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# Study of wet precipitation and its chemical composition in South of Brazil

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## ABSTRACT

The purpose of this study is to analyze the chemical composition of wet precipitation in samples collected at three stations in the Candiota region in the Brazilian state of Rio Grande do Sul (RS). Samples were collected in 2004. Variables analyzed in wet precipitation were pH, conductivity, and concentration of $Cl^-$, $NO_3^-$, $SO_4^{2-}$$F^-$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $NH_4^+$, Cu, Zn, Fe, Mn, Pb, Ni, Cd, Co, and Cr. $SO_2$ and $NO_2$ distribution over the time were also evaluated. Results have showed that pH $< 5.6$ are found mostly at Candiota airport (85%), followed by Aceguá (72%) and Três Lagoas (65%). Enrichment Factor of the studied ions in wet deposition revealed higher $Ca^{2+}$ and $SO_4^{2-}$ enrichment in Três Lagoas. Factor Analysis applied to metals and major ions allowed identifying the major sources. While $Cl^-$, $Na^+$, $Mg^{2+}$ are of marine origin, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, $F^-$ come from anthropogenic sources. Except for Fe and Mn originating from the soil dust, the metals studied showed to have anthropogenic influence The average $SO_2$ and $NO_2$ concentration, as well as $SO_4^{2-}$ and $NO_3^-$ in wet precipitation in the Candiota region showed higher concentrations during the warmer months.

**Key words:** wet precipitation, metals, factor analysis.

## INTRODUCTION

The increase in industrialization levels, as well as the growth of urban population, has increased the demand for energy, which in turn caused greater emission of atmospheric pollutants ($SO_2$, $NO_x$, VOCs and aerosols). Compounds like $SO_2$ and $NO_x$ are responsible for acid rain in the environment.

It is known that large quantities of pollutants including $SO_2$ are emitted from coal burning and other industrial activities. Many studies confirm that the amount of sulfur released by the emissions of coal combustion process is higher than that of other fossil fuels (e.g., Isobe et al. 2005). The acid deposition resulting from such source processes is currently considered as a potential damage; transformation of such chemicals into more stable end products, sulfuric acid, while posing a threat to vegetation and aquatic life in ecologically sensitive areas (Park et al. 2000), can also cause human organ damages (Pandey et al. 2005).

Precipitation is the most effective scavenging factor for the removal of particulate matter and gaseous pollutants dissolved in the atmosphere.

Atmospheric precipitation is slightly acid due to the presence in the air of natural occurrences of sulfur, nitrogen and carbon dioxide. However, an increase in its acidity, as well as alteration in its ionic composition, has been found.

The chemical composition of rain, influenced by natural and anthropogenic sources, is the result of the incorporation of pollutants and particles in the air into the raindrops. Although it is difficult to study experimentally both emission sources, the determination of the

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chemical composition of the rain, as well as the meteorological conditions, may help to understand the cause for its acidification (Sanusi et al. 1996).

Acidification and the ion concentration in the precipitation depend on the constituents of the pollution source, on its physical constitution in the hydrologic system, on the chemical transformation during the cloud development, and on the scavenging below the cloud (Kulshrestha et al. 2003).

The chemical characterization of precipitations continues to be under considerable investigation due to the increase in atmospheric inputs of substances and their effects upon earth, surface water, vegetation, and materials (Bravo et al. 2000).

The subject of acid precipitation and associated environmental problems has received special attention in recent decades and has been submitted to extensive investigation in several countries (Al-Momani et al. 1995).

Some studies have shown the environmental impact of the burning of fossil fuels, like coal, on atmospheric precipitation (Alastuery et al. 1999 and Flues et al. 2002). In the Candiota area, Rio Grande do Sul, Brazil, some research has been done to determine the existence of acid rain originated from the emissions of the biggest coal-fired power station located in Rio Grande do Sul (Migliavacca et al. 2004a, b). These studies measured bulk precipitation and wet precipitation at specific sites, and obtained partial data. The present study complements the study on wet precipitation at other sites under the influence of the power station and at the international border between Brazil and Uruguay, since acid rain possibly brought about by the coal-fired power station located in the area is reason of great concern of the governments of both countries. As a result, the present study aims at identifying physical and chemical parameters (pH, conductivity, major ions and trace elements) in samples of wet precipitation collected in Candiota in order to evaluate the influence of the main anthropogenic sources in the area. $SO_2$ and $NO_2$ distribution over the time were also evaluated in the Candiota region.

## STUDY AREA

The Candiota area, situated in the Southwest of the State of Rio Grande do Sul, Brazil – geographical coordinates 54°10'58"/ 53°18'35" West longitude and 31°17'35"/ 31°02'41" South latitude – about 420 km from the State capital of Porto Alegre, comprises totally or in part the counties of Aceguá, Bagé, Candiota, Herval, Hulha Negra, Pedras Altas and Pinheiro Machado (Fig. 1).

The biggest coal-fired power plant of Rio Grande do Sul, Usina Termoelétrica Presidente Médici (UPME), is located in Candiota. It is operated by Companhia de Geração Térmica de Energia Elétrica (CGTEE). There are plans to expand its capacity from 350 to 500 MW.

In terms of climate, the Candiota area is under the influence of tropical, as well as polar air masses from the sea. The wind blows predominantly from the NE quadrant all year round, although west winds are also present in all directions (Braga et al. 2004).

## MATERIALS AND METHODS

### SAMPLING SITES

The sampling sites for atmospheric precipitation (Aceguá, Candiota Airport and Três Lagoas) were chosen with the help of 1:50.000 cartographic charts, field job and GPS (Global Positioning System). The choice of the sampling sites followed some criteria, according to the ASTM D 5111 Standards (ASTM 1996a). These criteria were: i) predominant wind direction; ii) distance from polluting sources (approximately a radius of 50 km from UPME); iii) the distance from obstacles that could interfere in sampling (twice the height of obstacles); and iv) logistics (security, access, electric power supply).

### WET PRECIPITATION SAMPLER

The sampler for collecting wet precipitation consisted of a metallic protection box and a polyethylene collecting flask of 5-liter capacity, coupled to an acrylic funnel topped by a lid of the same material. The lid opens only during wet precipitation, closing after the precipitation has stopped. It runs on electric power or, in case of power failure, on a 12V battery.

### SAMPLING PERIOD

The cleaning of sampling and storing flasks was done with mil-Q water (type I) (conductivity $< 2\ \mu S.cm^{-1}$) (ASTM 1996b), rinsing several times (twice to 3 times) and leaving them stored with this water for at least 24 hours.

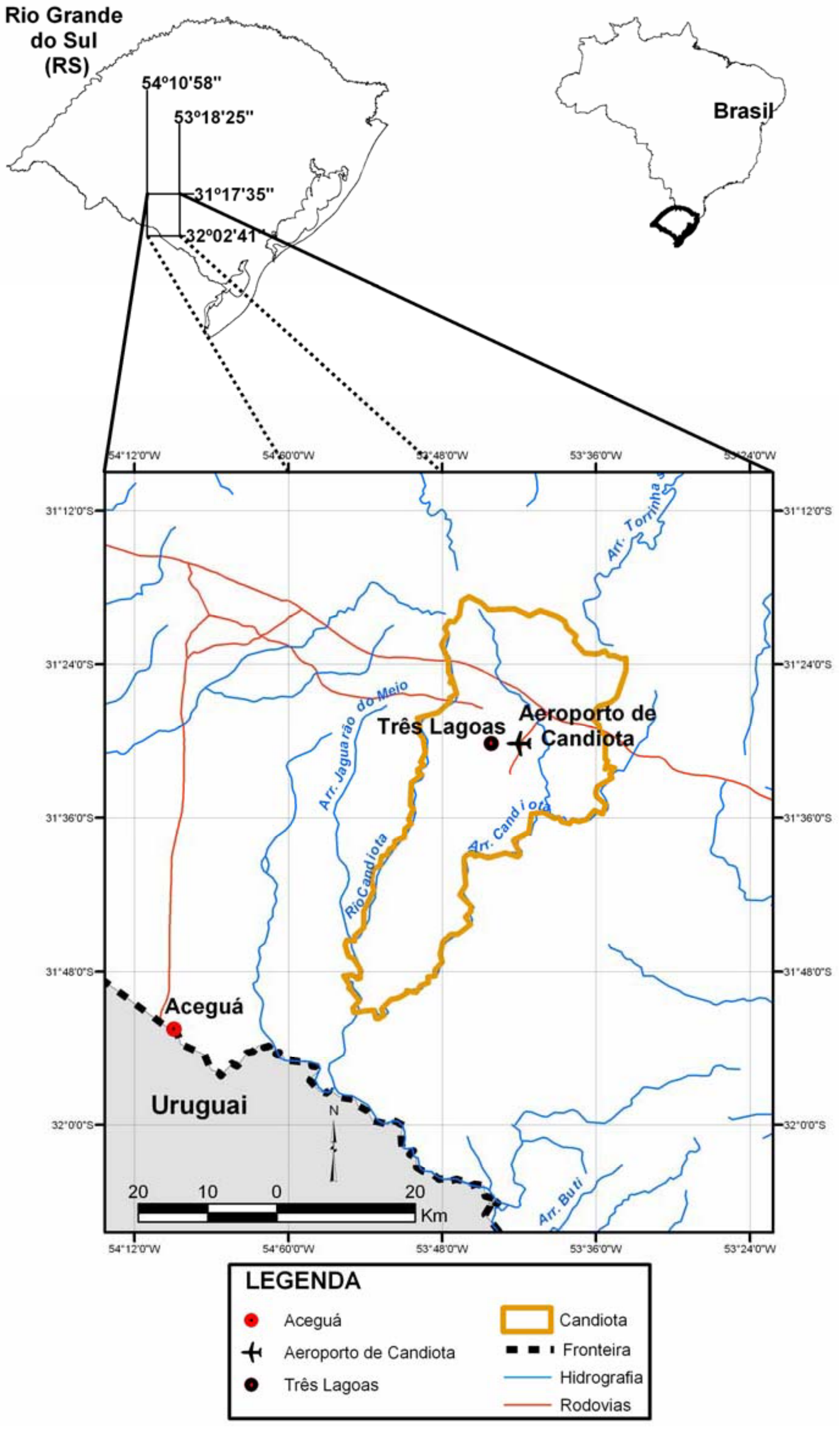


Fig. 1 – Map of the Candiota area.

Each sample was divided in the amounts required by the specific analytical methods to be performed. Unfiltered samples were used to determine pH, conductivity and alkalinity. Some sample amounts were filtered through a 0.22 $\mu$m membrane and divided into aliquots. The first aliquot, preserved in chloroform, was used to determine anions and cations. The second, preserved in $HNO_3$ (Merck) superpure at pH $< 2.0$, to determine metals. Both aliquots were stored at 4°C until chemically analyzed.

### CHEMICAL ANALYSIS

The unfiltered samples were determined in situ for pH (Mettler Toledo M 90 potentiometer, precision ± 0.01) and conductivity (Orion Model 105 Plus, readings range 0-100 $\mu S.cm^{-1}$).

At the laboratory, the volume of the samples was determined, as well as the pH and conductivity of unfiltered aliquots. The pH was determined with a digital pHmeter (Digimed DM-20, precision ± 0.01), and conductivity with an electric conductivimeter (Digimed DM-31), showing a 1% precision and range of 0-20 $\mu S.cm^{-1}$.

The major ions were determined through ionic chromatography (Dionex DX 500 with electric conductivity detector). The columns used were AS4A-SC CS12A (Dionex) to analyze anions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $F^-$) and cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $NH_4^+$), respectively. A cationic column CS12A with a $H_2SO_4$ 21.7 mmol $L^{-1}$ solution at a flow of 1.5 mL $min^{-1}$ was used to analyze the cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $NH_4^+$). The chromatographic conditions and the optimization of analytical methods are described in the studies of Barrionuevo et al. (2004).

Detection limits were: 0.061 $\mu$g/L for $F^-$; 0.051 $\mu$g/L for $Cl^-$; 0.28 $\mu$g/L for $NO_3^-$; $SO_4^{2-}$; $Na^+$; 0.26 $\mu$g/L for $NH_4^+$; 0.35 $\mu$g/L for $K^+$; 0.21 $\mu$g/L for $Mg^{2+}$; 0.17 $\mu$g/L for $Ca^{2+}$.

To evaluate the ionic balance, the sum of anions and cations was done. The calculation showed higher values for cations (64.1 $\mu$eq/L) than for anions (29.5 $\mu$eq/L). The deficit in anions is explained by the exclusion of some ionic species, like $HCOO^-$, $CH_3COO^-$ and $HCO_3^-$ that were not analyzed in the present work. The two main sources of organic acids in the atmosphere, the oxidized hydrocarbons emitted by the vegetation and the direct emission by industrial sources, both originating organic ions and bicarbonate, could have contributed with significant amounts to the wet precipitation samples of the Candiota area (Mouli et al. 2005).

The analysis of metals Cu, Zn, Fe, Mn, Pb, Ni, Cd, Co, Cr was done through the Plasma Emission Spectrometry method, Jobin Yvon, 38 S, coupled to an Ultrasonic Nebulizator. Certified standard solutions (PURE) were used.

Detection limits were: 0.5 $\mu$g/L for Cu, Ni, Cd, Co, Cr and 1.0 $\mu$g/L for Fe, Mn, Pb, Zn.

### $SO_2$ AND $NO_x$

Data were collected by $SO_2$ continuous samplers and analyzers (Horiba), model APSA 360, and $NO_x$ continuous samplers and analyzers, model APNA 360, which are the property of the Companhia de Geração Térmica de Energia Elétrica – CGTEE. The $SO_2$ continuous samplers were installed at three sites in Candiota (Candiota Airport, Três Lagoas, and Dario Lassance), while the $NO_x$ sampler was installed at one site (Candiota Airport). The data obtained for $SO_2$ and $NO_x$ are the average for the Candiota region.

### ENRICHMENT FACTOR

The Enrichment Factor (EF) was calculated according to the method suggested by several authors, and described in Keene et al. (1986).

$$EF = \frac{(X/C)_{\text{precipitation}}}{(X/C)_{\text{reference material}}} \tag{1}$$

where $X$ is the concentration of the ion of interest and $C$ is the concentration of the reference ion. In the present study, Na was used as the element of reference.

### STATISTICAL TREATMENT

In order to make the interpretation of data easier, statistical analysis was applied to the chemical variables. It also helped to determine the influence of natural and anthropogenic sources on the atmospheric precipitation of the area under study. The software SPSS for *Windows V.9.01* was used with the Factor Analysis technique.

The raw data was used to generate a correlation matrix (Pearson), which in turn was used to determine a new set of synthetic variables (common Factors) based on the interrelations of the original data. These resulting factors are associated to the characteristic roots $> 1.0$.

**TABLE I**
**Chemical composition (average, minimum and maximum) and average concentration pondered by the volume of ions ($\mu$eq $L^{-1}$) in the wet precipitation at Candiota region in 2004.**

| Station | | pH | Cond | $H^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $NH_4^+$ | $SO_4^{2-}$ | $NO_3^-$ | $Cl^-$ | $F^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aceguá n=23 | average | 5.63 | 7.51 | 3.18 | 2.42 | 7.79 | 5.41 | 15.2 | 31.4 | 11.7 | 2.15 | 14.7 | 3.18 |
| | minimum | 4.91 | 2.60 | 0.26 | 0.73 | 2.42 | 1.03 | 1.99 | 1.91 | 0.25 | 0.25 | 0.87 | 0.003 |
| | maximum | 6.59 | 22.4 | 12.3 | 5.97 | 30.3 | 14.9 | 61.9 | 210 | 33.5 | 7.37 | 73.3 | 24.5 |
| | MPV | | – | | 3.63 | 11.4 | 7.98 | 21.7 | 49.7 | 17.4 | 4.74 | 20.2 | 6.69 |
| Três Lagoas n=25 | average | 5.46 | 8.36 | 5.95 | 2.14 | 8.85 | 3.05 | 8.95 | 27.6 | 14.1 | 1.99 | 5.67 | 3.70 |
| | minimum | 4.40 | 2.70 | 0.46 | 0.76 | 2.21 | 1.06 | 2.35 | 0.63 | 0.73 | 0.33 | 0.66 | 0.003 |
| | maximum | 6.34 | 34.5 | 39.8 | 5.82 | 27.2 | 5.32 | 49.8 | 225 | 48.4 | 7.83 | 22.1 | 26.8 |
| | MPV | | – | | 3.88 | 17.7 | 6.95 | 18.5 | 41.6 | 38.5 | 3.81 | 12.8 | 16.1 |
| Airport n=19 | average | 5.47 | 8.11 | 4.23 | 2.42 | 9.37 | 4.39 | 11.3 | 40.5 | 15.9 | 2.63 | 9.47 | 3.98 |
| | minimum | 4.92 | 1.80 | 0.48 | 0.83 | 3.01 | 1.31 | 2.44 | 2.27 | 1.10 | 0.34 | 0.67 | 0.003 |
| | maximum | 6.32 | 25.4 | 12.0 | 6.34 | 21.0 | 8.18 | 25.4 | 234 | 48.5 | 7.84 | 24.9 | 10.9 |
| | MPV | | – | | 2.98 | 11.7 | 5.61 | 14.4 | 48.2 | 20.2 | 3.31 | 11.9 | 5.71 |

Spearman correlation was applied to the data of chemical elements using log-normal and normal distribution to measure the correlation between the ordinal variables. The values of each variable were ordered from lowest to highest for each selected case.

## RESULTS AND DISCUSSION

### MAJOR IONS

Table I shows average, minimum and maximum values of chemical composition and the average concentration pondered by the volume of major ions ($\mu$eq.$L^{-1}$) in samples of wet precipitation from the sites of Aceguá, Três Lagoas and Airport at Candiota, from January, 2004 to November, 2004.

The average pH value of the precipitation samples was lower than 5.6 at the three Candiota sites: Aceguá (pH = 5.32), Três Lagoas (pH = 5.46) and Airport (pH = 5.44). This indicates a slightly acid pH of the precipitation at Candiota area.

The pH data shows that rain with pH values below 5.6 occurs in higher percentages at Candiota Airport (85%), followed by Aceguá (72%) and Três Lagoas (65%).

Figures 2a, 2b, and 2c show the pH frequency for the three sites studied. Over 70% of events showed pH values below that for acid rain ($pH<5.6$), and about 15% of events were in the range of pH = 4.5-5.5. The pH value found at Aceguá is slightly higher than those determined in previous studies. However, this value is still lower than those found by Zunckel et al. (2003) at the border with Uruguay (Aceguá-Uruguay) between 1999 and 2000. The values found at the time were higher than 5.6.

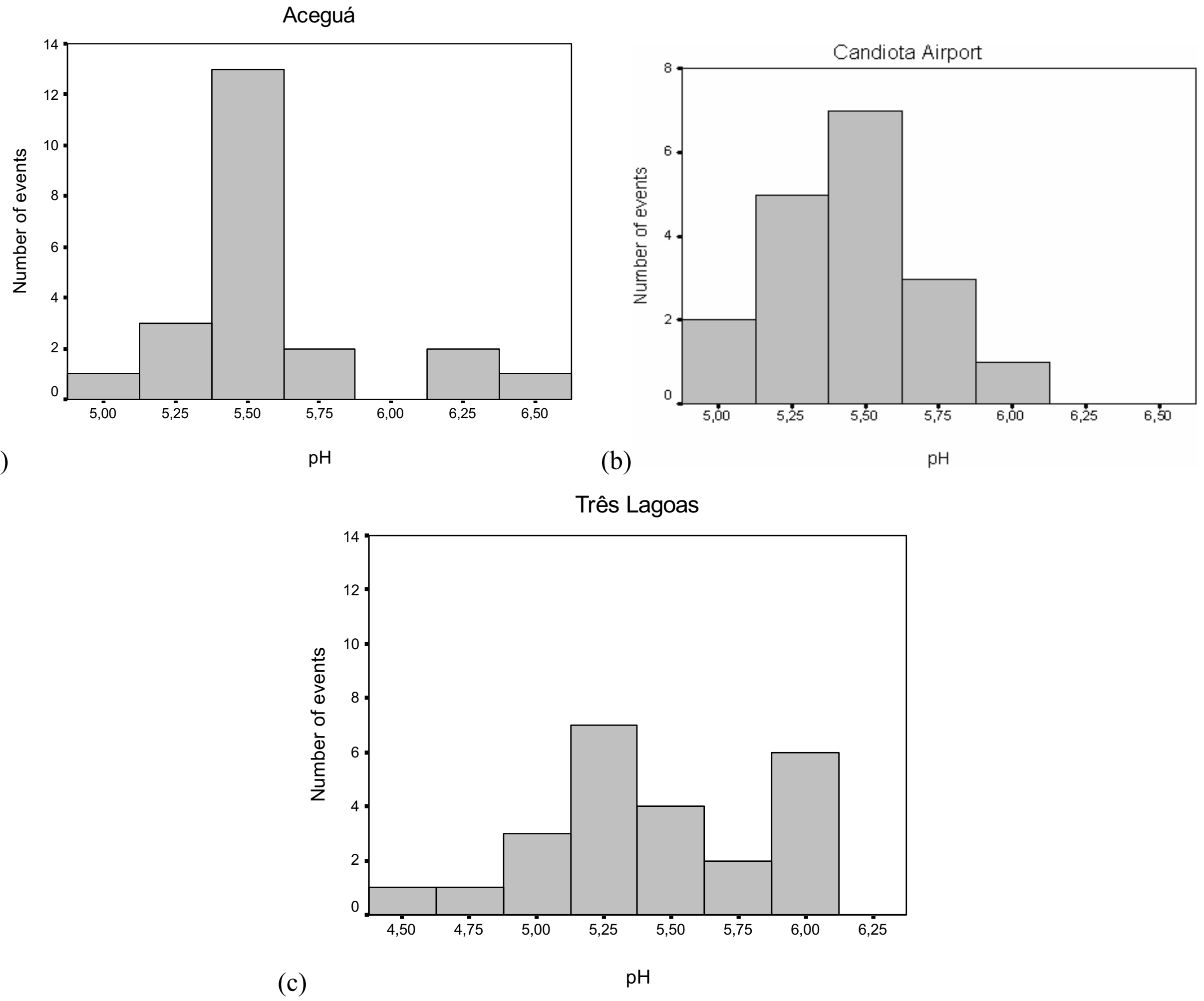
The average conductivity for the three sites was 7.25 (1.80-34.5) $\mu$S.$cm^{-1}$ and the maximum value for each site was 17.70, 34.5 and 15.60 $\mu$S.$cm^{-1}$, respectively, for Aceguá, Três Lagoas and Airport in Candiota area.

The average values for conductivity were similar to those found in other studies done on the same area, not showing significant variation (Migliavacca et al. 2004a, 2005).

The major ions presence (Table I) indicates that the presence of Cl in Candiota could be due to sea influence. In fact, this element is in higher concentration than those found in other studies for the Aceguá area Migliavacca et al. 2004b, 2005.

As the $SO_4^{2-}$ concentrations are far more significant than those of $NO_3^-$ (Table I), $H_2SO_4$ is probably the component responsible for the acidity in the precipitations in the Candiota area.

The higher average percentage of $NH_4^+$ presented at Candiota Airport can be due to the direct influence of agricultural and cattle raising activities in the region. According to Blume (1992) the high $NH_4^+$ concentrations found in rainwater might be related to ammonium gas ($NH_3$) introduced into the atmosphere mainly by cattle farming by the use of fertilizers (17%) and by industrial activities.



(a)

(b)

(c)

Fig. 2a – Histogram of pH values of the wet precipitation – Aceguá site. Fig. 2b – Histogram of pH values of the wet precipitation – Candiota Airport site. Fig. 2c – Histogram of pH values of the wet precipitation – Três Lagoas site.

The Factor Analysis explained 77% of total variance (Table II). Factor 1 shows significant values for variables $NO_3^-$, $NH_4^+$, $K^+$. As Candiota is an agricultural area, the use of fertilizers and animal excrements may have contributed to $NH_4^+$ increase. The high biogenic activity may be the cause for the relatively high load of $NH_4^+$ and $K^+$ (Migliavacca et al. 2004a, 2005). The presence of ions $NO_3^-$ e $SO_4^{2-}$ is characteristic of anthropogenic influence, probably the contribution of the power plants.

Ammonia usually occurs in the atmosphere as $(NH_4)_2SO_4$ and $NH_4NO_3$, and thus may be related to $SO_4^{2-}$ and $NO_3^-$, suggesting the influence of agricultural activity (Seinfeld and Pandis 1998).

Cape and Leith (2002), in their experiments, found that the quantity of $SO_2$ deposited on the surface of the wet funnel was related to the quantity of $NH_3$ deposited, attributing the fact to the oxidation of dissolved $SO_2$ that reacts with dissolved $SO_2$ producing $(NH_4)_2SO_4$ salts, non volatile during water evaporation.

As there are limestone mines in the area, $Ca^{2+}$, although showing load $< 5$, could be associated to this Factor.

Although $H_2SO_4$ and $HNO_3$ contribute to the acidification of rain water in this area, the presence of $Ca^{2+}$ results in diminished acidity. This element became evident through the Enrichment Factor.

Through Factor 2, 26% of the total variance of the raw data is explained. It shows higher loads for $Cl^-$,

**TABLE II**
**Matrix of factorial loads resulting from varimax rotation, applied to the wet precipitation – Candiota region (2004).**

| Variables | Factors | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $H^+$ | –0.284 | 0.00782 | **0.872** |
| $F^-$ | 0.153 | 0.120 | **0.796** |
| $Cl^-$ | –0.0264 | **0.949** | 0.0424 |
| $NO_3^-$ | **0.909** | –0.0642 | –0.0479 |
| $SO_4^{2-}$ | 0.641 | 0.0714 | 0.650 |
| $Na^+$ | –0.0286 | **0.933** | 0.0247 |
| $NH_4^+$ | **0.903** | –0.0582 | –0.0342 |
| $K^+$ | **0.882** | 0.167 | 0.0465 |
| $Mg^{2+}$ | 0.299 | **0.882** | 0.144 |
| $Ca^{2+}$ | 0.535 | 0.135 | 0.0462 |
| Extraction (%) | 33 | 26 | 18 |

$Na^+$ and $Mg^+$, probably indicating sea salt contribution in the area. This contribution could be explained mainly by $Na^+$ and $Cl^-$, originating in maritime tropical air and maritime polar air masses that exert influence on the area (Lee et al. 2000, Mello 2001, Lara et al. 2001). Other studies done in Candiota have shown the maritime contribution on this area (Migliavacca et al. 2004a, Braga et al. 2004). This last author demonstrated the influence of the sea breeze of SW direction in relation to the emission source, which is confirmed through the findings of the present study.

Factor 3 showed a variance of 19% characterized by the ions $SO_4^{2-}$ $H^+$ and $F^-$. Fluorides emission at the coal-fired power plant at Candiota were reported in some studies (Fiedler et al. 1990).

Figure 3a shows the scores distribution at the Três Lagoas site. The association of $H^+$, $F^-$ and $SO_4^{2-}$ in Factor 3 explains the acid pH values (4.67 and 4.40) occurred at Três Lagoas site on January 21, 2004 and January 24, 2004, respectively. On these occasions the concentrations of $F^-$ e $SO_4^{2-}$ were the highest during all the period under study.

At Aceguá site, there is a higher influence of ions of maritime origin. It shows higher scores for Factor 2 (Na, Cl and Mg). This result is confirmed by the fact that the highest concentrations for these ions were found at this site. Similar findings were obtained by Migliavacca et al. (2005) and Zunckel et al. 2003) in studies at the same site. As for Factors 1 and 3 (Fig. 3b), no significant variation was obtained; values in the range of –0,95 a 3,53, can be considered homogeneous.

At Candiota Airport site, the scores were more homogeneous, values varying from –0,976 a 2,94, (Fig. 3c). The highest value found was for Factor 1 ($NO_3$, $NH_4$, K, Ca,$SO_4$) on September 21, 2004, when an alkaline pH (6.32) and a high value for $NH_4$ ions (234 $\mu$eq/L) were determined.

## ENRICHMENT FACTOR

Table III shows the average, minimum and maximum values of EF. The highest values of EF were obtained for $Ca^{2+}$, $SO_4^{2-}$ and $K^+$ ions at Três Lagoas site. The explanation for this may be the fact that the sampling site is located in the main wind direction (NE-E).

However, $Ca^{2+}$ shows high values for EF at the three sites, a strong influence of the limestone mines in the area. The ion $Ca^{2+}$ could be neutralizing acidity, which could explain the fact that the pH of the atmospheric precipitation in the area is not as acid as in others. Furthermore, the ion $Ca^{2+}$ could be an original component from earth or dust (particulate material).

$SO_4^{2-}$ showed EF averages of 9.85; 18.64; 14.31 for Aceguá, Três Lagoas and Airport, respectively, in samples of wet precipitation. The coal fired power plant in the area produces $SO_2$; the major atmospheric oxidation of $SO_2$ occurs in the drop, either in the cloud or in the rain, when $SO_2$ dissociates to $HSO_3$. The latter is then quickly oxidized by $H_2O_2$ in the liquid phase, producing reaction of $HO_2$.

Studies on acid rain done in the area and other areas further south near coal fired power plants, showed significant concentrations of sulfate in deposition samples (Migliavacca et al. 2004a, Fiedler et al. 1990).

Just as other ions, $K^+$ also showed higher average values for EF at Três Lagoas site (EF: 17.8). At Aceguá and Airport the average values for EF were practically the same (EF: 14.0). The source that could explain the enrichment in $K^+$ is earth particles, quite significant in the area. Other studies done in the area and in a nearby State showed significant quantities for $K^+$ (Migliavacca et al. 2004b, Zunckel et al. 2003).

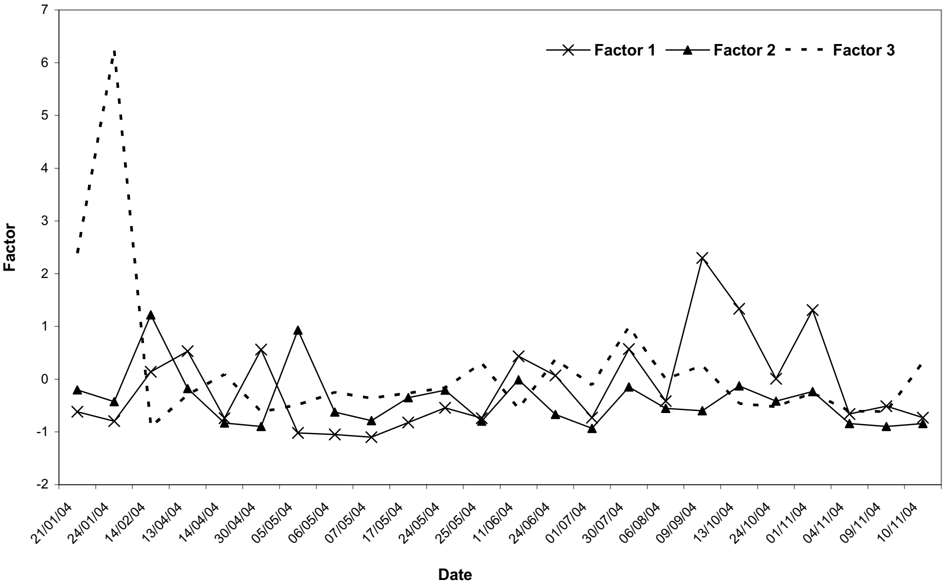


Fig. 3a – Temporal and spatial of Factors 1, 2 e 3 as observed for the ions at Tês Lagoas site for the studied period.

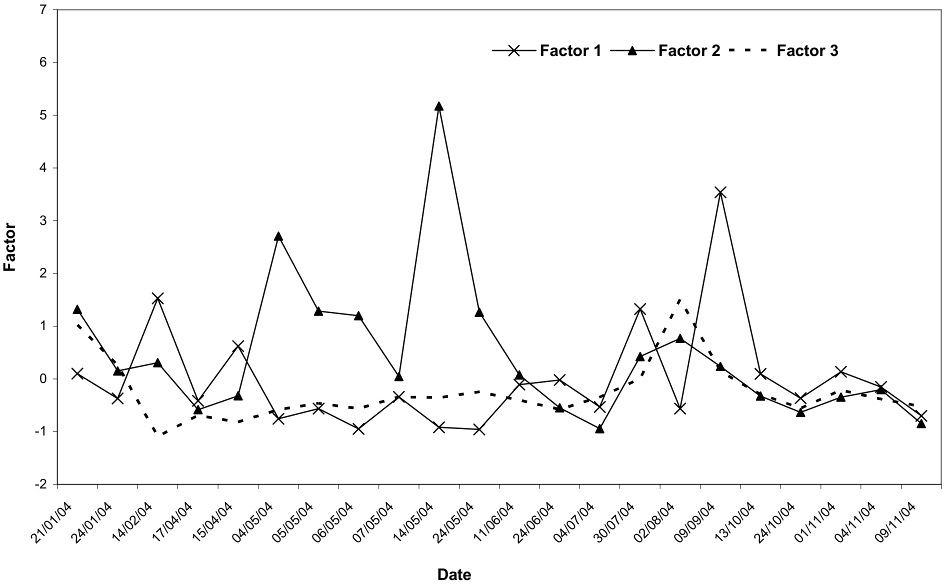


Fig. 3b – Temporal and spatial of Factors 1, 2 e 3 as observed for the ions at Aceguá site for the studied period.

## HEAVY METALS

Table IV and Figures 4a, b and c show the average concentration of metals at the three sampling sites from January to December, 2004.

The elements Ni, Pb, Cd, Co, Cr, Cu, Fe, Mn, and Zn showed higher concentrations in the wet precipitation samples from May to November. During these months, a higher precipitation level occurred, associated to an acid pH (pH < 5.6), dissolving the elements present on the ultra fine particles. Elements of anthropogenic and marine origin are more soluble in the precipitation than those derived from the soil dust.

Fe and Mn showed average concentrations of 7.53 e 5.43 ppb in Aceguá (Table IV and Fig. 4a). These concentrations were similar to those reported in other studies done in the same area, although the samples were collected differently (Migliavacca et al. 2004a). These

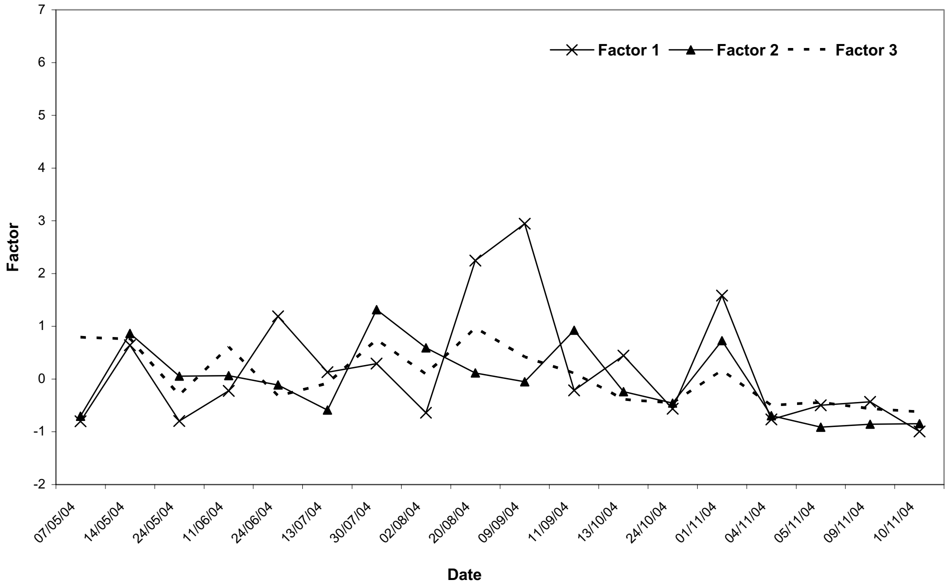


Fig. 3c – Temporal and spatial of Factors 1, 2 e 3 as observed for the ions at Candiota Airport site for the studied period.

**TABLE III**
**Enrichment Factor of wet precipitation samples.**

| | Aceguá | | Três Lagoas | | Candiota Airport | |
|---|---|---|---|---|---|---|
| | Averagand | Minimum-Maximum | Average | Minimum-Maximum | Average | Minimum-Maximum |
| $SO_4^{2-}$ | 10.9 | (0.146-34.3) | 18.64 | (0.122-53.7) | 14.31 | (3.25-33.7) |
| $Cl^-$ | 0.765 | (0.325-1.22) | 0.652 | (0.0774-1.22) | 0.670 | (0.234-1.09) |
| $K^+$ | 13.92 | (1.67-31.9) | 17.81 | (2.29-63.0) | 13.60 | (3.35-32.0) |
| $Ca^{2+}$ | 26.34 | (2.07-144) | 31.45 | (3.75-69.8) | 26.02 | (9.63-47.5) |
| $Mg^{2+}$ | 2.36 | (0.797-7.30) | 2.15 | (0.368-4.67) | 2.086 | (1.06-3.77) |

**TABLE IV**
**Average, minimum and maximum concentrations of metallic elements in wet precipitation samples ($\mu$g L$^{-1}$) at Candiota region (2004).**

| | Aceguá (n=18) | | | Candiota Airport (n=20) | | | Três Lagoas (n=14) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Average | Minimum | Maximum | Average | Minimum | Maximum | Average | Minimum | Maximum |
| Cu | 0.296 | 0.020 | 1.25 | 0.516 | 0.020 | 1.83 | 0.509 | 0.020 | 3.03 |
| Fe | 2.35 | 0.005 | 9.19 | 4.16 | 0.005 | 12.8 | 2.92 | 0.005 | 20.7 |
| Mn | 2.22 | 0.360 | 8.32 | 3.33 | 0.480 | 8.79 | 1.58 | 0.120 | 4.46 |
| Ni | 0.639 | 0.010 | 2.27 | 0.499 | 0.010 | 1.89 | 0.023 | 0.010 | 0.070 |
| Pb | 0.131 | 0.050 | 0.570 | 0.286 | 0.050 | 1.17 | 0.153 | 0.050 | 0.900 |
| Zn | 10.3 | 3.80 | 21.3 | 11.1 | 4.75 | 28.3 | 6.86 | 0.950 | 25.7 |
| Cd | 0.0636 | 0.005 | 0.240 | 0.177 | 0.005 | 0.830 | 0.011 | 0.005 | 0.030 |
| Co | 0.199 | 0.005 | 0.50 | 0.194 | 0.005 | 0.620 | 0.072 | 0.005 | 0.310 |
| Cr | 0.152 | 0.010 | 0.450 | 0.133 | 0.010 | 0.620 | 0.0764 | 0.010 | 0.760 |

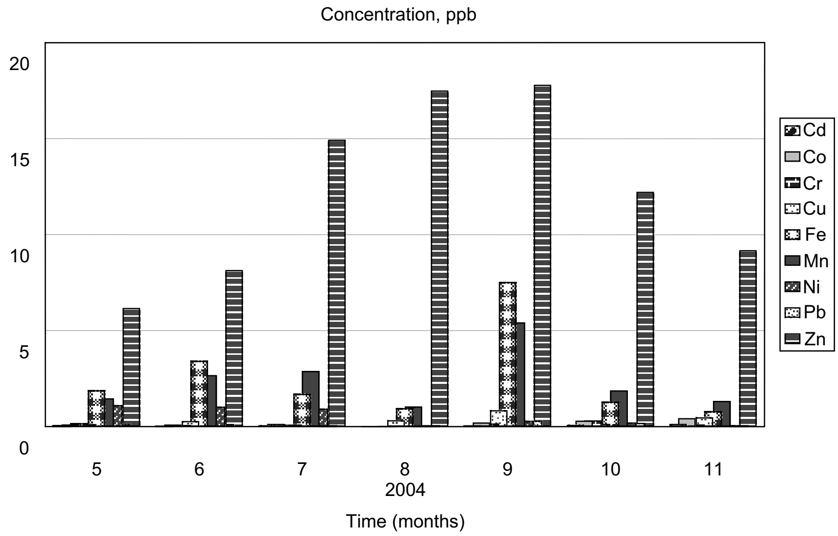


Fig. 4a – Concentration of metallic elements varying with time in wet precipitation at Aceguá – Candiota region (2004).

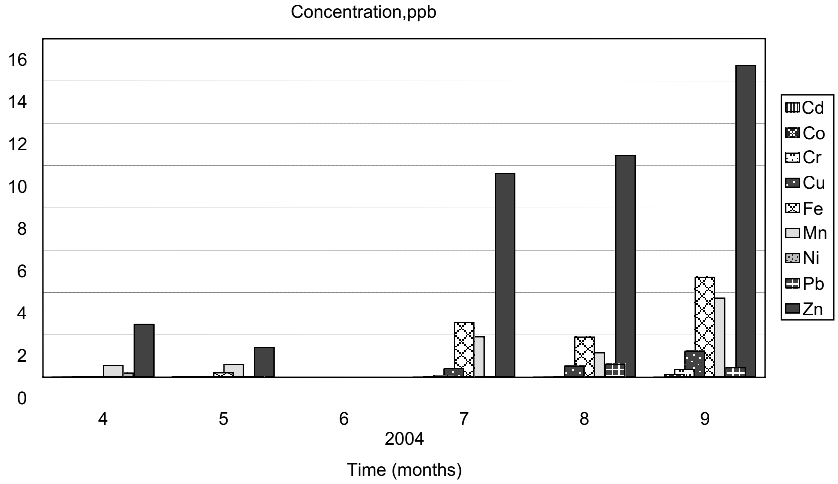


Fig. 4b – Concentration of metallic elements varying with time in wet precipitation at Três Lagoas site – Candiota region (2004).

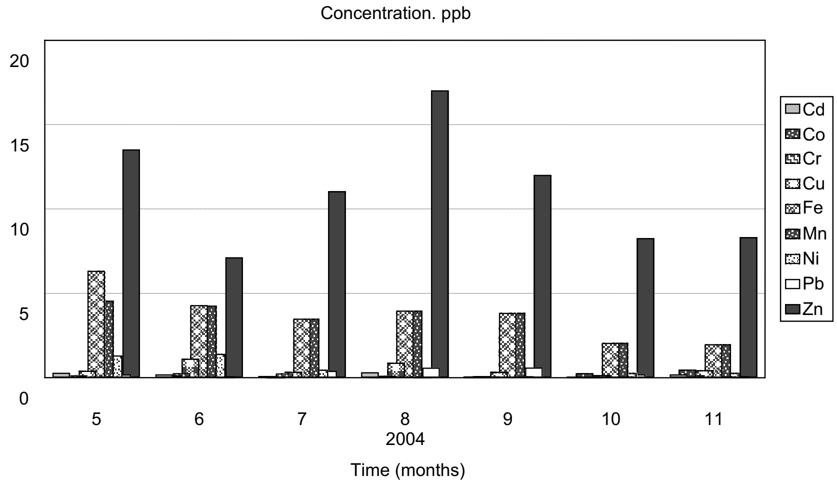


Fig. 4c – Concentration of metallic elements varying with time in wet precipitation at Candiota Airport site – Candiota region (2004).

elements and others which have a major crustal component tend to have a lower solubility, although they show a variable characteristic in the precipitation (Spokes and Jickels 1995). However, the anthropogenic metals tend to show a higher solubility under most of the conditions (Spokes and Jickels 1995), as it is dependent on the type of aerosol and on the pH, important variables controlling solubility.

Zn was the element that showed the highest concentration during the period under study (Figs. 4a, b and c). This data confirm the findings of other studies in Candiota, which report high concentrations of Zn (Migliavacca et al. 2004a). This indicates strong emission of Zn from anthropogenic source (coal fired power plant).

Elements Cu and Zn, removed through precipitation, and their concentrations may depend on the sampling site, as well on collection weather. On rainy days, there was higher solubilization of the elements adsorbed to the fine particles, enhanced also by the acid pH of the rain (pH < 5.6). At the Aceguá and Três Lagoas sites, the highest concentration of the anthropogenic metals occurred during the rainy period in the month of September.

The Correlation of Spearman was applied to the whole set of data of the chemical elements, synthesizing the whole data into three Factors, representing a total variance of 77% of raw data (Table V).

**TABLE V**
**Matrix of factorial loads resulting from varimax rotation applied to wet precipitation samples – Candiota region (2004).**

| Variable | Component | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Cd | 0.166 | 0.383 | **0.650** |
| Co | 0.129 | 0.210 | **0.721** |
| Cr | 0.317 | **0.697** | 0.170 |
| Cu | **0.866** | –0.115 | 0.127 |
| Fe | **0.759** | 0.375 | –0.234 |
| Mn | **0.809** | 0.259 | 0.047 |
| Ni | –0.098 | **0.859** | 0.206 |
| Pb | 0.393 | 0.336 | –0.516 |
| Zn | **0.875** | 0.017 | 0.176 |

Factor 1 was represented by the variables Cu, Zn, Fe and Mn. The elements Cu and Zn are originated in anthropogenic sources and their wet inputs are usually in a dissolved state, especially under pH < 5 values (Migon et al. 1996). Fe and Mn are originated from the soil dust, and show low solubility. Fe and Mn are mainly introduced into the atmospheric aqueous phase by influence of particulate re-suspension of soil particles. About 80% of the total Fe content is present in an atmospheric particulate sample in the form of various oxides (goethite – 60,8%, hematite – 7,5%, magnetite – 9,8%), whereas 10% were found to be present as ionic Fe (III) and 10% were found to be ionic Fe (II) (Hoffmann et al. 1994).

Cu and Zn are available into the atmospheric aqueous phase from the coal burning and enriched in the surface of fine particles such as oxides (volatilization – condensation mechanism) and may easily dissolve in contact with the rain, which doesn't happen to Fe and Mn elements (Swaine and Goodarzi 1995, Clarke and Sloss 1992, Davidson and Clarke 1996).

Fe and Mn can be available in soil dust such as hydroxides, oxyhydroxides, silicates, sulfides, etc., which are less soluble than oxides of elements that are commonly found in anthropogenic emission (Kaya and Tuncel 1997).

Studies have shown that in the rainwater Fe element was particulate, and not soluble in 0.03 M $HNO_3$, implying that Fe-bearing mineral aerosol had not been modified during atmospheric transport, and that very little of the total Fe would be bioavailable (Halstead et al. 2000).

Some authors (Spokes and Jickels 1995), using the critical stability constant, have shown that, while Mn II and Ni II occurred almost entirely as ion hexaqua, Fe can occur in atmospheric droplets as $[Fe(OH)(H_2O)_5]^+$, $[Fe(OH)(H_2O)_4]^+$, and $[Fe(SO_3)(H_2O)_4]^+$, the partition of which is a function of pH.

These same authors (Spokes and Jickels 1995) suggest that the anthropogenic elements Cu, Pb and Zn are controlled by the adsorption/desorption process, when rain water supplies sorption sites on the active surface.

Factor 2 is represented by the variables Cr and Ni. These elements, originating in the coal fired power plant, are adsorbed on the ultra fine particles such as oxides (volatilization – condensation mechanism), probably showing solubility with atmospheric precipitation (Swaine and Goodarzi 1995, Clarke and Sloss 1992, Davidson and Clarke 1996).

The solubility of anthropogenic elements agrees with that reported in various studies, in which the majority classifies Zn as the most soluble. Other elements like Ni, Cr, Cu and Pb, however, are reported to show variable solubility, either high or moderate, and authors refer to a variety of influencing conditions, as pH of the rain and the type of particle these elements are associated to in the atmosphere (Al-Momani et al. 1995, Chester et al. 1993). The solubility of elements is higher in samples of $pH < 5$. However, highly soluble elements are not significantly affected by the pH, because they usually may be soluble in water.

The pH value of the cloud and of the rain drop can be extremely low. In the cloud occurs the oxidation of $SO_2$ and $NO_x$, which can be catalyzed by the transition metals. Falconer and Falconer (1980) reported pH values of rain water below 2.2, and suggest that wet aerosols can show values of up to 0.1 (Zhu et al. 1993). That means that the ultimate pH of the precipitation (between 4 and 6) may not reflect the pH conditions to which the aerosol is subjected in the atmosphere.

Factor 3 is represented by variables Cd and Co. These are elements of anthropogenic origin (burning of coal), and are controlled by the adsorption/desorption process dependent on pH.

### $SO_2$ AND $NO_2$

The area under study is highly influenced by the burning of coal that throws particulate matter in the atmosphere as well as great quantities of acidity generating gases, $SO_2$ and $NO_x$, which contribute to the development of acid rain. These acidity developing gases are dissolved in the clouds, generating sulfuric and nitric acid.

Figure 5 shows the influence of $SO_2$ and $NO_2$ average concentration in relation to the weather (2004) in Candiota. $SO_2$ and $NO_x$ concentration peaks have been reported during spring and summer, while autumn and winter months showed intermediate concentrations. The high concentration in summer may be caused by increased power consumption due to higher temperatures during that season.

Concerning $SO_4^{2-}$ and $NO_3^-$ average concentration in wet precipitation (Fig. 6) the trend is that summer, winter and spring months show peak concentrations. A higher $SO_4^{2-}$ concentration in summer may be partly due to higher temperature and incidence of solar radiation, increasing photochemical activity and especially OH levels (Gupta et al. 2003). Despite July and August being winter months, they have shown atypical high temperatures for the period.

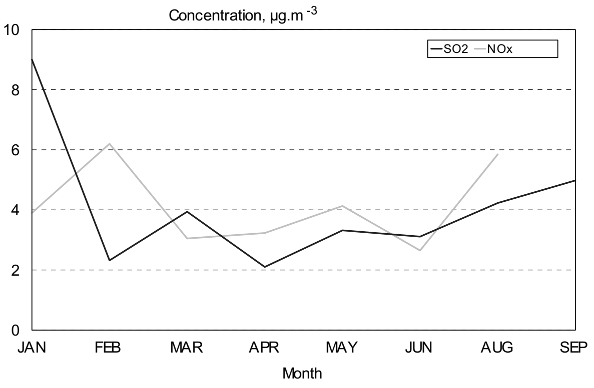


Fig. 5 – Average concentration of $SO_2$ and $NO_2$ in function of time in the Candiota region.

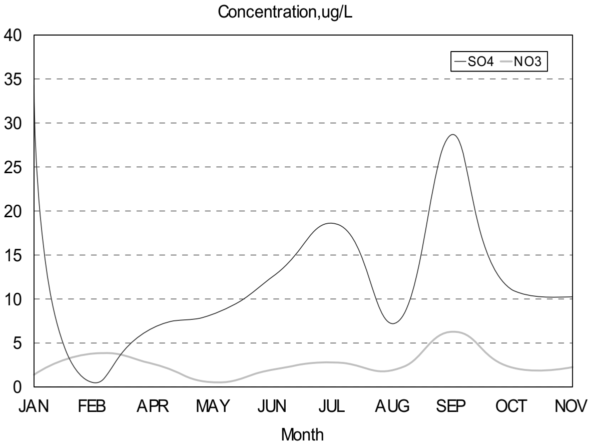


Fig. 6 – Average concentration of $SO_4^{2-}$ and $NO_3^-$ in the wet precipitation in function of time in the Candiota region.

Although gas data in this study are only partial, $SO_2$, $SO_4^{2-}$ and $NO_2$, $NO_3^-$ tend to show a relation among them. The average $SO_2$ concentration was highest amongst other values reported (Table VI), signaling evidence of acid precipitation. This is confirmed by the pH of wet precipitation, whose average value is approximatly 5.5 for the Candiota region.

According to some authors (Igarashi et al. 2006), $SO_2$ in the free troposphere is converted to $SO_4^{2-}$ if cloud processes are involved during transport, and some of the

**TABLE VI**
**Comparison of average concentration of gaseous $SO_2$. $NO_2$ ($\mu$g/m$^3$).**

| Site | $SO_2$ | $NO_2$ | Reference |
|---|---|---|---|
| Candiota | 8.91 | 4.33 | Present study |
| Nguyen; Kim | 3.7 | 7.3 | Gupta et al. 2003 |
| Turkey (coastal ) | 2.03 | – | Erduran and Tuncel 2001 |

sulfate is likely to be removed from the polluted air by precipitation.

$SO_2$ may react with hydroxyl radical in the atmosphere to produce $SO_3^-$, which in turn reacts with water vapor to produce sulfuric acid. $SO_2$ may react with hydroxyl radical in the atmosphere to produce $SO_3^-$, which in turn reacts with water vapor to produce sulfuric acid.

The oxides of nitrogen, $NO_x$ mainly emitted in the atmosphere as NO, which is subsequently transformed into $NO_2$ and other nitrogenous species are very important constituents of air pollution. During daytime the most important source of nitric acid is the reaction of $NO_2$ with hydroxyl radical. During the night $NO_3$ free radical is the source of tropospheric $HNO_3$. $NO_3$ is relatively unimportant during daylight as it is destroyed through its rapid photolysis in sunlight and by its rapid reaction with NO (Stockwell et al. 1997).

Table VI shows $SO_2$ and $NO_2$data compared with other studies. The data showing a higher $SO_2$ concentration reveals the influence of the coal power station.

## CONCLUSIONS

Results showed that over 70% of events had pH values below 5.6 (below the limit for acid rain), and about 15% of them presented pH between 4.5 and 5.0. Thus, it is not unreasonable to say that the pH of the atmospheric precipitation around the area of Candiota is acidified.

The major ions, through the statistical analysis, showed that $NO_3^-$ (Factor1), $F^-$ and $H^+$ (Factor 3), and $SO_4^{2-}$ in both Factors (Factors 1 and 3) characterized the anthropogenic influence, probably originating in the coal fired power plant. $Ca^{2+}$ (Factor 1) is originated, probably, in the limestone mines. Besides, this ion as $NH_4^+$ and K, respectively, might depend on the use of fertilizer or of soil neutralizers (frequently $CaCO_3$), on the soil composition itself, through re-suspension, or on the deposition of the coal plant fly ash. $Cl^-$, $Na^+$ and $Mg^{2+}$ are due to marine influence.

The highest EF in the wet precipitation being represented by $Ca^{2+}$, confirms the strong influence of the limestone mines, earth and dust (particulate matter) on the area.

The wet precipitation tends to easily remove Ni, Pb, Cd, Co, Cr, Cr, Cu and Zn of anthropogenic origin than Fe and Mn elements originated from soil dust. Metals of anthropogenic origin, especially Zn, showed high concentration levels which are controlled by the adsorption/desorption processes and pH. Metals soil dust are mainly associated to minerals and its precipitation removal is essentially pH controlled.

Candiota area shows problems with acid precipitation and the contribution of ions sulfate and metals in the precipitation. This tendency will probably get worse with the implantation of the Candiota III power plant. More ions will be emitted and metals will be adsorbed to ultra fine particulate matter that escapes the control equipment.

The average $SO_2$ and $NO_2$ concentration, as well as $SO_4^{2-}$ and $NO_3^-$ in wet precipitation in the Candiota region showed higher concentrations during the warmer months. Nevertheless, gases should be studied for a longer period to better assess distribution of $SO_2$ and $NO_2$ over the time in relation to ions ($SO_4^{2-}$ and $NO_3^-$) in wet precipitation.

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## RESUMO

O objetivo deste estudo é analisar a composição química da precipitação úmida em amostras coletadas em três estações na região de Candiota no Estado do Rio Grande do Sul (RS) Brasil. Amostras foram coletadas em 2004. Variáveis analisadas na precipitação úmida foram pH, condutividade e concentração de $Cl^-$, $NO_3^-$, $SO_4^{2-}$ $F^-$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $NH_4^+$, Cu, Zn, Fe, Mn, Pb, Ni, Cd, Co e Cr. Distribuição no tempo de $SO_2$ e $NO_2$ também foi avaliada. Resultados mostraram que pH < 5,6 são encontrados em sua maioria no aeroporto de Candiota (85%), seguidos pelo Aceguá (72%) e Três Lagoas (65%). Fator de Enriquecimento dos íons estudados na deposição úmida revelou maior enriquecimento de $Ca^{2+}$ e $SO_4^2$ em Três Lagoas. Análise Fatorial aplicada aos metais e íons maiores permitiu identificação de fontes maiores. Enquanto $Cl^-$, $Na^+$, $Mg^{2+}$ são de origem marinha, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, $F^-$ são provenientes de fontes antropogênicas. Exceto Fe e Mn originários de poeira do solo, os metais estudados mostraram ter influência antropogênica. A média da concentração de $SO_2$ e $NO_2$, bem como $SO_4^{2-}$ e $NO_3^-$ na precipitação úmida na região de Candiota mostrou maiores concentrações durante os meses mais quentes.

**Palavras-chave:** precipitação úmida, metais, análise fatorial.

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