

IPEN-DOC-

4805



CONCENTRATIONS OF SOME IONIC SPECIES IN
 RAINFALL FROM SAO PAULO

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SUMMARY. Rainfall samples were collected during the period March until December of 1991 in Sao Paulo city. The samples were analyzed for pH and the species Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ and Ca^{2+} were determined using ion chromatography. The data set was evaluated by means of correlation coefficients and regression analyses. The results obtained showed that the ions sulfate appeared to be more closely associated with Ca^{2+} and NH_4^+ than with H^+ .

Key words: wet deposition, ionic species, anions, cations, acidity.

INTRODUCTION

Air pollution is a permanent problem for industrialized cities like Sao Paulo with 15 million inhabitants, 4.5 millions cars and industries of all types and kinds. Eighty percent of these industries are pollutants such as cement, chemical fertilizer, metal and wood pulping plants. Information on chemical composition of precipitation is necessary due to the increasing concern about atmospheric out from the industries of substances and their effects on land surface waters. Several works suggest that acidity and concentrations of sulfate, nitrate and some other components of precipitation in big cities have been increasing in recent years as a result of man's activities^{1,2}.

Interest in acid precipitation was further stimulated by the discovery that acid rainfall contained a pH substantially below 5.65, the value expected from kinetic equilibrium of precipitation with atmospheric carbon dioxide³.

In this study, precipitation samples were collected on an event basis and analyzed using ion chromatography to determine Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ and Ca^{2+} .

The city of Sao Paulo is located on the Atlantic Plateau, 700 to 900m above sea level, on the Tropic of Capricorn, 80km from the Atlantic coastline. The general topography is rather complex and the air flow is strongly influenced by local conditions. The mean temperature is 24°C during the summer months of December until March which falls within the rainy season (October-March) and 12°C during the winter months of June until September which falls within the cold dry season (April-September).

MATERIALS AND METHODS

The sampling period extended from March until December 1991. The rainfall samples were collected using a polyethylene funnel and a polyethylene collector reservoir, 2m above land-level, in the western periphery of the city. The polyethylene funnel was tightly covered by polyethylene and opened manually to the atmosphere immediately prior to each event to prevent dry deposition of particles before the onset of the rainfall. Immediately prior to the rainfall, the funnel was rinsed thoroughly with deionized distilled water. Measurements of precipitation pH were made immediately upon collection of an entire precipitation event. Precipitation quantity was crudely estimated by measuring the volume of the collected sample. pH measurements were made with a pH meter (Metronal E-120). Before each measurement, the pH meter and the electrode were calibrated with standard buffer solutions at pH 4 and 7, and the electrode was then thoroughly rinsed with deionized distilled water. The samples were filtered using a 0.45 μm Millipore filter, bottled in polyethylene containers, and maintained at 4°C. The species were measured by ion chromatography (Dionex 10). Analytical details on IC technique are

provided in Pires et al.⁴. All the samples were analyzed within 7 days of collection.

RESULTS AND DISCUSSION

In Table 1 are given the arithmetic mean, standard deviations, ranges and the volume-weighted mean of the entire data set. Over the collection period, the H^+ concentration of precipitation collected varied from 0.10 to 72.44 μM , with a mean of $8.1 \pm 14.5 \mu M$. The results of the precipitation volume-weighted mean (VWM) of each specie were calculated using the equation⁵:

$$\left[\bar{X} \right]_{VWM} = \frac{\sum_{i=1}^n [X_j]_i V_i}{\sum_{i=1}^n V_i}$$

Where X_j is the j^{th} ionic species

$[X_j]_i$ is the concentration of X_j in the i^{th} of n samples

V_i is the precipitation volume collected for the i^{th} sample

Table 1. Arithmetic means, standard deviations, ranges and volume weighted mean data, μM ($n=53$)

Ion	Mean \pm SD	Minimum	Maximum	VWM
H^+	8.1 ± 14.5	0.10	72.44	2.42
Cl^-	57.7 ± 62.3	0.28	195.20	0.74
NO_3^-	74.7 ± 72.6	1.13	263.22	1.04
SO_4^{2-}	49.1 ± 61.3	17.50	404.60	0.53
Na^+	33.1 ± 45.7	1.70	253.60	0.40
K^+	21.8 ± 38.9	0.26	148.60	0.22
Ca^{2+}	29.9 ± 72.7	0.50	521.70	0.30

The VWM normalizes the precipitation concentration by precipitation amount, in real sense. The means concentration resulting from this calculation is equivalent to that which would

have been obtained by mixing the n samples and the composition determined. The unweighted means gives more importance to extreme values with low volume.

The mean volume-weighted pH precipitation over the period was 5.62 ($2.42\mu\text{M}$). Although there is a high concentration of SO_4^{2-} and NO_3^- , 0.53 and $1.04\mu\text{M}$ respectively, the rainwater cannot be considered acid, because simultaneously the Na^+ , K^+ and Ca^{2+} ionic content is also higher. In acid rain, the decrease in pH is usually caused by the increased concentration of NO_3^- and SO_4^{2-} from the acid precursors, SO_2 and NO_x . However, in our case these precursors were not sufficiently high enough to decrease the pH which was produced by elevated concentrations of cations which provoked a neutralization in the precipitation. The ammonium ion was not included in the data set because 20% of the samples were missing the ammonium values, even though the detection limit of the technique was $2.22\mu\text{M}$. In 40 samples the VWM for NH_4^+ was $1.9\mu\text{M}$. The excess of NO_3^- and SO_4^{2-} may be linked to the exhausts of vehicle motors and the combustion of fossil fuels⁶.

The correlation coefficients for this data set showed that there is no correlation between H^+ and SO_4^{2-} , whereas there is a correlation between H^+ and NO_3^- . This indicates that sulfate ions occurred as salts associated with other cations, i.e. CaSO_4 and $(\text{NH}_4)_2\text{SO}_4$. In atmosphere of Sao Paulo, the total Ca concentration is higher than 1000 ng/m^3 with the principal sources being soil dust and resuspension of urban surface dust⁶. Chloride ions found no correlation with H^+ , SO_4^{2-} and NO_3^- showing that it does not contribute to the acidity of rainfall in Sao Paulo. However, Na^+ and Cl^- ions have a high correlation.

Using principal factors analysis, Paiva et al.⁷ found that the source of Cl^- and Na^+ in the Sao Paulo aerosol is from seawater, which was confirmed in this study. This conclusion indicates that little of the acidity in rainfall is due to Cl^- .

Correlations 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 $[\text{H}^+]$ on $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ are : $[\text{H}^+]=0.35[\text{SO}_4^{2-}]+12.1$ and $[\text{H}^+]=0.46[\text{NO}_3^-]+13.2$. If

the source of all the NO_3^- and SO_4^{2-} were emissions of NO_x and SO_2 , then every equivalent of NO_3^- and SO_4^{2-} should have one equivalent of H^+ originally associated with it, and the slopes of these regression lines should be 1. However, the slopes of the $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$ lines are significantly different from 1. The slope of $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ regression are 0.35 and 0.46 respectively, implying that 35% of the SO_4^{2-} ion is derived from SO_2 oxidation and 46% 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 oxidised in the atmosphere to NO_2 and thence to nitric acid and possibly nitrate aerosol; this results ultimately in precipitation as the nitrate ion.

The wet deposition is the most effective component of the atmospheric self-cleaning. The ionic content of precipitation is influenced by both meteorological parameters and emission patterns of the areas in which the rain air masses have crossed. Both of these factors are able to modify the wet deposition individually as well as jointly. These factors as well as the complex general topography of Sao Paulo have a great influence in the local rainfall where frequently rainfall is present in one area and not in another, modifying the atmospheric chemistry.

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