CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES IN URBAN AREAS OF RIO GRANDE DO SUL, BRAZIL – PRELIMINARY STUDY

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ABSTRACT

This work reports the determination of the concentration and chemical composition of atmospheric particles in the urban districts of Charqueadas and Sapucaia do Sul, State of Rio Grande do Sul, Brazil. Chemical composition, morphology and particle size were analyzed using a scanning electron microscope with energy dispersive x-ray microanalysis (SEM-EDS). Cluster analysis showed that there were six types of particles: Fe-Zn, Fe, Si-Al, Si, Ca-S and Na. Factorial analysis from cluster data showed that particles rich in Fe-Zn, Si-Al and Ca-S appeared more frequently, indicating anthropogenic influence (vehicles, steel plant, coal fired power station). The experimental results and consideration of the wind directions show that the main source of pollution in Charqueadas appears to be due to coal mining and steel industries, while in Sapucaia do Sul due to steel plants and vehicles.

RESUMO

Este trabalho trata da determinação da concentração e composição química de partículas atmosféricas nos distritos urbanos de Charqueadas e Sapucaia do Sul, Estado do Rio Grande do Sul, Brasil. A composição química, morfologia e tamanho das partículas foram analisados usando um microscópio eletrônico de varredura acoplado com microanálise com energia dispersiva de raios-x (MEV-MED). Análise de enxames mostrou a existência de seis tipos de partículas: Fe-Zn, Fe, Si-Al, Si, Ca-S e Na. Análise fatorial indicou que partículas ricas em Fe-Zn, Si-Al e Ca-S eram mais frequentes, indicando influência antropogênica (veículos, indústria siderúrgica e usina termoeletrica). Análise dos resultados experimentais, junto com a consideração da direção dos ventos indica que as fontes principais de poluição em Charqueadas são a mineração do carvão e a indústria do aço, enquanto em Sapucaia do Sul são as siderúrgicas e o transito de veículos.

INTRODUCTION

Anthropogenic sources may discharge fine particles of heterogeneous chemical composition into the atmosphere. These particles can cause a severe impact on human health due to the presence of organic and inorganic pollutants that may be deposited in the human respiratory system.

The type of particles present in the atmosphere originating from stationary emissions and mobile sources varies from country to country. These particles present heterogeneous characteristics, the larger ones usually originating from soil and the finer ones from emissions of anthropogenic sources.

Particulate concentration, regulated in most countries by environmental legislation is a pollution indicator but it does not specify chemical composition. Knowledge of the chemical composition of aerosols allows in many cases the identification of the source of pollution that may be anthropogenic. Many studies have been done in the past that identified chemicals species in atmospheric particles in urban and non-urban areas.¹

The many techniques used to determine particle composition however failed to determine the speciation and distribution of elements in the aerosols.

Scanning electron microscopy with energy-dispersive x-ray microanalysis (SEM-SED) and particle induced x-ray emission (PIXE) have been used for particle characterization.²⁻⁶ The results of these studies have permitted the determination of the size and type of particles as well as the relation of these characteristics to anthropogenic sources.

In Southern Brazil, particulate matter has been an issue of concern, specially due to the low efficiency of emission control systems for fine particles. The activity of coal processing and steel plants has been responsible for alterations in the air quality in some areas of the State of Rio Grande do Sul. In particular, the counties of Charqueadas and Sapucaia do Sul, located in the Baixo Jacuí Region, have shown problems with particulate contamination.^{7,8} In both counties there are anthropogenic sources with emissions that have produced alterations in the air quality (steel industry and coal-fired power station). In Sapucaia do Sul, the main source of atmospheric pollutants is the Riograndense Steel Plant but heavy vehicular traffic was also verified at the place where the sampling was done.

The main purpose of this work is to study the chemical composition of the atmospheric particles in Charqueadas and Sapucaia do Sul, associate these data with the size of the particles and wind direction and identify and confirm the anthropogenic sources.

STUDY AREA

The area studied included the districts of Charqueadas (Figure 1a) and Sapucaia do Sul (Figure 1b) in the State of Rio Grande do Sul, Brazil. Both districts, as mentioned above present several economic activities that lead to significant emissions of particulate matter in the atmosphere. The sampling points were established with the aid of a GPS and the coordinates were as follows for Charqueadas (29°57'12,8"S and 51°37'21,4"W), west of the steel plant and southeast from the power plant. In this area there are mineral coal reserves and a coal mine, power plant and steel plant, all in operation. For Sapucaia do Sul the coordinates were 29°49'11,4"S and 51°09'39,0"W. The sampling site is situated 1km east of the main highway BR-116 and 1,7km northwest of the steel plant. The economic activity in this area includes metallurgy,

leather and other industries. The general area studied has subtropical humid climate (Cfa type) with average temperatures between -3°C and 18°C for the coldest month and above 22°C for the hottest month. The total precipitation is superior to 1200mm and is well distributed through the year.

Figure 1a. Map Illustrating Sampling Site in Charqueadas, RS, Brasil

Figure 1b. Map Illustrating Sampling Site in Sapucaia do Sul, RS, Brasil

EXPERIMENTAL PROCEDURE**Sampling**

High Volume Samplers (Hi Vol type) were used to collect atmospheric particles <100µm. The sampler consisted of a filter bearer that aspirated air through a filter with a flow varying between 1,13 and 1,70m³/min for 24 hours.⁹ The samples were collected using 0,4µm pore size polycarbonate membrane filters.¹⁻¹⁰ Eight samples were collected at each site leading to a total of sixteen (16) for the period from May 1997 to May 1998.

Analysis of samples using a scanning electron microscope equipped with energy dispersive x-ray microanalysis

The samples were analyzed with a LEO 440 Scanning Electron Microscope (SEM) with an energy dispersive x-ray detector (EDX) and an Inquant image analyzer at the Center of Mineral Technology (CETEM) in Rio de Janeiro. The specifications for EDS (energy dispersion spectroscopy) were as follows: Link ISIS L300 SiLi Pentafet detector, ATW ultrafine window with resolution of 133 eV for 5,0keV with ZAF correction, focal distance of 25mm, approximately 4000 counts for 5 seconds with a Co analytic window.

The procedure for the obtention of the EDS analysis consisted basically of the image of the retro-dispersed electrons (BSD), processing of the image for the individuality of the grains, EDs analysis of each one of the identified grains and storage of the results.

The quantification of the elements from the spectra took into consideration ZAF corrections (atomic number and mass fluorescence) and used the program SEMQUANT, Oxford ISIS 3. The elements analyzed were the following: Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn and Pb. The perimeter of the particles was defined and the average diameter was calculated. It is important to observe that the particle diameter used was obtained from microscopy and is not an average aerodynamic diameter.

Statistical analysis

The statistical treatment was carried out with a computer using the software Statistics for Windows 4.3TM and SPSS for Windows, first for Cluster Analysis followed by Factorial Analysis using the Principal Components Method.

Cluster analysis using the K method is not hierarchic and consists of grouping cases with similar profiles and a series of definite features. In the present study three stages were used for the grouping of elementary composition in the atmospheric particles: identification of the type of particles present in the aerosols (each type of particle was represented by a group – cluster), reduction of the volume of data without a significant loss of the data set and exclusion of particles that presented maximum seed points, not exceeding 10% of the data set. Only particles with diameter <10 were considered for cluster analysis. This corresponded to a total of 5057 particles from Charqueadas and 4913 particles from Sapucaia do Sul.

This analysis was applied to the elements Al, Si, S, K, Ca, Mn, Fe and Zn. Magnesium was excluded due to the maximum distance of the seed points. Factorial analysis through the principal component method was applied for Si, Al, Fe, Zn, Ca, S and Na.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the general characteristics of the samples obtained in Charqueadas and Sapucaia do Sul, respectively. Properties such as average particle concentration, wind direction, wind speed, number of particles and average diameter.

Table 1. Genertal Characteristics of the Samples Collected in Charqueadas.

Filer	Sample date	Season date	Wind direction	Wind speed (m/s)	Average concentration ($\mu\text{g.m}^{-3}$)	Particle number	Average diameter (μm)
1	11/06/97	winter	NW	0,24	112	570	2,46
2	14/07/97	winter	SE	0,61	148	569	3,06
3	16/09/97	winter	NW	0,88	103	599	2,46
4	03/10/97	spring	SE	3,68	303	809	1,66
5	03/03/98	summer	NW	0,58	107	542	2,59
6	21/03/98	summer	SE	2,20	131	797	2,00
7	08/04/98	autumn	W	2,23	94,3	484	2,82
8	21/05/98	autumn	SE	0,96	206	702	2,34

Primary standard : $240 \mu\text{g.m}^{-3}$ (Conama, 1992)

Secondary Standard : $150 \mu\text{g.m}^{-3}$ (Conama, 1992)

Table 2. General Characteristics of the Samples Collected in Sapucaia do Sul.

Filer	Sample date	Season date	Wind direction	Wind speed (m/s)	Average concentration ($\mu\text{g.m}^{-3}$)	Particle number	Average diameter (μm)
1	11/06/97	Autumn	NW	0,60	139	646	2,58
2	14/07/97	winter	NW	1,39	300	569	2,37
3	16/09/97	winter	E	1,01	208	606	2,91
4	03/10/97	spring	E	5,71	244	634	2,45
5	03/03/98	summer	SE	0,59	121	490	2,33
6	21/03/98	spring	W	2,17	92,8	761	2,73
7	08/04/98	Autumn	W	3,50	276	484	2,43
8	21/05/98	Autumn	NW	0,26	290	759	2,24

Primary standard : $240 \mu\text{g.m}^{-3}$ (Conama, 1992)

Secondary Standard : $150 \mu\text{g.m}^{-3}$ (Conama, 1992)

Characterization of Atmospheric Particles

Eight different filters were used at both locations. An average size of $<10\mu\text{m}$ prevailed and accounted for more than 98% of the total of all particles ($1-100\mu\text{m}$) Figure 2 and 3 show the average percentage values for the elements studied found at the two sampling sites.

Figure 2. Average Percentage of the Elements Studied for Each Filter for Charqueadas.

Figure 3. Average Percentage of the Elements Studied for Each Filter for Sapucaia do Sul.

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For the case of Charqueadas, higher particulate concentrations were observed for the SE direction, corresponding to filters 4 ($303\mu\text{gm}^{-3}$) and 8 ($206\mu\text{gm}^{-3}$) for spring (October 3, 1997) and autumn (May 21, 1998), respectively. The value observed for filter 4 was above that allowed by Brazilian Legislation, $240\mu\text{gm}^{-3}$ for 24 hours.⁹

For these filters, as well as for filters 2 and 6 that correspond to the direction of the SE quadrant, the percentage of Fe and Zn were higher, while Mn was lower (Figure 2). The steel plant is located in the SE direction in relation to the sampling station and this fact in addition to the higher concentration of the two elements and particularly Fe, point to the steel plant as the contamination source for this type of particulate.

The filters 1 (112mgm^{-3}), 3 (103mgm^{-3}) and 7 ($94,3\text{mgm}^{-3}$) showed smaller concentrations than the others, however, the preferential NW/W direction of the winds and the presence of Si and Al point to the coal power plant as the main anthropogenic source (Figure 2). Particles of Al/Si (aluminosilicate) and Si (quartz) have been identified in ashes derived from coal combustion by several authors.^{11,12} They consist mainly of fine particles in spherical form, being characterized as fly ash.^{10,11,13}

S presented a similar behavior in all filters studied, except for filter 8 where the wind direction was in the SE quadrant with respect to the receptor source and the S percentage was higher. In this case both anthropogenic sources in Charqueadas are responsible for the presence of S, however higher emissions of SO_2 are probably from the steel plant.

In Sapucaia do Sul high particulate concentration was verified for filters 2 ($300\mu\text{gm}^{-3}$), 7 ($276\mu\text{gm}^{-3}$) and 8 ($290\mu\text{gm}^{-3}$). In all three cases the concentration was above the air quality standard for particulates required by Brazilian legislation ($240\mu\text{gm}^{-3}$) for 24 hours.⁹

The elements Fe-Zn/Mn and Si-Al were identified in different wind directions, probably indicating that several local sources were responsible for these emissions. However, filters 6 and 8 that correspond to the directions W/NW, respectively, showed higher percentages of Fe, Zn and Mn (Figure 3) probably indicating that the emissions originated from Riograndense Steel Plant.

Silicon and aluminum showed higher percentages for filters 2, 4 and 5 in the directions NW, E and SE with reference to the receptor source, indicating contribution from several anthropogenic sources (Figure 3). The experimental results obtained for Sapucaia do Sul did not allow a clear identification of the anthropogenic contribution. The particles in this region are more heterogeneous and due to several sources such as automobile exhausts, steel plants, refineries, etc. Besides, the sampling point was close to the BR-116 Highway with intense automobile traffic. Further studies are needed.

Cluster Analysis

Cluster analysis was applied to the experimental data obtained for atmospheric particles ($<10\mu\text{m}$) collected at both sites. The total number of particles considered corresponded to 5057 for Charqueadas and 4913 for Sapucaia do Sul.

Table 3 summarizes the results obtained for Charqueadas, where six different groups of particles were obtained. Group 1 was characterized by particles rich in silicon (69,0%). Group 2 was characterized by particles rich in Ca (33,0%), S (19,0%) and associated with Na (19,0%). Group 3 contained large amounts of Na (48,0%). Group 4, that may be called the aluminosilicate group contained 33,0% Si and 26,0% Al. Group 5 contained mainly Fe (44,0%) and Zn (16,0%) and Na (19,0%). Group 6 contains mainly iron (73,0%) and the Fe particles are very small and generally present in spherical

form.^{10,11,13} For Sapucaia do Sul, cluster analysis also resulted in six groups (Table 4) and they were similar to the ones found for Charqueadas.

Table 3. Element Centroids Determined for Particle Samples from Charqueadas.

Elements (%)	Group 1: * Si	Group 2: * Ca e S	Group 3: * Na	Group 4: * Al e Si	Group 5: * Fe e Zn	Group 6: * Fe
Total number cases	417	359	804	1515	1157	805
Al	6,8	4,2	6,9	26	1,9	0,9
Si	69,0	5,4	9,0	33,0	3,4	1,7
S	1,8	19	6,2	3,0	3,3	1,2
K	1,4	1,4	2,4	2,7	0,8	0,4
Ca	0,8	33,0	2,4	1,6	1,7	0,9
Cr	0,4	0,5	1,0	0,5	1,0	0,9
Mn	0,4	0,7	1,2	0,6	2,2	1,6
Fe	2,9	4,6	7,7	6,3	44	73,0
Co	0,5	0,7	1,0	0,6	0,7	0,7
Ni	0,5	0,7	1,3	0,7	0,6	0,6
Cu	0,7	0,9	1,4	0,8	0,7	0,5
Zn	1,0	2,8	3,7	1,6	16	5,5
Sn	0,8	1,5	1,8	1,1	0,8	0,5
Pb	1,0	3,0	2,1	1,2	1,6	0,8
Na	11	19,0	48,0	17,0	19,0	9,4

*Rich particle

Table 4. Element Centroids Determined for Particle Samples from Sapucaia do Sul.

Elements (%)	Group 1: * Si	Group 2: * Ca e S	Group 3: * Fe e Zn	Group 4: * Fe	Group 5: * Na	Group 6: * Al e Si
Total number cases	735	254	427	661	651	2185
Na	9,0	21,6	25,7	15,4	46,4	14,3
Al	9,4	2,3	1,5	2,3	4,7	16,1
Si	66,2	3,7	3,8	5,3	8,7	29,4
S	1,3	21,9	3,5	1,5	6,9	2,1
K	3,2	1,3	1,2	0,7	2,2	2,6
Ca	1,2	29,1	0,7	1,0	2,9	2,5
Cr	0,3	0,5	0,4	0,4	0,6	0,3
Mn	0,4	0,6	1,6	1,9	1,0	0,5
Fe	2,9	2,3	23,2	54,2	7,4	7,9
Co	0,5	0,7	0,6	0,7	0,9	0,5
Ni	0,4	0,7	0,6	0,4	1,1	0,5
Cu	0,6	0,8	0,8	0,8	1,6	0,6
Zn	1,1	2,5	28,8	8,7	5,9	1,7
Sn	0,8	1,8	0,9	0,6	1,7	0,9
Pb	0,7	3,3	1,5	1,2	2,2	0,8

*Rich particle

Group 1 contained mainly silicon (66,2%) and group 2 was characterized by Ca (29,1%), S(21,9% and Na (21,6%). Group 3 consisted mainly of Fe (23,2%) and Zn (28,8%) while group 4 was mainly iron (54,2%Fe). Group 5 consisted predominantly of Na (46,4%) and group 6 was the aluminosilicate group (16,1%Al and 29,4%Si).

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The results from the two sampling sites were similar. However, particles containing Fe and Zn were present in larger numbers in Charqueadas, while in Sapucaia do Sul the Si and Si-Al groups prevailed.

The iron particles in pure form and also associated with Zn prevail in small particle size ($<2,5\mu\text{m}$) and are present in spherical form. This morphology size was also verified by other authors.^{2,13} Teixeira and coworkers confirmed the presence of iron particles in Charqueadas and pointed the steel plant present in the region as the possible source of emission. This hypothesis was confirmed visually by the emission of red smoke, indicating the presence of iron oxides.

The most abundant among the analyzed particles were those containing Al and Si (aluminosilicates). These particles (~66-69%Si) were identified as quartz in submicron size and originated from coal combustion.¹⁰

The particles rich in S and Ca may originate from various sources, including coal combustion, when CaSO_4 is present in fly ash.¹² In the case of Charqueadas, the particles rich in Ca and S originate from the coal power plant and the steel plant, both using fossil fuels for energy generation.

The distribution of particle size in relation to elementary composition is illustrated in Figures 4 and 5 for the sampling sites of Charqueadas and Sapucaia do Sul, respectively.

Figure 4. Variation of Particle Diameter with Elementary Composition – Charqueadas

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Figure 5. Variation of Particle Diameter with Elementary Composition-Sapucaia do Sul

Of the elements studied (Al, Si, Fe, Zn, Ca and S) all were found in higher concentration in the finer particles (2,5 μ m), indicating anthropogenic sources. The contribution of the coarse particle fraction (2,5 -10 μ m) was less significant and was attributed to the soil natural source.

Factorial Analysis

The statistical methods were carried out in the computer using the *Statistics for Windows 4.3*™ software. The procedure used applied the factor analysis technique through the principal component method to the data sets obtained through cluster analysis for Charqueadas and Sapucaia do Sul.

For Charqueadas, these sets resulted in three factors associated with characteristic eigenvalues $>1,0$, that synthesized, after the application of the Varimax Rotation normalized to the factor loadings of 76,16% of the total variance. The factor loadings for variables studied in the particle samples from Charqueadas are shown in Table 5.

Table 5. Factor Loadings for the Variables \studied in Particle Samples from Charqueadas.

	Factor 1	Factor 2	Factor 3
Na	0,04	0,02	0,77
Al	0,79	-0,16	-0,16
Si	0,82	-0,20	-0,20
S	0,00	0,87	0,01
Ca	0,00	0,90	-0,18
Fe	-0,79	-0,27	-0,22
Zn	-0,64	-0,13	-0,08
Variância total (%)	33,58	24,70	17,88

* Factor loading $\geq 0,50$

The first factor (33,58 of the total variance) was attributed to the elements that presented a higher frequency in the group of data. This factor had higher loads for Si, Al, Fe and Zn. For the last two elements the signs presented were the opposite. The results show that the two different groups, Si-Al and Fe-Zn, originated from two different sources, from the power plant and the steel plant, respectively. These elements had shown predominance of more than 50% in the fine fraction ($2,5\mu\text{m}$) as was seen in Figure 5. The second factor, with high factorial load for S and Ca, explained 24,70% of the total variance of the data. This factor is represented by original particles of the two

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local sources, that are responsible for the emissions of S. The third factor, characterized by particles containing Na revealed the contribution of natural sources.

For Sapucaia do Sul, the data sets resulted in two factors associated with characteristic eigenvalues $>1,0$ that synthesized after application of the Varimax Rotation normalized to the factor loadings of 59,01% of the total variance. The factorloadings fro the variables studied in particle samples from Sapucaia do Sul are shown in Table 6.

Table 6. Factor Loadings for the Variables Studied in Particle Samples from Sapucaia do Sul.

	Factor 1	Factor 2
Na	0,44	0,34
Al	-0,67	-0,16
Si	-0,79	-0,28
S	0,14	0,90
Ca	-0,06	0,84
Fe	0,64	-0,39
Zn	0,69	-0,12
Variância total (%)	31,3	27,8

* Factor loading $\geq 0,50$

The first factor, characterized by the higher factorial loads for Si and Alk and with negative signs for Fe and Zn, explained 31,29% of the total variance. In spite of the fact that the elements presented opposite signs for this factor, as in Charqueadas, indicating two different anthropogenic sources, it was not possible to clarify the origin of the emissions of these species. In Sapucaia do Sul, the collector was located in a place of intense vehicular traffic, being subject to a significant influence of mobile sources. Figure 6 shows the relation between wind direction and the average composition for the elements characterized by cluster analysis of the eight filters used for collection in Charqueadas. The presence of Fe in high concentration in the SE direction point to the steel plant as the emission source, while the high concentrations of Si and Al in the NW direction indicate the coal power station plant as the source of emissions.

Figure 6. Relation between Wind Direction and Average Composition for Charqueadas for the Eight Filters Employed.

Figure 7. Relation between Wind Direction and Average Composition for Sapucaia do Sul for the Eight Filters Employed.

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Figure 7 shows the average composition and wind direction for Sapucaia do Sul. As can be seen, the samples containing Fe and Zn concentrate in the SE direction, where the steel plant is located. On the other hand, the Si-Al samples are more dispersed, indicating the contribution of several sources.

CONCLUSIONS

The experimental results obtained in this study showed that the quality of air in Charqueadas and Sapucaia do Sul was affected mostly by fine atmospheric particles ($<2,5\mu\text{m}$)

Cluster analysis indicated the presence of six distinct groups in both locations: Fe-Zn, Fe, Si-Al, Si, Ca-S and Na.

Factorial analysis through the Principal-Components Method applied to the data sets from cluster analysis resulted in three factors for Charqueadas and two for Sapucaia do Sul.

For Charqueadas, Factorial analysis indicated that Fe and Zn have anthropogenic origin and the steel plant can be considered as the responsible source. Particles rich in aluminosilicates and quartz were identified as fly ash originating from the coal power plant. Both the steel plant and the power plant in Charqueadas also contributed to the formation of particles containing Ca and S.

For Sapucaia do Sul it was not possible to determine the source of Si-Al rich particles. They may be due to vehicles, suspension matter or other sources. The steel plant was characterized as the source of particles rich in Fe and Zn and for the case of wind in the W and NW directions during the sampling days, the steel plant was also the source of the emission of particles rich in Ca-S. For other wind directions it was not possible to define the source, however one possibility being automobile traffic. The identification of anthropogenic sources in Sapucaia do Sul requires additional studies.

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