publicado em: Fresenius Environmental Bulletin 6(9/10) 508-513, 1997

A PRELIMINARY STUDY OF THE ANTHROPOGENIC CONTRIBUTION TO SÃO PAULO RAINFALL

R.P. Paiva[1], M.A.F. Pires[1], C.S. Munita[1], M.F. Andrade[2], F.L.T. Gonçalves[2], O. Massambani[2]
[1]Instituto de Pesquisas Energéticas e Nucleares-CNEN/SP,
C.P. 11049, CEP 05422-970, São Paulo, SP, Brasil
[2]Instituto Astronômico e Geofísico - USP
C.P. 9638, CEP 01065-904, São Paulo, SP, Brasil

SUMMARY. Rainwater samples were collected and analyzed to provide information about its composition and contamination. The samples have being collected since September 1993. Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-} contents were determined in rainwater samples. Surface meteorological information are also being analyzed to interpret the information regarding the characteristics of Sao Paulo rain chemistry. This study suggests that the precipitation is strongly influenced by anthropogenic and marine sources.
Key words: Precipitation, rain water contamination, air pollution, ionic species, acidity.

INTRODUCTION

The acid precipitation, in several regions of the world, is an atmospheric contamination, mainly due to anthropogenic activity. The rainwater composition depends on the pollutant load on the atmosphere and on meteorological conditions, such as type, rainfall rate, wind direction and season of the year. The city of São Paulo is located 80 km away from the Atlantic Ocean and is 700 to 900 m high. The topography of the city is complex and the air flux is strongly influenced by local conditions.

The weather in the São Paulo Metropolitan Area (SPMA) presents a dry winter and a wet summer. August precipitation (winter month) is about 40 mm, while February (summer month) precipitation is about 200 mm. The winds blow predominantly from the northwest to southeast and from the southeast to northwest during the afternoon, due to the sea breeze circulation. The average temperatures are 22°C, in summer, and 16°C, in winter.

In São Paulo city there are many heavy industries, such as: siderurgic, metallurgic, cement, cellulose and paper, oil refinery; 4.5 million vehicles and a population of 16 million inhabitants, whose compounds released by their activities contaminate the atmosphere.

In this study, rainwater samples were collected on an event basis and analyzed for pH and SO_4^{2-}, NO_3^-, Cl^-, F^-, Na^+, NH_4^+, Ca^{2+} and Mg^{2+} species by ionic chromatography.

MATERIALS AND METHODS

Samples are being collected in an event basis, just after the precipitation, since September 1993 at the top of the building of the Astronomy and Geophysics Institute, located at the campus of the University of São Paulo, using a Thies Clima automatic sampler, which separates wet and dry depositions.

Wet deposition samples were filtered in 0.4 µm Nuclepore filters and pH was measured. One fraction was acidified to pH 1.5 with purified nitric acid and stored at 4°C for later metal analysis. The other fraction was stored at 4°C for ionic species analysis by ionic chromatography. The analytical procedure was the same used and described in a previous work[2].

RESULTS AND DISCUSSION

Analytical quality control

The analytical quality control was carried out by means of the analysis of the Simulated rainwater (NIST-SRM-2694II) reference material. Results obtained are in good agreement with certified values, as shown in Table 1. Precision and accuracy were lower than 5.8% and 4.6%, respectively.

Table 1. Results obtained for NIST-SRM-2694II reference material, mg L^{-1}

Specie	Mean ± SD	Certified values	RSD, %	Error, %
Na^+	0.420 ± 0.007	0.423 ± 0.012	1.7	0.7
NH_4^+	1.07 ± 0.03	(1.06)	2.8	
K^+	0.106 ± 0.005	0.108 ±0.003	4.7	1.8
Mg^{2+}	0.049 ± 0.002	0.0484 ± 0.0010	4.1	1.2
Ca^{2+}	0.036 ± 0.002	0.0364 ± 0.0006	5.5	1.1
F^-	0.103 ± 0.006	0.108 ± 0.004	5.8	4.6
Cl^-	0.96 ±0.03	(0.94)	3.1	
NO_3^-	7.12 ± 0.15	7.19 ± 0.16	2.1	1.0
SO_4^{2-}	10.5 ± 0.06	10.6 ± 0.1	0.6	0.9

RSD - Relative standard deviation

Rainwater results

The method was applied to the analysis of 26 samples collected from September/93 to May/94. Table 2 presents range, arithmetic means and volume weighed means (VWM) for each analyzed specie in $\mu eq\ L^{-1}$.

Table 2. Range, arithmetic means and volume weighed means (VWM) for each specie analyzed in São Paulo rainwater samples, in $\mu eq\ L^{-1}$.

Specie	Range	Mean ± SD	VWM
pH	4.05 - 6.28	4.54 ± 0.50	4.47
Na^+	0.35 - 56.11	11.47 ± 13.48	10.45
NH_4^+	0.22 - 409.65	34.85 ± 78.70	26.13
K^+	0.13 - 65.73	10.74 ± 14.19	8.51
Mg^{2+}	0.08 - 34.56	6.75 ± 10.00	4.83
Ca^{2+}	0.30 - 270.96	22.44 ± 54.23	12.06
F^-	0.53 - 22.11	3.65 ± 4.68	2.44
Cl^-	0.56 - 188.98	21.85 ± 47.40	17.07
NO_3^-	0.15 - 61.45	28.37 ± 16.67	26.14
SO_4^{2-}	5.0 - 89.32	38.73 ± 21.32	34.59

The expression "acid rain" is applied when the rainwater pH is lower than 5.6, which is the pH of water in equilibrium with carbon dioxide at atmospheric concentration. The VWM for the period was 4.47, corresponding to a hydrogen concentration of 33.9 $\mu eq\ L^{-1}$.

Nitrate, sulphate and chloride are the principal anions found in these São Paulo rainwater samples. Nitrate and sulphate are correlated with hydrogen ions, being considered responsible for rainwater acidity. Probably, chloride ions do not contribute to rainwater acidity as there is no correlation between the chloride and the hydrogen ions.

Although a high sulphate and nitrate concentrations have been observed in the same events, the pH was not acid, probably due to high Ca^{2+} and NH_4^+ contents, which neutralize the precipitation.

Figure 1 presents the temporal variation of ammonium, nitrate and sulphate rainwater concentrations (in μeq/ml), characterizing high Pearson correlation coefficient values, around 0.80. This result is an indication that they are presented in the SPMA atmosphere in the form of ammonium nitrate and of ammonium sulphate, which can be verified using stechiometric equilibrium. The amount of precipitation presents a significative negative correlation with those species due to the high solubility of all of them.

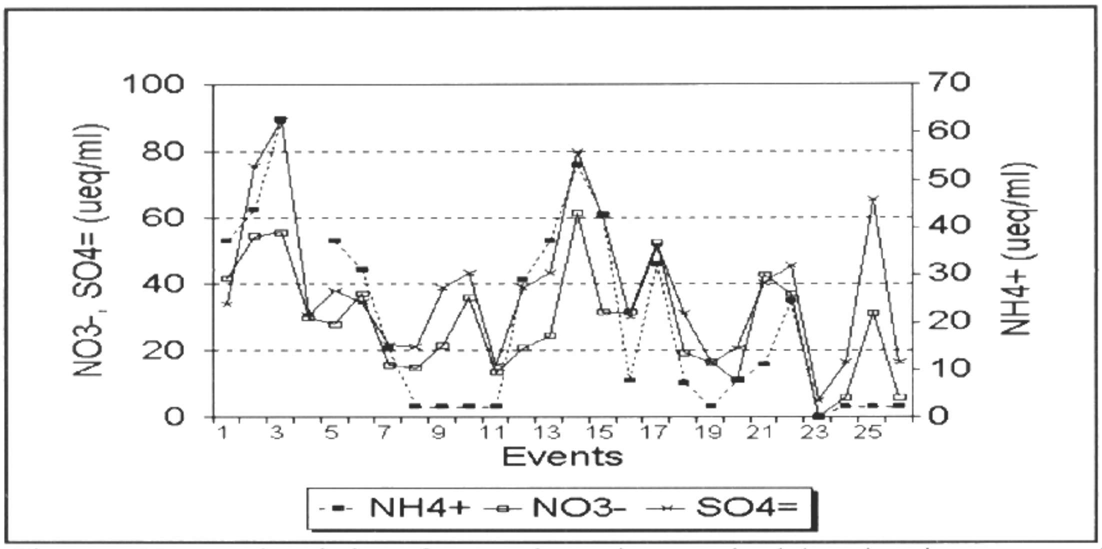

Figure 1. Temporal variation of ammonium, nitrate and sulphate in rainwater samples.

A positive relationship between chloride and the southeast wind was found. Figure 2 shows the event variations of chloride in rainwater samples and the wind directions. Except for the two initial values, the highest values are associated with southeast winds (100-170°), indicating the marine aerosol contribution to the chemical rainwater composition. The two high initial values are probably associated with contamination of samples.

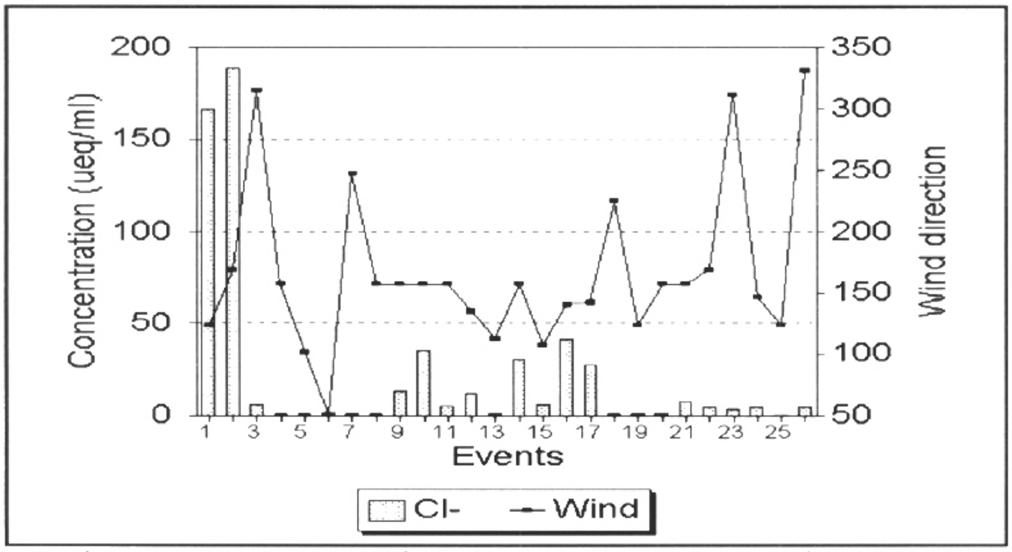

Figure 2. Temporal variation of chloride and wind direction.

Sodium ions are strongly correlated with Mg^{2+}, for this reason it was considered of marine origin.

Results obtained in this work were compared with others obtained in several cities of the United States[4] and also with another study carried out in the city of São Paulo[5]. Figure 3 shows this comparison.

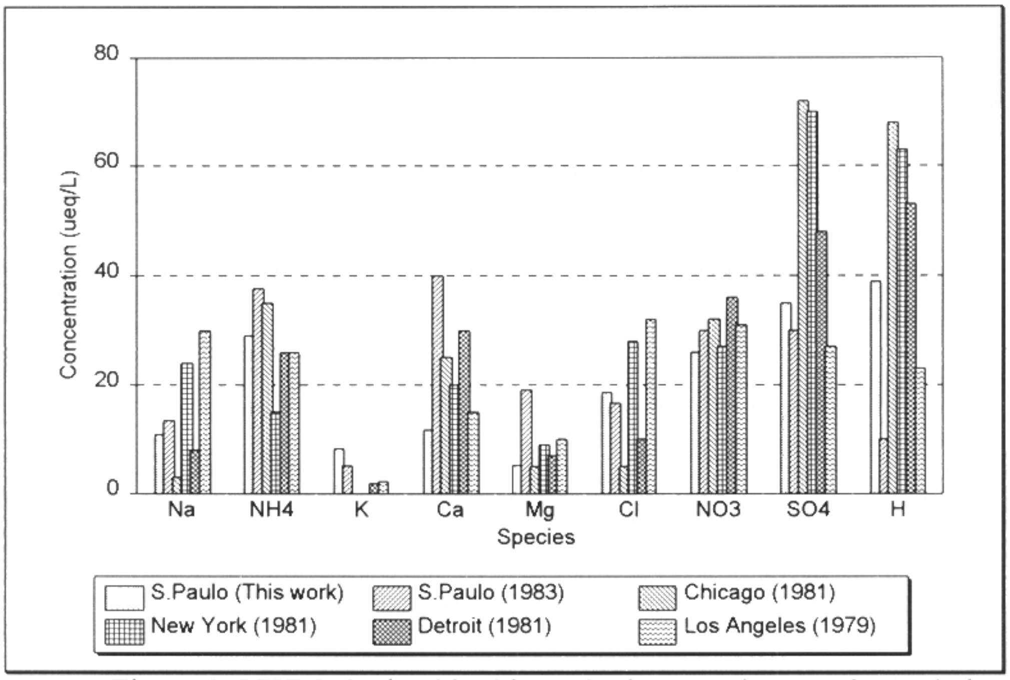

Figure 3. VWM obtained in this study, in a previous study carried out in São Paulo[5] and in several cities of the United States[4].

In general, the concentration of ionic species in São Paulo are lower than in four American cities (New York, Chicago, Detroit and Los Angeles), mainly, by the species that contribute to the acidity (sulphate and nitrate). This can be related to the major contribution of these pollutants to the atmosphere in that country.

Forti et al[5] found a higher pH for São Paulo precipitation than the one obtained in this work. It can be due to the use of different kinds of precipitation collectors. Forti et al used a collector that do not separate the dry fraction of the precipitation. According to Hansey and Hidy[6], alkaline species as Mg^{2+}, Ca^{2+} and K^{+}, that are normally found in coarse particles of resuspended soil, are collected with higher efficiency in this kind of collector than fine aerosol particles containing SO_4^{2-} and NO_3^{-}, and this tends to increase the pH of the wet precipitation.

Figure 4 shows the relation between the amount of precipitation and sulphate concentration in rainwater. The highest values of precipitation are related to the lowest sulphate concentrations, indicating a negative correlation.

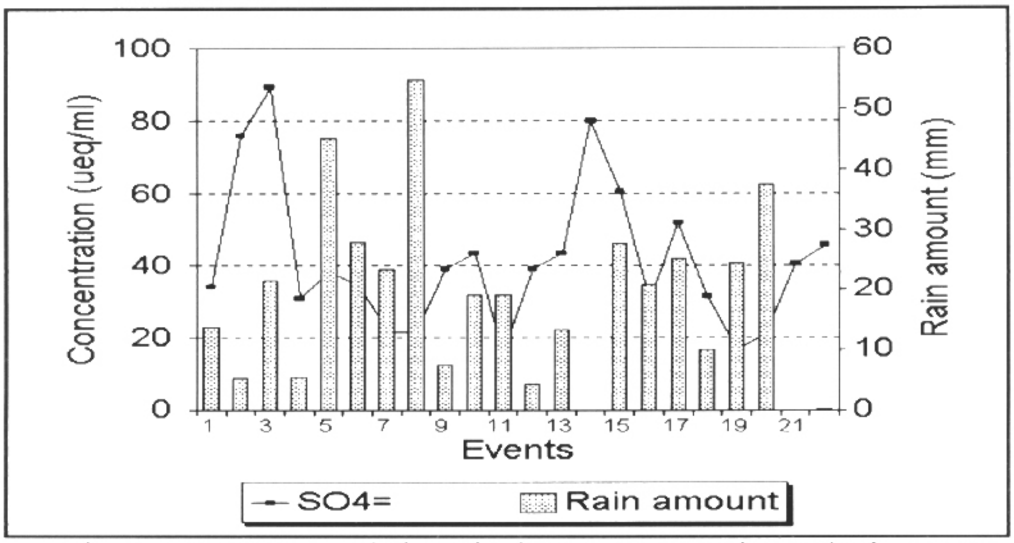

Figure 4. Temporal variation of sulphate concentration and rain amount.

A predominance of events associated with winds coming from southeast and moderate correlation between this direction and higher sulphate contents were observed. Convective rain seems to be associated with higher ionic species contents, as other authors[4, 7] have also observed. Although several meteorological data are available, we can not take conclusions about the sources of the precipitation contents. Due to the small number of samples collected and analyzed, it is impossible to apply multivariate statistical treatments normally used in this kind of study.

REFERENCES

1. Kasina, S., 1980. On precipitation acidity in southeastern Poland. Atm. Env. 14: 1217- 1221.
2. Pires, M.A.F.; Dantas, E.S.K., Munita, C.S., 1995. An attempt to identify commercial drinking water through means of some ionic species. Fresenius Envir. Bull. 4: 673-678.
3. Paiva, R.P.; Munita, C.S.; Cunha, I.L.; Alonso, C.D.; Romano, J.; Martins, M.H.R., 1993. A contribution to the characterization of aerosol sources in São Paulo. J. Radioanal. Nucl. Chem., Articles 167: 295-307.
4. Gatz, D.F., 1991. Urban precipitation chemistry: a review and synthesis. Atm. Env. 25B: 1-15.
5. Forti, M.C.; Moreira-Nordemann, L.M.; Andrade, M.F.; Orsini, C.Q., 1990. Elements in the precipitation of São Paulo city (Brazil). Atm. Env. 24B(2): 355-360.
6. Hansen, D.A.; Hidy, G.M., 1982. Review of questions regarding rain acidity data. Atmos. Environ. 16(9): 2107-2126.
7. Wolff, G.T.; Lioy, P.S.; Golub, H.: Hawkins, J.S., 1979. Acid precipitation in the New York Metropolitan area: Its relationship to meteorological factors. Environ. Sci. Techn. 13(2): 209-212, 1979.