Chemical Composition of São Paulo Atmospheric Wet Precipitation

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Abstract: Rainwater samples of the city of São Paulo collected from December 1993 to April 1995 were analyzed for sulfate, nitrate, chloride and amonium ions by ion chromatography, for Al, As, Cr, Fe, K, La, Mn, Na, Sm and Zn by instrumental neutron activation analysis, and pH. Correlation and regression analysis indicated that H+ is more closely associated with nitrate than with sulfate ions. Sulfate ions are associated with ammonium, probably as $(NH_4)_2SO_4$. Statistical analysis suggest that Al, Fe and Mn in precipitation are soil derived and nitrate and sulfate ions are associated with anthropogenic sources.

Key words: Acid rain, acid precipitation, anions, cations, ion chromatography, instrumental activation analysis

INTRODUCTION

During the last decades, characterization of the chemical nature of precipitation has been widely investigated in many industrialized areas of the world(1-7). Several studies have demonstrated that the anthropogenic activities can affect precipitation composition and subsequently affect aquatic and terrestrial ecosystems.

Recent evidence suggests that organic acids are one of many dominant classes of

organic compounds found in the atmosphere in a variety of phases. These organic acids, in particular, formic and acetic acids, play a major role in precipitation acidity observed in both urban and remote areas of the world(8-10)

The rainwater pH value alone provides a rather incomplete information on the acid properties of rain, which usually is an unbuffered solution that changes its composition with time after the precipitation event.

This paper presents data on the composition of 25 precipitation events collected over a 16 month period, from December 08, 1993 to April 20, 1995 in the city of São Paulo. The purposes of this study is to determine the relationship between the acidity (H⁺) and other ions. As precipitation consists of a mixture of ions, largely in free solution, and there is no way of definitely associating H⁺ with any of strong acid anions, statistical analysis can, however, provide some indication of the likely source of some of the acidity in rainwater. A high correlation coefficient value between elements is indicative of a common source and similar behavior.

MATERIALS AND METHODS

Sampling and Analysis Procedure

Rainwater samples were collected in a wet-only sampler, on an event basis at the top of the building of the Astronomy and Geophysics Institute, located at the campus of the University of São Paulo, in the western periphery of the city, using a Thies Clima automatic sampler, which separates wet and dry deposition. Immediately after collection, the samples were filtered through a Nuclepore filter 0.45 μm pore size and pH was measured. The samples were divided in two fractions and stored in polyethylene bottles with screw cap at 4°C. One fraction was acidified to pH 1.5 with purified nitric acid to determine Al, As, Cl, Cr, Fe, K, La,

Mn, Na, Sm and Zn by instrumental neutron activation analysis, INAA. In the other fraction the concentration of NH_4^+, SO_4^{2-} and NO_3^- was measured by ion chromatography, IC.

The analysis procedures are described elsewhere*(11-13)*.

RESULTS AND DISCUSSION

The analytical chemical methods were evaluated with standard reference materials. Precision and accuracy were lower than 10% for INAA, and lower than 6% for IC *(11-13)*.

The range, mean and standard deviation of chemical components are shown in Table 1.

Correlation coefficients between all ion concentrations are shown in Table 2. Sulfate, NO_3^- and NH_4^+ species form a highly correlated group. Hydrogen ions correlate with SO_4^{2-} and NO_3^-, and do not correlate with Cl^-. Chloride ions correlate weakly with SO_4^{2-}, NO_3^- and NH_4^+ showing that they do not contribute to the acidity of rainfall in São Paulo. This bears out the conclusion that little of the acidity is due to Cl^-. However, NO_3^- correlates better with H^+ than it does with SO_4^{2-}. This indicate that SO_4^{2-} occurred as salts associated with other cations, i.e $(NH_4)_2SO_4$, $CaSO_4$.

In Table 3 the correlation coefficients between H^+ and SO_4^{2-}, and NO_3^- as a function of pH are shown. In samples with pH<4.5, the correlation coefficients are high for NO_3^-. This indicate that in the majority of the rain events, most of the NO_3^- were associated with hydrogen ions and the SO_4^{2-} are associated with other cations.

To clarify the relationship between the various ions, the deposition was calculated. As the deposition is the product of volume by concentration all deposition rates naturally correlate with volume. The results showed that events with a high NO_3^- deposition have a strong tendency to have a high SO_4^{2-} deposition, and events with a high H^+ deposition tend to have

high NO_3^- and SO_4^{2-} depositions. The exception is again Cl^-. There is no relationship between events with high Cl^- and those with high NO_3^- and SO_4^{2-}.

Correlation analysis demonstrates the degree of covariance of two quantities, but in order to estimate how the change in one quantity is associated with the change of the other quantity, regression analysis is necessary.

The regression of $[H^+]$ on $[NO_3^-]$ is $[H^+]=0.70[NO_3^-]+17.4$. If the source of all the NO_3^- is emission of NO_x, then every equivalent of NO_3^- should have one equivalent of H^+ originally associated with it, and the slop of this regression line should be 1. However, the slop is 0.70 implying that 70% of NO_3^- is derived from NO_x oxidation. Nitrogen oxides are first largely emitted as nitric oxide (NO), with some nitrous oxide (N_2O). Nitric oxide is oxidized in the atmosphere to NO_2 and therefore to nitric acid and possibly nitrate aerosol; these finally result as nitrate ion precipitation.

The SO_2 and NO_x gases that are mostly emitted by industries and anthropogenic activities. Nitrate ions are the major sources the acid rain in industrialized areas, such as the city of São Paulo.

The concentration of NH_4^+ could be measured in only 40% of the events, the rest are missing values. The NH_4^+/SO_4^{2-} ratio average of the samples was around 0.4. In these rainwater samples Cl correlates well with Na, the correlation coefficient was 0.7, indicating that main source for these elements was marine.

From Table 2, a strong correlation coefficient exists between Fe and Al, Mn, La, As, K and Zn. This suggests a common source for these metal pairs. A further comparison of the data with concentration of metals in the earth's crust expressed in ppm[14]: Al, 81,300; Mn, 950; La, 30; Fe, 50,000; K, 25,900 ; Sm, 6.0; Zn, 70.0, indicates soil is the source of these elements. Of these metals Al and Fe are highest in the earth's crust. Definitely, colloidal soil-borne dust

particles entrapped in precipitation contribute to the high relationships exhibited between these metal pairs in this study.

Acknowledgements

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Table 1. Range, arithmetic mean and standard deviation of São Paulo rainwater chemical components, in $\mu eq\ L^{-1}$.

Specie	Range	Mean ± SD
Al	3.11 – 40.25	9.5 ± 9.2
As	0.0047 – 0.11	0.018 ± 0.020
Cl	6.09 – 75.12	30.46 ± 21.5
Cr	0.040 – 0.87	0.12 ± 0.09
Fe	0.127 – 79.82	13.44 ± 21.43
H^+	0.52 – 60.25	28.87 ± 17.03
K	5.98 – 121.66	29.56 ± 27.72
La	0.00071 – 0.063	0.0105 ± 0.0178
Mn	0.040 – 0.87	0.206 ± 0.17
Na	0.26 – 48.98	9.37 ± 9.5
NH_4^+	0.22 – 42.68	11.85 ± 13.76
NO_3^-	0.15 – 52.58	23.5 ± 15.35
Sm	0.000064 – 0.0122	0.000562 ± 0.00065
SO_4^{-2}	1.46 – 60.59	29.23 ± 18.78
Zn	0.091 – 10.07	1.23 ± 1.98

Table 2. Correlation matrix of the São Paulo rainwater chemical components.

	Al	As	Cl⁻	Cr	Fe	H⁺	K	La	Mn	Na	NH₄⁺	NO₃⁻	Sm	SO₄⁻²
As	0.59													
Cl⁻	0.66	0.21												
Cr	0.38	0.25	0.07											
Fe	0.86	0.88	0.86	0.32										
H⁺	0.02	0.36	0.02	0.01	0.52									
K	0.52	0.80	0.32	0.32	0.96	0.58								
La	0.60	0.84	0.12	0.52	0.79	0.40	0.75							
Mn	0.32	0.21	0.49	0.05	0.65	0.46	0.50	0.30						
Na	0.33	0.25	0.43	0.01	0.24	0.24	0.14	0.01	0.22					
NH₄⁺	0.28	0.10	0.15	0.18	0.15	0.63	0.16	0.15	0.08	0.10				
NO₃⁻	0.11	0.16	0.16	0.38	0.29	0.44	0.43	0.19	0.16	0.07	0.54			
Sm	0.53	0.87	0.19	0.38	0.80	0.52	0.74	0.89	0.37	0.15	0.10	0.27		
SO₄⁻²	0.24	0.01	0.39	0.09	0.11	0.40	0.30	0.12	0.27	0.46	0.54	0.69	0.12	
Zn	0.64	0.87	0.35	0.27	0.91	0.40	0.81	0.80	0.35	0.16	0.10	0.21	0.83	0.11

Table 3. Hidrogén, nitrate and sulfate ion correlations as pH function

Relationship	pH < 4.5	$4.5 \leq pH \leq 5.0$
H⁺ vs SO₄⁻²	0.37	0.29
H⁺ vs NO₃⁻	0.44	0.19