

## RAINWATER CHEMICAL COMPOSITION AND ANNUAL ATMOSPHERIC DEPOSITION IN SOROCABA, (SÃO PAULO STATE), BRAZIL

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**ABSTRACT.** This work evaluated the rainwater chemical composition and the annual atmospheric deposition in Sorocaba, (São Paulo State), Brazil. One sampling point was chosen and forty samples were collected between January and December 2006. The analyses were performed for pH, electrical conductivity, sodium, calcium, potassium, magnesium, sulphate, nitrate, phosphate, alkalinity and chloride. The rainwater pH varied from 5.20 to 6.40, being  $\text{Ca}^{2+}$  the main ion responsible for controlling the rainwater pH. The ionic concentration decreases in the following order:  $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$  for cations and  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{PO}_4^{3-}$  for anions. The annual atmospheric deposition appears to be controlled by the following sources: mining activities and cement factories ( $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ ), agricultural activities ( $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ), soil dust ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$ ) and fossil fuel burning ( $\text{SO}_4^{2-}$ ).

**Keywords:** Sorocaba, rainwater composition, air pollution.

**RESUMO.** Este trabalho avaliou a composição química das águas pluviais e a deposição atmosférica anual na cidade de Sorocaba (SP). Um ponto de amostragem foi escolhido e quarenta amostras foram coletadas entre janeiro e dezembro de 2006. As amostras foram caracterizadas em relação ao pH, condutividade elétrica, sódio, cálcio, potássio, magnésio, sulfato, nitrato, fosfato, alcalinidade e cloreto. O pH das águas de chuva variou entre 5,20 e 6,40, sendo o  $\text{Ca}^{2+}$  o principal íon responsável pelo controle do pH das águas de chuva. A concentração iônica diminui na seguinte ordem:  $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$  para os cátions e  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{PO}_4^{3-}$  para os ânions. A deposição atmosférica anual parece ser controlada pelas seguintes fontes: minerações e fábricas de cimento ( $\text{Ca}^{2+}$  e  $\text{HCO}_3^-$ ), atividades agrícolas ( $\text{K}^+$ ,  $\text{NO}_3^-$  e  $\text{PO}_4^{3-}$ ), poeira de solo ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  e  $\text{HCO}_3^-$ ) e queima de combustíveis fósseis ( $\text{SO}_4^{2-}$ ).

**Palavras-chave:** Sorocaba, composição da água de chuva, poluição atmosférica.

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## INTRODUCTION

Water is one of the most important substances that exists in nature, not only for covering about 70% of the Earth surface, but also for being fundamental for the survival of living beings. Fresh water represents only 3% of the total water in nature, and the remaining 97% are found in oceans and salt seas. From this total, only 0.3% represents the exploitable fresh water. Part of this exploitable resource is confined as groundwater in the phreatic zone and deep aquifers, in the polar ice caps, glaciers and permanent snow and other reservoirs, usually of difficult access. Additionally, the contamination of the springs prevents the use of this fresh water for human consumption, turning this resource even scarcer.

Water is a renewable natural resource through the hydrologic cycle. Evaporation and precipitation can act as a distiller, but many substances arising from air pollution can also be poured in the aquatic medium by the same way. Gases and particulate matter in the atmosphere are dissolved in the raindrops, during condensation (rainout process) and precipitation (the washing of the atmosphere called washout) (Berner & Berner, 1996), and are deposited in the exploitable fresh water reserves. The dissolved substances in rainwater can be divided into three groups: (a) derivatives of marine aerosols; (b) derivatives of terrestrial aerosols (soil dust and biological emissions), and (c) derivatives of anthropic sources (Négre & Roy, 1998).

Many human activities are significant sources of element/compound emissions to the atmosphere, like the burning of fossil fuels, industrial emissions, waste incineration, and agriculture and mining, placing these compounds locally or transporting them for long distances (Molinari et al., 1999). For these reasons, a chemical analysis of the precipitation composition spatial distribution is essential, since it can have important influence in the agriculture, in the water quality of springs and of the reservoirs in hydroelectric plants, preventing problems in electricity supply due to eutrophication. Anthropic changes in the atmospheric system also directly interfere in the trophic status of the system, generating many effects on human health.

Taking into account the anthropic influences, the south and southeast regions of Brazil are considered potentially problematic areas, specially in São Paulo state due to the intense industrial activities. Only some studies have documented the chemical composition variation of the rainwater in these regions of Brazil (Forti et al., 1990; Danelon & Moreira-Nordemann, 1991; Gonçalves et al., 2000; Lara et al., 2001; Mello, 2001; Rocha et al., 2003; Conceição & Bonotto, 2004; Leal et al., 2004; Mello & de Almeida, 2004; Migliavacca et al., 2004, 2005; Fornaro

& Gutz, 2006; Pelicho et al., 2006; Fontenele et al., 2009; Conceição et al., 2010).

Therefore, the purpose of this work is to analyze the rainwater chemical composition and the annual atmospheric deposition in Sorocaba, which is the most important city located at the southeast of São Paulo state. Furthermore, this city presents a recent growth in relation to the number of industries, fossil fuel burning and inhabitants (more than 600,000 inhabitants). The presented results explain how the anthropogenic influences can affect the atmospheric system in Sorocaba, and provide important subsidies for its sustainable development.

## CHARACTERIZATION OF THE STUDY AREA

Sorocaba city belongs to the Sorocaba Middle Tietê hydrographic basin, and is located nearly 90 km at the southeast from the capital city of São Paulo state (S latitude: 23°37' and 23°50'; W longitude: 47°27' and 47°50'), Brazil (Fig. 1). Sorocaba has more than 600,000 inhabitants and approximately 1,500 medium to large-sized industries, which are located near the residential areas. Topographically, Sorocaba average altitude is 600 m with the maximum altitude reaching 1,028 m at the southeast of the municipality. Sorocaba presents a Cwb climate, that is, a hot humid climate with dry winter. The prevailing winds originate from the southeast (SSE) and northeast (WNW) quadrants, respectively, during the dry and rainy period, respectively (IPT, 2005). The average annual temperature is 20°C and during the dry season evaporation is greater than precipitation.

Sorocaba is located partially in the Paraná sedimentary basin, regionally presenting outcrops of the Itararé Subgroup and partially over crystalline basement rocks of the São Roque Domain. The Itararé Subgroup is constituted mainly by glacial sandstones (arkoseans), massif or stratified siltstones and argillites, as well as rithmites, varvites with dropstones and diamictites (IPT, 2005). The São Roque Domain presents low grade metamorphic rocks of the São Roque Group (phyllites and metabasic) and a granitoid complex called Granito Sorocaba (syenogranites) (Godoy, 2003). The region presents three classes of soils, that is, Argisols, Latosols and Cambisols (IPT, 2005).

The average annual precipitation between 1960 and 2004 was 1,493 mm, and January was the rainiest month (the average was 248 mm) and August was the driest month (the average was 43 mm) (Fig. 2a). The rainiest year during this period was 1983 (2,540 mm) and the less rainfall occurred in 1963 (969 mm). According to Figure 2a, the precipitation values in 2006, when this study was carried out, are above the historical monthly average in January, February, April, May, July, October and November, while



**Figure 1** – Map of Sorocaba location highlighting the sampling point of rainwater and minings and cement factories located at the southeast of this city.

the values below the average occurred in March, June, August, September and December in this same year. Besides, the total precipitation in 2006 was 1,559 mm, that is, a value that is only 4% superior than the historical annual average.

The frequency distribution for precipitation values with 5, 20, 50, 80 and 95% of occurrence probability based on the historical data from 1960 to 2004 can be viewed in Figure 2b. For 5%, corresponding to a 20 year recurrence period (TR), we can find the value 428, 244 and 355 mm by month for January, June and December, respectively. In contrast, for 95% of probability (1 year TR) the values 57, <1 and 108 mm by month for January, June and December, respectively. Thus, we can conclude that despite the observed variations in 2006, this year presented the majority of the precipitation values within the 20 and 80% (5 and 1.25 year TR, respectively) of occurrence ranges and near to the historical precipitation average in Sorocaba, considering the 1960 to 2004 data.

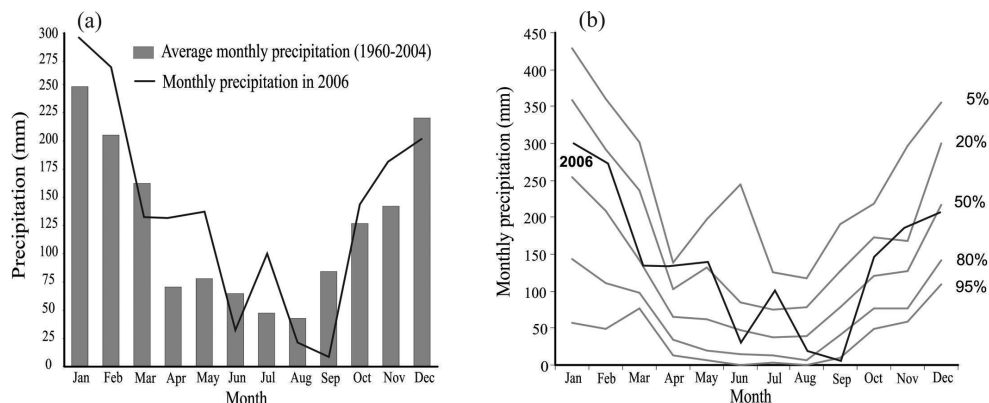
Average annual Sorocaba river discharge between 1960 and 2004 was 12.7 m<sup>3</sup>/s. The year 1983 presented the highest river discharge (36.3 m<sup>3</sup>/s), corresponding exactly to the year with the highest precipitation. The year 1969 presented the lowest average discharge (6.18 m<sup>3</sup>/s). The months with the highest and lowest average discharges are October (13.6 m<sup>3</sup>/s) and May (11.2 m<sup>3</sup>/s) (Fig. 3a), respectively. In spite of presenting a precipitation slightly higher than the historical average in 2006, the monthly average discharge of Sorocaba river in this same year

was 11.7 m<sup>3</sup>/s, a value lower than the historical average, and only October and December presented values higher than the historical monthly average (Fig. 3a). This is due the damming of the Sorocaba river water in the Itupararanga reservoir, located upstream the Sorocaba city, controlling the water flow to the Sorocaba urban area. Figure 3b presents the Sorocaba river permanence curve created from the frequency diagram resulted from the annual average values between 1960 and 2004. For each duration, we can note the corresponding discharge probability being equalized or exceeded. We can observe that Sorocaba river has between 10 and 15 m<sup>3</sup>/s discharge in approximately 25 to 60% of the time. Also, the 12.7 m<sup>3</sup>/s annual average discharge has an occurrence probability around 40% of the time.

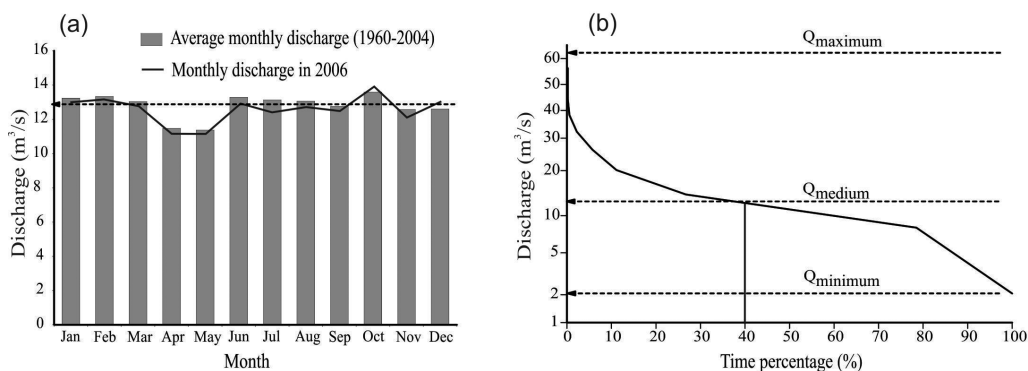
## METHODOLOGY

### Sampling

The methodological approach used in this work aimed to evaluate the rainwater chemical composition and the annual atmospheric deposition at a sampling point at Universidade Estadual Paulista (UNESP), Campus Experimental de Sorocaba, which is approximately 3 km away from downtown Sorocaba and from the industrial district (Fig. 1). The choice of the sampling location was due to its distance from the he pollution sources, to the wind direction and to logistics. The sampling interval occurred from 20<sup>th</sup> of January, 2006 to 20<sup>th</sup> of December, 2006, when 40 total



**Figure 2** – Average monthly precipitation between 1960 and 2004 and monthly precipitation in 2006 in Sorocaba (a); relative frequency distribution with equalized or exceeded monthly rain value between the same years according to the indicated probability (b) (CBA, 2007).



**Figure 3** – Average monthly discharge of Sorocaba river between 1960 and 2004 and average monthly discharge in 2006 (a); Sorocaba river permanence curve between the same years (b) (CBA, 2007).

deposition samples (humid + dry) were collected, without pre-defining the time interval among the collections. The collected samples corresponded to a single precipitation event that generated a minimum volume of 500 mL, which was enough to carry out all chemical analyses. In less than 12 hours after the precipitation event conclusion, the rainwater samples were transferred and stored in 500 mL polyethylene bottles (Nalgon).

A bulk collector with a 22 cm diameter polyethylene funnel attached to a 2 L polyethylene container fixed at 2 m from the soil. The funnel was covered with a nylon mesh to avoid the contamination (leaves, insects, etc.). After each collection, the collector was washed from two to three times with distilled and deionized water. The rain volume was recorded to subsequently calculate the volume weighted average (VWA) concentrations using Equation 1:

$$C_E = \frac{\sum_{i=1}^n C_i \cdot V_i}{\sum_{i=1}^n V_i} \quad (1)$$

where:

$C_E$  = weighted average of  $E$  (mg/L) parameter;

$C_i$  = parameter concentration in the  $i^{\text{th}}$  sample (mg/L);

$V_i$  = total volume of rain during the event preceding the  $i^{\text{th}}$  sample collection (mm).

### Chemical analyses

The electrical conductivity ( $\mu\text{S}/\text{cm}$ ) and hydrogenionic potential (pH) measurements were carried out using direct reading equipments at the sampling local on unfiltered samples, with YSI equipments, models YSI 85 and YSI 100, respectively. The pH electrode is a combined one and the highest purity standards used for calibration were: pH 4.00 ( $4.005 \pm 0.010$  at  $25^\circ\text{C} \pm 0.2^\circ\text{C}$ ) and 7.00 ( $7.000 \pm 0.010$  at  $25^\circ\text{C} \pm 0.2^\circ\text{C}$ ). The conductivitymeter was calibrated with the standard KCl solution of known conductivity (1.0 mmol/L), that is,  $147 \mu\text{S}/\text{cm}$  at  $25^\circ\text{C}$ .

The rainwater samples, stored in polyethylene bottles, were taken to the Laboratório de Geoquímica Ambiental (LAGEA) of the Departamento de Engenharia Ambiental of UNESP in Sorocaba

(SP), and in the same day they were filtered using Millipore membranes with a 0.45  $\mu\text{m}$  pore diameter size, to determine the following chemical parameter: alkalinity, chloride, sulphate, phosphate and nitrate. In another bottle, the rainwater samples were first filtered through the same membrane, and conserved with  $\text{HNO}_3$  ( $\text{pH} > 2$ ) in order to quantify the content of sodium, potassium, calcium and magnesium.

The alkalinity was determined by titration with 0.01 N sulphuric acid and concentration between 1 and  $500 \pm 0.2$  mg/L. The content of sulphate (turbidimetric method of barium sulphate, from 1 to  $70 \pm 0.6$  mg/L), phosphate (ascorbic acid method, from 0.02 to  $2.5 \pm 0.01$  mg/L) and nitrate (cadmium reduction method, from 0.1 to  $10 \pm 0.3$  mg/L) were quantified by a *Hach Company DR 2800* spectrophotometer (Hach, 1992). Sodium, potassium, calcium and magnesium were quantified by atomic absorption spectrometry (AAS – *Varian 240-FS*), with the following detection limits:  $\text{Ca}^{2+}$  – 0.05 mg/L,  $\text{Na}^+$  and  $\text{K}^+$  – 0.02 mg/L and  $\text{Mg}^{2+}$  – 0.01 mg/L. For the chloride determinations, the potentiometric method ( $0.1$  to  $100 \pm 0.02$  mg/L) was used, with an *Orion model 94-17B* ion sensitive electrode and an *Orion model 90-02* reference electrode (double junction) and the *Analion model IA-601* analyzer.

**Result validation and statistical analyses**

The used criterion to control the quality of the obtained results for the Sorocaba rainwater was based on the ionic mass balance and on the comparison between the measured and calculated conductivity. The mass balance ( $\Delta Ion$ ) was calculated according to Equation 2, and the calculated conductivity of each rainwater sample was obtained using Equation 3. From the total forty quantified precipitation events, four events were discarded, as they showed an ionic balance greater than 25%, according to the suggested criterion for samples presenting ionic strength greater than  $100 \mu\text{eq/L}$  (Mosello et al., 1996). After discarding, all remaining samples presented a percentage difference between the measured and calculated conductivities smaller than 50%, for the conductivities calculated with values up to  $30 \mu\text{S/cm}$ , and not rejecting any other sample using this criterion (Migliavacca et al., 2004).

$$\Delta Ion \text{ (in \%)} = \frac{[(\Sigma_{cations} - \Sigma_{anions}) \cdot 100]}{(\Sigma_{cations} + \Sigma_{anions})} \quad (2)$$

where:  $\Sigma_{cations} = [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Na}^+] + [\text{Mg}^{2+}] + [\text{K}^+]$   
 $\Sigma_{anions} = [\text{HCO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$

$$k = \Sigma c_i \cdot \Lambda_i^o \quad (3)$$

where:

$k$  = calculated conductivity ( $\mu\text{S/cm}$ );

$c_i$  = ionic concentration of the  $i^{\text{th}}$  ion (mmol/L);

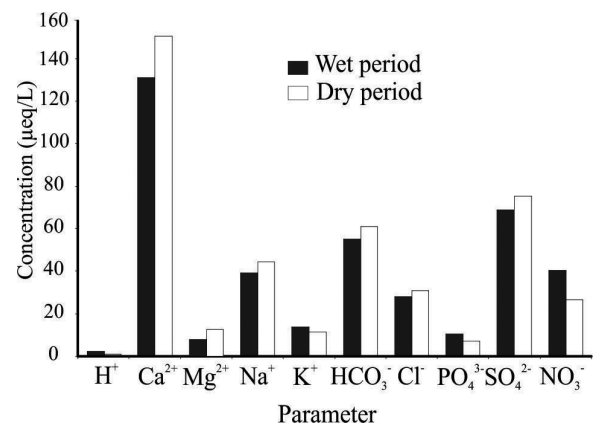
$\Lambda_i^o$  = molar ionic conductance of the  $i^{\text{th}}$  ion ( $\text{S/cm}^2/\text{mol}$ ) in an infinite dilution at  $25^\circ\text{C}$ .

To obtain the correlations and the factor analysis (using the principal component method) among the quantified parameters in this work, the *Statistica for Windows 4.3™* software was used. The Pearson linear correlation analysis is a statistical method frequently used to identify the behaviour of a variable in relation to other and allows checking if the variables are dependent or independent. The factor analysis is a statistical method that allows identifying the main emission sources and also working with large variable groups with distinct units.

**RESULTS AND DISCUSSION**

**Ionic composition**

Table 1 presents the analysis results of the physical-chemical and chemical parameters of the Sorocaba rainwater collected during 2006. The rain period was established from October to March and the dry period from April to September (Fig. 2a). The ionic concentration variation in the rainy and dry periods is shown in Figure 4. The electrical conductivity results were practically constant during all year, with  $23.3 \mu\text{S/cm}$  volume weighted average (VWA), and the greater and smaller volume weighted average values were in the rainy ( $24.0 \mu\text{S/cm}$ ) and dry ( $21.7 \mu\text{S/cm}$ ) periods, respectively.



**Figure 4** – Concentration variation of the inorganic ions in Sorocaba rainwater in the dry and rainy periods during 2006. The values were calculated based on the volume weighted averages of each period.

The pH values of the samples collected in Sorocaba vary between 5.20 and 6.40, and the greatest values were obtained in the rainy period. The pH VWA, calculated from the VWA concentrations of  $\text{H}^+$ , was 5.90 for Sorocaba, indicating a free acidity

**Table 1** – Rainwater chemical composition in Sorocaba ( $\mu\text{eq/L}$  concentration,  $n = 36$ ).

Parameter	VWA <sup>1</sup>	Minimum	Maximum	Dry period <sup>3</sup>	Rainy period <sup>4</sup>
Conductivity <sup>2</sup>	23.3	15.0	30.0	21.7	24.0
pH	5.9	5.2	6.4	5.6	6.1
H <sup>+</sup>	1.3	6.0	0.4	2.8	0.8
Ca <sup>2+</sup>	141.0	32.5	299.0	130.0	154.0
Mg <sup>2+</sup>	11.4	3.3	18.7	7.4	12.1
Na <sup>+</sup>	43.3	4.3	72.2	38.0	45.4
K <sup>+</sup>	12.3	7.7	53.8	14.1	10.9
HCO <sub>3</sub> <sup>-</sup>	60.3	24.5	88.2	56.3	61.2
Cl <sup>-</sup>	31.2	18.5	67.7	27.4	33.1
PO <sub>4</sub> <sup>3-</sup>	8.4	3.4	23.1	10.0	6.4
SO <sub>4</sub> <sup>2-</sup>	70.9	20.8	158.0	67.3	76.1
NO <sub>3</sub> <sup>-</sup>	33.4	14.2	74.3	39.7	29.7
$\Sigma$ of cations	209.3	—	—	192.3	223.2
$\Sigma$ of anions	204.2	—	—	200.7	206.5

<sup>1</sup> Volume weighted average for 2006. <sup>2</sup>  $\mu\text{S/cm}$ . <sup>3</sup> Volume weighted average for the dry period.

<sup>4</sup> Volume weighted average for the rainy period.

of 1.25  $\mu\text{eq/L}$ . The 5.6 pH value for “clean” rainwater is a function of the partial solubilization of the carbon dioxide ( $\text{CO}_2$ ) and by the partial dissolution equilibrium of the formed carbonic acid ( $\text{H}_2\text{CO}_3$ ). However, the pH lower limit for rainwater acidified by natural processes corresponds to 5.0 (Galloway et al., 1982). For Sorocaba, there were not pH values lower than 5.0.

Although there is not the determination of ammonium ion ( $\text{NH}_4^+$ ), Table 1 also shows, based on the VWA concentrations, that the sum of cations ( $\Sigma$  of cations) and of anions ( $\Sigma$  of anions) analyzed in the rainwater was 209.3  $\mu\text{eq/L}$  and 204.2  $\mu\text{eq/L}$ , respectively. With these values, we can note that the sum of cations was greater than the sum of anions in Sorocaba, and this relation has already been observed in other areas when only the inorganic ions are analyzed (Galloway et al., 1982; Moreira-Nordemann et al., 1997; Lara et al., 2001; Conceição & Bonotto, 2004). However, in the dry period, the VWA sum of anions (200.7  $\mu\text{eq/L}$ ) is greater than the VWA sum of cations (192.3  $\mu\text{eq/L}$ ).

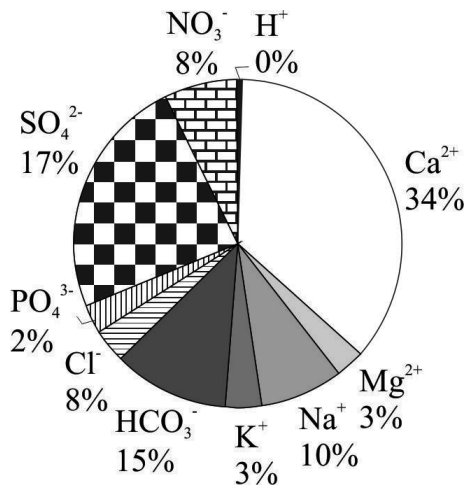
Sorocaba city is located at the southeast region of Brazil, in São Paulo state, with the Atlantic Ocean situated to the East, and it is around 100 km far from the ocean. Thus, the rainwater samples should present a smaller influence of sea salt on their chemical composition in relation to the coastal areas, due the distance of the collecting sites from the sea. This fact is demonstrated by the smaller values of the VWA concentrations of  $\text{Na}^+$ , that is, 43.3  $\mu\text{eq/L}$ , when compared to the values obtained for Ilha Grande (RJ) – 142.2  $\mu\text{eq/L}$  (Souza et al., 2006), Niterói

city (RJ) – 62.6  $\mu\text{eq/L}$  (Mello, 2001) and Cubatão city (SP) – 82.0  $\mu\text{eq/L}$  (Danelon & Moreira-Nordemann, 1991).

Furthermore, the ionic ratios ( $\mu\text{eq/L}$ ) found in this work, except the  $\text{Cl}^-/\text{Na}^+$  ratio, also confirm the little marine influence ( $\text{Ca}^{2+}/\text{Na}^+ = 3.26$ ;  $\text{Mg}^{2+}/\text{Na}^+ = 0.26$ ;  $\text{K}^+/\text{Na}^+ = 0.28$ ;  $\text{Cl}^-/\text{Na}^+ = 0.72$ ;  $\text{SO}_4^{2-}/\text{Na}^+ = 1.64$  and  $\text{HCO}_3^-/\text{Na}^+ = 1.39$ ) in relation to the rainwater collected near the ocean ( $\text{Ca}^{2+}/\text{Na}^+ = 0.04$ ;  $\text{Mg}^{2+}/\text{Na}^+ = 0.23$ ;  $\text{K}^+/\text{Na}^+ = 0.02$ ;  $\text{Cl}^-/\text{Na}^+ = 1.16$ ;  $\text{SO}_4^{2-}/\text{Na}^+ = 0.12$  and  $\text{HCO}_3^-/\text{Na}^+ < 0.01$ ) (Wilson, 1975). With the same exception, the other ratios are also greater than the ratios presented by Danelon & Moreira-Nordemann (1991) for Cubatão city (SP), and they reflect the introduction of terrestrial or anthropic elements and compounds in the chemical composition of the Sorocaba rainwater.

Table 1 indicates that there is a great variation in the ionic concentration, and the  $\text{H}^+$  and  $\text{Na}^+$  ions are the ions which presented greater variability in Sorocaba. The VWA concentrations indicated that  $\text{Ca}^{2+}$  (67% of the total cation sum) and  $\text{SO}_4^{2-}$  (35% of the total anion sum) are the most abundant ions found in the rainwater in Sorocaba, indicating the following tendency:  $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$  for cations and  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{PO}_4^{3-}$  for anions (Table 1). As we can see in Figure 5, the content of  $\text{Ca}^{2+}$  in the rainwater in Sorocaba represents more than 34% of the sum of all elements and compounds analyzed in this work, suggesting that it is controlling this rainwater pH, as the presence of this ion plays an important role in controlling the rainwater pH (Manahan, 1994).

Correlation statistical tests (Table 2) did not indicate that there is correlation among the VWA concentrations of  $H^+$  with any cation or anion, indicating that the analyzed ions must be conditioning the pH values, besides the possible organic acids and ammonia ( $NH_3$ ) that were not quantified in this work.



**Figure 5** – Percentage distribution of the inorganic ions in Sorocaba rainwater. The values were calculated based on the VWA concentrations.

There were not correlation among the other cations or anions (Table 2), and only the correlations between  $K^+$  and  $PO_4^{3-}$  ( $r = 0.88$  and  $P \leq 0.01$ ),  $K^+$  and  $NO_3^-$  ( $r = 0.82$  and  $P \leq 0.01$ ) and  $PO_4^{3-}$  and  $NO_3^-$  ( $r = 0.86$  and  $P \leq 0.01$ ) were found for the collected samples in Sorocaba. The greatest weighted average values of  $K^+$ ,  $PO_4^{3-}$  and  $NO_3^-$  were obtained in the rainy period, when there is a greater concentration of these ions in the rainwater of Sorocaba city (Table 1). Table 3 presents the results of the factor analysis applied to the original data of each parameter measured in this work, indicating that the adjustment for five factors explains 94.40% of the total variance for Sorocaba, with the variables grouped in the same factor, only altering the total variance of factor, that is,  $Ca^{2+}$  (24.90%);  $K^+$ ,  $PO_4^{3-}$  and  $NO_3^-$  (20.40%);  $Mg^{2+}$ ,  $Na^+$  and  $HCO_3^-$  (18.00%);  $Cl^-$  (15.70%) and  $SO_4^{2-}$  (15.40%).

**Cation and anion annual deposition**

The annual atmospheric depositions were obtained multiplying the VWA concentration of each ion by the total precipitation that occurred between January and December in 2006, that is, 1,559 mm. Table 4 presents the annual deposition results in different Brazilian regions, which refer to different years of sampling, but all years comprise at least one complete hydrologic cycle. It is worth highlighting that it was used the wet only sampling in almost all places presented in Table 4, that is, only humid

deposition, and the exceptions are the bulk samples carried out in Campo Grande and Rio Claro, as in this work. Thus, a relative comparison among the results was carried out in order to obtain information about the different influences that exist in rainwater in Sorocaba.

$Ca^{2+}$  is associated to the first factor of the main factor analysis. Apart from Rio Claro, the greatest  $Ca^{2+}$  annual depositions occurred in Sorocaba. The high  $Ca^{2+}$  annual depositions in Rio Claro were attributed to the intense activities of the civil construction that occur in this city (Conceição & Bonotto, 2004). The first explanation for the high  $Ca^{2+}$  atmospheric depositions in Sorocaba would be the  $CaCO_3$  dissolution ( $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ ) deriving from the limestone region soil dust, as it is already described in other areas (Moreira-Nordemann et al., 1997; Lara et al., 2001). The second explanation for the  $Ca^{2+}$  inflow can be attributed to the particulate matter spread in the atmosphere resulting from the largest limestone minings and cement factories of Brazil which are located at the southeast of Sorocaba city (Fig. 1). The  $CaCO_3$  dissolution derived from these anthropic activities in the atmosphere explains the high  $Ca^{2+}$  VWA concentrations (Table 1), mainly in the rainy period due the prevailing direction of the WNW wind, that in turn play an important role as a rainwater pH controller in Sorocaba.

The second variable group found by the main factor analysis is formed by  $K^+$ ,  $PO_4^{3-}$  and  $NO_3^-$ . Among the discussed cities, the greatest  $K^+$  annual atmospheric depositions were in Candiota due the biomass burning (Migliavacca et al., 2004), followed by Manaus and Sorocaba. The  $NO_3^-$  annual atmospheric deposition values were only smaller than the values found for Rio Claro and Candiota. The  $NO_3^-$  atmospheric inflow in Rio Claro occurs due the sugar cane burning, and it corresponds to a  $1 \times 10^5$  tons of organic matter or  $5 \times 10^4$  tons of C for the atmosphere in the period of drought (Lara et al., 2001). In Candiota in contrast, the use of coal in a thermoelectric plant is the main responsible for the elevated  $NO_3^-$  annual deposition values (Migliavacca et al., 2004). In relation to  $PO_4^{3-}$ , the values obtained in this work are higher than Manaus values and lower than Rio Claro values, and this value was attributed to the use of phosphate fertilizers (Conceição & Bonotto, 2004). In Sorocaba there is not burning, and the high annual atmospheric depositions of these elements and compounds can be attributed to the intense agriculture activity which applies NPK fertilizers (where  $N = NH_4Cl$  and  $(NH_4)_2HPO_4$ ,  $P = (NH_4)_2HPO_4$  and  $K = KCl$ ) (Fig. 1), mainly in the Itupararanga reservoir region, located at the southeast of Sorocaba, near the minings and cement industries. This fact is confirmed by the correlations presented in Table 2.

**Table 2** – Correlation ( $P \leq 0.01$ ) among all parameters obtained for rainwater in Sorocaba.

	H <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>
H <sup>+</sup>	1.00									
Ca <sup>2+</sup>	0.12	1.00								
Mg <sup>2+</sup>	-0.23	-0.15	1.00							
Na <sup>+</sup>	-0.35	0.06	0.45	1.00						
K <sup>+</sup>	-0.11	0.04	0.52	-0.02	1.00					
HCO <sub>3</sub> <sup>-</sup>	-0.09	-0.29	-0.45	0.01	0.01	1.00				
Cl <sup>-</sup>	-0.14	-0.29	-0.35	-0.11	-0.19	-0.47	1.00			
PO <sub>4</sub> <sup>3-</sup>	-0.20	-0.33	-0.21	-0.24	0.88	0.36	0.39	1.00		
SO <sub>4</sub> <sup>2-</sup>	0.03	-0.07	-0.49	0.17	-0.28	-0.34	0.53	0.59	1.00	
NO <sub>3</sub> <sup>-</sup>	0.56	-0.17	-0.52	0.21	0.82	0.29	0.38	0.86	0.25	1.00

**Table 3** – Main factor analysis among all parameters obtained for rainwater in Sorocaba.

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Ca <sup>2+</sup>	0.86	0.34	0.03	-0.18	-0.21
Mg <sup>2+</sup>	0.11	0.15	0.95	0.27	0.13
Na <sup>+</sup>	0.14	-0.42	0.87	0.12	-0.18
K <sup>+</sup>	-0.09	0.79	0.26	0.08	0.17
HCO <sub>3</sub> <sup>-</sup>	0.12	-0.21	0.68	-0.02	-0.24
Cl <sup>-</sup>	-0.25	0.20	-0.34	0.97	0.13
PO <sub>4</sub> <sup>3-</sup>	0.05	0.98	0.21	-0.07	-0.10
SO <sub>4</sub> <sup>2-</sup>	-0.06	0.16	0.18	0.39	0.92
NO <sub>3</sub> <sup>-</sup>	0.01	0.90	-0.11	0.09	0.01
Total variance (%)	24.90	20.40	18.00	15.70	15.40

**Table 4** – Cation and anion annual atmospheric deposition (ton/km<sup>2</sup>/year) in some Brazilian regions.

Ion	Manaus <sup>a</sup>	Rio Claro <sup>b</sup>	Piracicaba <sup>c</sup>	Campo Grande <sup>d</sup>	Cubatão <sup>e</sup>	Londrina <sup>f</sup>	Candiota <sup>g</sup>	Sorocaba
Ca <sup>2+</sup>	0.13	10.42	0.12	0.24	—	—	2.06	4.39
Mg <sup>2+</sup>	0.03	1.12	0.03	0.04	—	—	0.34	0.21
Na <sup>+</sup>	0.15	1.52	0.07	0.26	5.06	0.19	1.97	1.55
K <sup>+</sup>	0.90	0.41	0.13	0.24	—	0.04	1.20	0.75
HCO <sub>3</sub> <sup>-</sup>	—	2.24	—	—	—	—	—	5.73
Cl <sup>-</sup>	0.45	3.46	0.28	1.00	12.39	0.71	3.75	1.72
PO <sub>4</sub> <sup>3-</sup>	<0.01	0.55	—	—	—	—	—	0.42
SO <sub>4</sub> <sup>2-</sup>	0.26	3.46	0.99	0.48	7.54	1.07	7.97	5.31
NO <sub>3</sub> <sup>-</sup>	0.72	7.09	1.11	0.79	1.99	1.06	4.02	3.23

<sup>a</sup>Williams & Fisher (1997). <sup>b</sup>Conceição & Bonotto (2004). <sup>c</sup>Lara et al. (2001). <sup>d</sup>Moreira-Nordemann et al. (1997).

<sup>e</sup>Danelon & Moreira-Nordemann (1991). <sup>f</sup>Pelicho et al. (2006). <sup>g</sup>Migliavacca et al. (2004).

The inland water quality reported by CETESB (CETESB, 2008) shows that the Sorocaba river basin fluvial waters, even on their headstreams, always had high content of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> (above the allowed value for Class 4), and these values are attributed to

the anthropic input related to the use and occupation of the soil in this basin. However, the high rates obtained for the K<sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> annual atmospheric deposition indicate that a large part of the concentration of these elements/compounds in the



Sorocaba river basin fluvial waters must be from rainwater, that, in turn, is already polluted. Thus, the  $K^+$ ,  $PO_4^{3-}$  and  $NO_3^-$  atmospheric inflow is also contributing to the eutrophication process of the Itupararanga reservoir, an important water spring for approximately 1,000,000 inhabitants that live in the Sorocaba region.

The third variable group of the main factor analysis is formed by  $Mg^{2+}$ ,  $Na^+$  and  $HCO_3^-$ . In Table 4 we can note that the  $Mg^{2+}$  annual atmospheric deposition was smaller only than the depositions in Rio Claro and Candiota. The greatest  $Na^+$  annual atmospheric deposition occurred in Cubatão, a fact already expected, as Cubatão is closer to the Atlantic Ocean, and the prevailing marine origin of  $Na^+$  (Moreira-Nordemann & Girard, 1996). In relation to the  $HCO_3^-$  annual atmospheric deposition, in contrast, Sorocaba presents the greatest values in comparison to Rio Claro. The first explanation for the high  $HCO_3^-$  annual depositions can also be the  $CaCO_3$  dissolution emitted to the atmosphere by the limestone mining and cement manufacture activities. But, there was not correlation between  $Ca^{2+}$  and  $HCO_3^-$  (Table 2), indicating that the suggested sources must not be the main  $CO_3^{2-}$  sources for the Sorocaba rainwater. Therefore, the explanation for the  $HCO_3^-$ ,  $Mg^{2+}$  and  $Na^+$  annual atmospheric depositions is associated to the dust of the soils derived from the alteration of the sedimentary, magmatic and metamorphic rocks in this area.

The  $Cl^-$  is associated to the fourth factor of the main factor analysis. The  $Cl^-$  annual atmospheric depositions in Sorocaba are smaller than the depositions in Rio Claro, Cubatão and Candiota, where the  $Cl^-$  atmospheric inflow is attributed to the same  $SO_4^{2-}$  sources. Besides, the greatest atmospheric deposition rate found in Cubatão for  $Cl^-$  is related to the strong marine influence of this anion, as it is also demonstrated for  $Na^+$  (Danelon & Moreira-Nordemann, 1991). The values found for the  $Cl^-$  annual atmospheric depositions in Sorocaba can be explained by the marine input and by many anthropic pollution sources, like the fossil fuel burning, charcoal plants and the combustion or decomposition of chloro-organic compounds (Sanusi et al., 1996; Conceição & Bonotto, 2004; Pelicho et al., 2006).

Finally, the fifth factor of the main factor analysis is associated to  $SO_4^{2-}$ . The  $SO_4^{2-}$  annual atmospheric depositions in Sorocaba were greater than the depositions in Manaus, Rio Claro, Piracicaba, Campo Grande and Londrina and smaller than the depositions in Candiota and Cubatão, the cities where there were high annual depositions due the extensive fossil fuel burning in thermoelectric plants (Migliavacca et al., 2004) and industries (Danelon & Moreira-Nordemann, 1991), which are the main and permanent  $SO_x$  sources, that is removed as  $H_2SO_4$  by the rainwater. The  $SO_x$  annual depositions in Sorocaba can be attributed

to natural (pyrite oxidation –  $FeS_2$  in limestones, producing  $SO_2$  or sulphate particles) or anthropic factors. The cement production process that uses coking coal in the furnaces can explain the elevated  $SO_4^{2-}$  levels found in Sorocaba rainwater, as there are  $SO_2$  emissions from this fossil fuel burning for the calcination of limestone. The diesel burning from the trucks that circulate in the mining internal area and on the roads accessing the mining can also be contributing to increase the  $SO_4^{2-}$  annual atmospheric depositions. Furthermore, Sorocaba has approximately 1,500 medium to large-sized industries, which can also contribute to the  $SO_x$  emission and, consequently, the annual depositions of this compound.

## CONCLUSIONS

The solid, liquid and gas materials present in the atmosphere can chemically modify the rainwater and, consequently, change the quality of surface and groundwater and soils. The results of the rainwater analyses of Sorocaba city showed a pH variation between 5.20 and 6.40 (5.90 for VWA), corresponding to a free acidity of 1.25  $\mu eq/L$ . In contrast, the VWA conductivity was 23.3  $\mu S/cm$ , and the greatest values were obtained during the rainy period. The ionic concentrations ( $\mu eq/L$ ) decreased in the following order:  $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$  for cations and  $SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > PO_4^{3-}$  for anions. The  $Na^+$  VWA concentrations were smaller than the values obtained for the oceanic regions located at the Brazilian southeast. The  $Ca^{2+}$  and  $HCO_3^-$  annual atmospheric depositions occur due the  $CaCO_3$  dissolution ( $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ ) in the atmosphere, possibly deriving from the limestone mining and cement factory activities. Furthermore, the high  $Ca^{2+}$  VWA concentrations associated to the wind direction play an important role as a rainwater pH controller in Sorocaba. Dust of soils derived from the sedimentary, magmatic and metamorphic rocks found in Sorocaba is responsible for the  $Mg^{2+}$ ,  $Na^+$  and  $HCO_3^-$  annual depositions. The elevated values obtained for the  $SO_4^{2-}$  annual atmospheric deposition can be attributed to the coking coal burning in the furnaces during the cement production and to the diesel from the trucks that circulate in the mining internal area and on the roads accessing the mining, and also to the industries located in Sorocaba. The dust from agriculture soils, where the phosphate fertilizers are used, can be the mainly responsible for the high atmospheric deposition rates of  $K^+$ ,  $NO_3^-$  and  $PO_4^{3-}$ , that should intensify the eutrophication process of the Sorocaba river basin fluvial waters, mainly in the Itupararanga reservoir, that supplies nearly 1,000,000 inhabitants of this important inland region of the São Paulo state.

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