (233.43-772.60)
Ba	104.15	57.99	76.62	98.27	136.76	150.79	104.10 (57.99-150.79)
Cd	0.06	0.06	0.05	0.05	0.04	0.04	0.05 (0.04-0.06)
Cr	2.50	6.55	2.12	13.77	2.82	3.81	5.26 (2.12-13.77)
Cu	6.13	4.44	16.29	20.69	16.35	22.65	14.42 (4.44-22.65)
Fe	298.72	153.30	103.47	381.15	186.10	194.23	219.49 (103.47-381.15)
Mn	147.86	75.12	203.41	263.74	201.63	208.70	183.41 (75.12-263.74)
Ni	3.99	3.03	2.93	7.34	8.91	12.41	6.43 (2.93-12.41)
Pb	15.99	5.94	12.67	8.28	16.28	22.30	13.58 (5.94-22.30)
Zn	77.66	56.90	97.10	135.55	87.07	78.52	88.80 (56.90-135.55)
Hg	74.94	72.40	73.90	21.64	62.99	38.18	57.34 (21.64-74.94)

*The concentrations were expressed in mg kg^{-1} (dry basis), except for Hg, which is expressed in µg kg^{-1} (dry basis).

Table 4. Mean concentrations of the metals (µg g^{-1}, dry basis) and the pollution categories proposed by Klumpp et al. (2004).

Class / Sample	Metal						
	Cd	Pb	Cr	Ni	Cu	Zn	Fe
Class 1 - Very Low	≤ 0.04	≤ 0.8	≤ 0.8	≤ 5.5	≤ 7.1	≤ 31.7	≤ 180
Class 2 - Low	0.05-0.07	0.9-1.6	0.9-1.5	5.6-9.3	7.2-11.6	31.8-45.1	181-309
Class 3 - High	0.08-0.10	1.7-2.4	1.6-2.3	9.4-13.1	11.7-16	45.2-58.6	310-438
Class 4 - Very high	> 0.10	> 2.4	> 2.3	> 13.1	> 16.0	> 58.6	> 438
Campo Bom, RS, Brazil	**0.05**	**13.58**	**5.26**	**6.43**	**14.42**	**88.80**	**219.49**

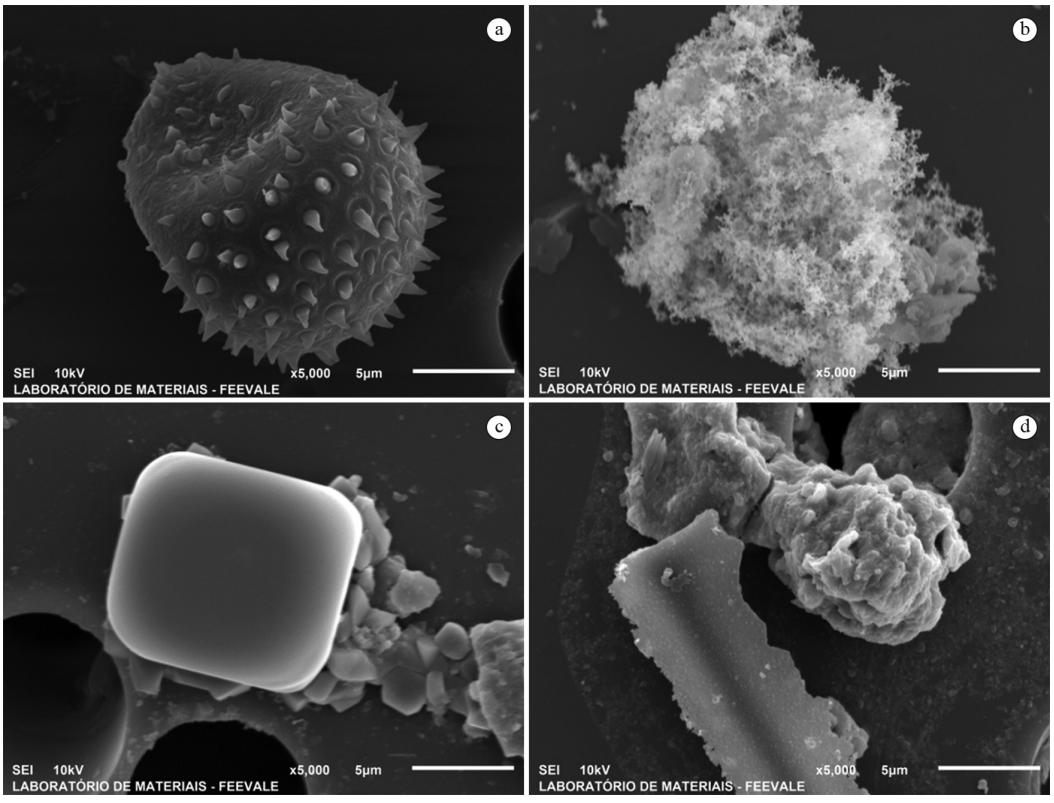

Figure 3. Particle of biological origin, identified in the $PM_{2.5-10}$ of sample III (a), soot particle, identified in the $PM_{2.5-10}$ of sample III (b), cubic-shaped particle, identified in the $PM_{2.5-10}$ of sample I (d) and particle characteristic of soil resuspension (above) and particle possibly originated from anthropic sources (bellow), both identified in the$PM_{2.5-10}$ of sample I (d).

of $PM_{2.5-10}$ exhibited a trend, with results that were greater than or equal to the concentrations of $PM_{2.5}$ and peaks in samples I and III, with 15.4 μg m^{-3} and 12.3 μg m^{-3}, respectively. The type of particles that comprise $PM_{2.5-10}$ normally enter the atmosphere by resuspension of soil and from natural sources (fragments of biological origin), as has been demonstrated by Wimolwattanapun et al. (2011). High concentrations of $PM_{2.5-10}$ are compatible with the study area, since the presence of particles with aerodynamic diameter greater than 2.5 μm is more common in semi-urban locations (Micic et al., 2003; Rosasco, et al., 2011).

In Brazil, the national environmental regulator's (CONAMA - Conselho Nacional de Meio Ambiente) ruling on air quality parameters and standards (CONAMA Resolution 03/90) does not specify measurement of $PM_{2.5-10}$ or $PM_{2.5}$, but just the PM_{10}, which is identified in the regulation as Inhalable Particles (IP), and therefore it is not possible to compare the results of this research with the standard defined in Brazilian legislation (Brasil, 1990).

In view of this, $PM_{2.5}$ results were compared with international air quality standards (EPA standard). The results observed in this research do not exceed the limit laid down in EPA standard, which is 35 μg m^{-3}. It is important to assess both $PM_{2.5-10}$ and $PM_{2.5}$, since the $PM_{2.5}$ is primarily produced by anthropic sources, such as industrial and vehicular emissions (burning of fuels). Additionally, it is in $PM_{2.5}$ that heavy metals such as Cd, Cr, Cu, Mn, Ni, and Pb and other toxic substances are generally concentrated, which exacerbates further still the potential risks of this fraction of airborne particles (Allen et al., 2001; Espinosa et al., 2001; Hieu and Lee, 2010; Teixeira et al., 2011).

4.2. Biomonitoring

With the exceptions of Al, Cr, Fe, Ni and Hg, it was observed that the concentrations of the metals measured in ryegrass leaves were lower for exposure II. The large volume of rainfall recorded during exposure II was the main contributing factor in reducing the concentrations of metals during this exposure, since rain can remove pollutants from the air (Seinfeld and Pandis, 2006; Gomes, 2010). The exception to this trend observed for Cr is related to the fact that this element is normally associated with the fine fraction of PM and can be absorbed more easily by the plant, even in the presence of rain. Furthermore, Cr and Fe concentrations could also be affected by their greater solubility for plants in aqueous medium (Migliavacca, 2009). Exposure III had the lowest observed rainfall and the greatest concentration of Al, which is an element normally associated with the coarse PM fraction and one that has lower mobility. The higher concentration of Al may be related to its lower mobility, which results in particles remaining deposited on the ryegrass leaf surface, enabling greater absorption.

Comparing the mean concentrations of the metals analyzed, Ba had the fourth highest concentration, exceeded only by Al, Fe and Mn. This finding may be related to the existence of an electrostatic paint business located close to the sample point and/or pollution from automotive vehicles. Electrostatic painting employs powdered paint that can contain loads that are added with the pigments. Baryte (barium ore) is one of the most common loads employed (Camargo, 2002). Ba is also used in the form of barium salts in brake lines. In areas exposed to vehicle traffic, it is likely that brake dust is the primary source of Ba in the atmosphere. Gietl et al. (2010) have suggested the use of Ba as a quantitative marker of brake dust in urban areas, since there are similarities between the particle size distribution of PM from highways and background concentrations in urban areas.

Mn had the third highest concentration of the metals analyzed and is used in gasoline/petrol as a lead substitute, in the form of the organic compound methylcyclopentadienyl manganese tricarbonyl, as an octane-boosting additive (Nogueira, 2006; Kabata-Pendias, 2011).

The concentration of Hg in ryegrass leaves was similar over the six exposures, with the exceptions of exposures IV and VI. Hg can be found in fluorescent lamps, hospital waste and fossil fuels and burning of these fuels has been identified as the principal anthropic source of Hg in the atmosphere (Cooper and Alley, 2002; Manahan, 2005; Migliavacca, 2009; Moreira, 2010).

When the concentrations of Cd, Pb, Cr, Ni, Cu, Zn and Fe were classified according to the pollution categories proposed by Klumpp et al. (2004), it was observed that Cd, Ni and Fe were at Class 2 – Low pollution level. Cd is used in the manufacture of tires and the friction of the rubber in the traffic can be one of the causes of the presence of this element in the atmosphere (Manahan, 2005; Moreira, 2010). Ni is a component used in nickel-cadmium batteries and both elements can enter the environment as a result of its incorrect disposal. Additionally, Ni can be emitted during burning of coal and petroleum-based products (Manahan, 2005; Nogueira, 2006; Kabata-Pendias, 2011). Fe occurs naturally in the environment and is present in the soil, from where it can be resuspended. Additionally, this element is present in many metal alloys and can be emitted into the air when these are abraded (Manahan, 2005; Migliavacca, 2009; Kabata-Pendias, 2011).

Cu concentration was in Class 3 – High pollution. Atmospheric Cu can come from brake wear and use of copper parts in automotive vehicles (Manahan, 2005; Nogueira, 2006; Kabata-Pendias, 2011).

Concentrations of Pb, Cr and Zn were at the Class 4 – Very High pollution level. For many years Pb was used as an additional additive to gasoline/petrol, to increase its octane rating, and was released into the atmosphere as fuel was burnt. Despite the fact that adding lead to fuel was banned in the 1990s, Pb that is still present in the atmosphere may still be related to residual levels of the metal (Migliavacca, 2009). Furthermore, Pb is still part of the chemical composition of fuels and is used in recycled tires and automotive batteries (Manahan, 2005; Moreira, 2010). The primary uses of Cr are related to industrial activities (metal working, steel making, chemical factories and the leather industry), in applications such as making

stainless steel, paint pigments, varnishes and paper and for curing hides for leather. Cr can be found in the atmosphere in the form of trivalent chrome (Cr^{+3}) and hexavalente chrome (Cr^{+6}). These two species differ considerably in terms of toxicity and behavior in the environment, and Cr^{+6} is considered the more toxic of the two ones (USDHHS, 2012). Zn is used in lubricating oils for automotive vehicles and in the manufacture of tires and can be released into the atmosphere as tire rubber is abraded by road surfaces (Manahan, 2005; Nogueira, 2006; Kabata-Pendias, 2011).

Comparing the results of the biomonitoring with the occurrence of metals detected in samples of water collected from the headspring of the Schmidt Stream between July and September of 2012 (Kieling-Rubio et al., 2015), it was observed that concentrations of Cd, Pb, Cu, Mn and Ni were all within the permissible limits for Class I fresh water, according to CONAMA resolution 357/2005 (Brasil, 2005), and only Fe, which is a known component of the soils in this region, was beyond the limit, while Cr, reported as Total Cr, was not detected in the samples tested. These contrasting observations confirm the different behavior of these metals in the environment, in terms of distribution.

4.3. Analysis by SEM/EDS

The chemical and morphological characteristics of particles detected in PM were identified using SEM/EDS analysis, as a mean of assessing integration of PM data and quantification of metals in ryegrass. This analysis revealed that particles of natural origin were also present (Figure 3a). Despite the lack of quantitative representation, in epidemiological terms such particles play an important role because they are responsible for allergies (Micic et al., 2003).

Figure 3b shows a cluster of fine soot particles with the metals Na, Mg, Al, Cr, Mn, Fe, Ni, Zn, Cd, Hg and Pb all present in its composition. This type of particle originates from burning fuel at high pressures and temperatures in internal combustion engines (Micic et al., 2003; Rosasco, et al., 2011; Chithra and Shiva Nagendra, 2013). The presence of these particles can be linked to the sampling point's proximity to major roads such as the *Avenida dos Municípios* and the RS 010 highway. Figure 3c shows a salt crystal mainly composed of the elements Cl and K. The presence of K can be attributed burning of biomass, in the form of agricultural waste, in addition to its natural occurrence in the earth's crust (Chow et al., 2007; Begum et al., 2007). Figure 3d (above) shows a typical particle of natural origin (soil resuspension), presenting predominantly Al and Si in its composition. The composition of the particle shown in Figure 3d (bellow) includes Na, Al, Mn, Fe, Ni, Zn, Hg and Pb, with emphasis on the metals Ni, Zn, Hg and Pb, because their presence is suggestive of anthropic sources (Espinosa et al., 2001; Hieu and Lee, 2010).

5. Conclusion

$PM_{2.5}$ concentration (24 hours) was below the limit set out in EPA standard. When dealing with air quality standards, Brazilian legislation does not mandate monitoring $PM_{2.5}$, in contrast with standards such as those from the United States, which cover monitoring of $PM_{2.5}$. The legislation also fails not requiring chemical analysis of PM thrown up into the atmosphere, which can constitute an important source of pollution.

It was found that the concentrations of certain metallic elements in ryegrass leaves were influenced by the volume of rainfall during the period of exposure. This is because rain interferes on metals' bioavailability characteristics and can also change the concentrations of PM in the atmosphere, since rain can trap the particles.

The concentrations of metallic elements detected in the ryegrass leaves, especially Pb, Cr and Zn, indicate a very high degree of pollution (Class 4), according to the classification proposed by Klumpp et al. (2004).

Chemical and morphological analysis of particles of $PM_{2.5-10}$ and $PM_{2.5}$ and identification of their sources of emission (natural or anthropic) are prerequisites for the construction of wide-ranging environmental diagnoses and provide the information needed for development of precautionary measures to reduce the effects of pollution that take into consideration both the environment's supportive capacity and environmental quality.

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