Chemical characterization of São José dos Campos and Cachoeira Paulista (Sao Paulo-Brazil) atmosphere using denuderes system: preliminary results.

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Objective: Study the chemical composition of the São Paulo state atmosphere using a system of low cost based on sampling denuder[1] and implementing a strategy for quantifying the concentration of various chemical species especially reactive nitrogen (Nr). Here it is presented the preliminary results for São José dos Campos (SJC) and Cachoeira Paulista (CP) respectively, sites 3 and 2 on figure 1.

Introduction: The content of nitrogen reactive forms in excess in the atmosphere negatively influences the environment, human health and climate leading to severe environmental changes. This study presents the preliminary results of a study conducted at São Paulo State to characterize chemically the apportionment between the particulate and gaseous phases examining some inorganic chemical species.

Method: This study presents results from São José dos Campos/SP-Br: SJC – urban site and Cachoeira Paulista/SP-Br: CP-rural site.

- Studied period: August 2013 until July 2014.
- Sampling technique: train of denuders and stacked filters[1] for gas-particles phase on active substrate (DELTA*) and dichotomous stacked filter unit (SFU) for $PM_{2.5}$ and $PM_{2.5-10}$ on neutral substrate.
- Gas phase chemicals: HNO_3, NO_x as NO_3^-; SO_2 as SO_4^{2-}, HCl as Cl^- and NH_3 as NH_4^+.
- Particulate phase: NH_4^+, NO_3^-, SO_4^{2-} and Cl^- ionic soluble forms.

Figure1 – Sites location of DELTA* systems in São Paulo State where: 1: Cunha; 2: Cachoeira Paulista; 3: São José dos Campos; 4:São Paulo; 5: São Carlos; 6: Assis e 7: Teodoro Sampaio
* **DE**nuder for **L**ong-**T**erm **A**tmospheric sampling

Results – Figure 1 and Table 1 presents time evolution and the statistics, respectively for the sites considered in this study. As the SFU system samples a larger particle spectrum as well as the product of gas-particle conversion, the volumetric concentrations are, as expected, larger than the ones obtained with the DELTA, which collects a narrow particle size spectrum as well as the apportionment between the gas phase from the particle ones.
Both phases presents lower concentration during rainfall events, however, particle-NH_4^+ concentration has a peak after rainfall period probably due to soil emission. Unexpected is the fact that the gas-phase in CP is higher than in SJC reflecting the presence of sources of gases such as SO_2, NO_x and NH_3 which can be confirmed by the results obtained with the SFU system whose values for the fine and coarse particles presents no statistically significant differences being the fine ones mainly derived from gas-particle conversion.

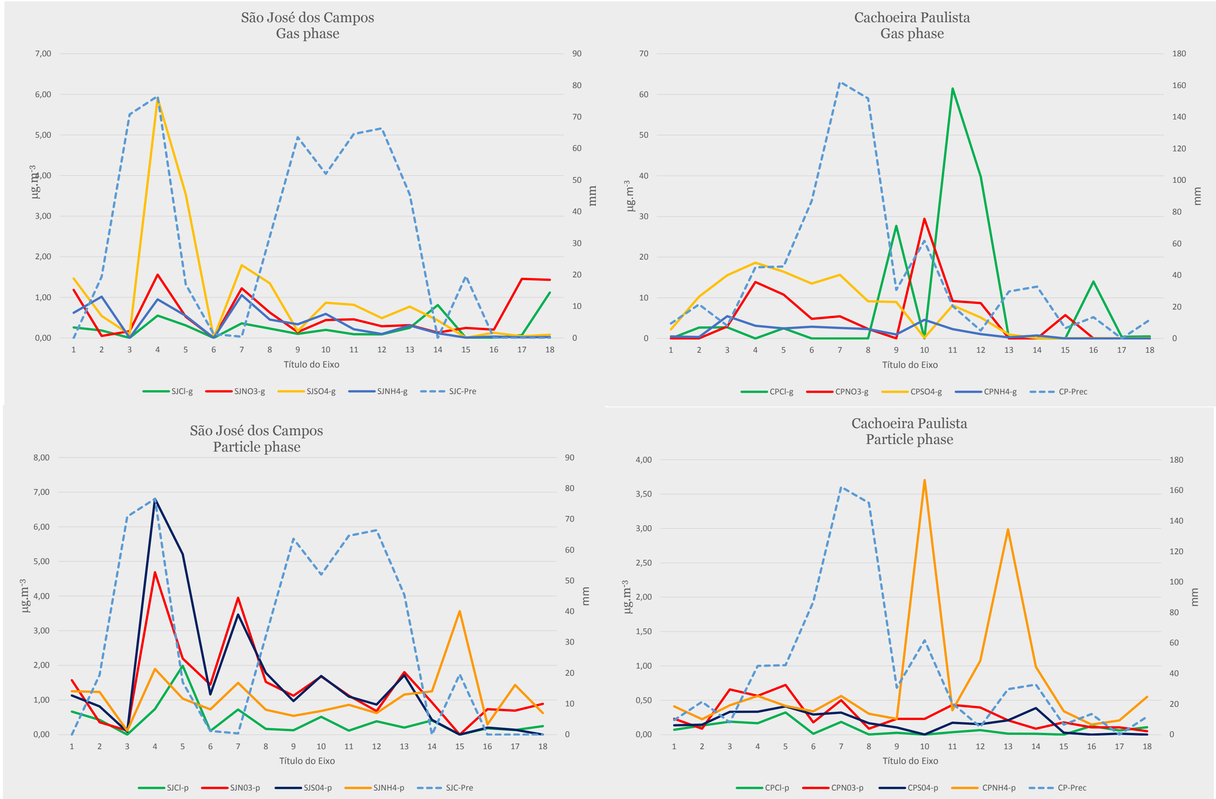

Figure 1 – Concentration time evolution (ng.m^{-3}) for the gas and particle phase for both sites: Aug2013- Jul2014

Table 1 – Statistics for the observed values for the DELTA (g-gas and p-particle phases) and SFU (fine - $MP_{2.5-10}$ and coarse - MP_{10} fractions) systems in ng.m^{-3}, where AVG: mean values, STD: standard deviation, Count: observation number, Min: minimum value and Max: maximum value. Underlined pair presents statically significant difference.

	São José dos Campos					Cachoeira Paulista				
	DELTA									
	Gas phase									
	Count	AVG	STD	Min	Max	Count	AVG	STD	Min	Max
	µg.m^{-3}					µg.m^{-3}				
Cl-	17	0.207	0.217	0.000	0.811	17	8.90	17.7	0.003	61.5
NO_3^-	17	0.531	0.506	0.001	1.56	17	5.50	7.59	0.012	29.4
SO_4^{2-}	17	1.08	1.53	0.004	5.91	17	7.35	6.77	0.051	18.6
NH_4^+	17	0.374	0.370	0.001	1.06	17	1.74	1.66	0.004	5.49
	Particle phase									
Cl-	18	0.396	0.462	0.000	1.99	18	0.085	0.088	0.000	0.323
NO_3^-	18	1.42	1.21	0.000	4.69	18	0.280	0.212	0.050	0.723
SO_4^{2-}	18	1.53	1.86	0.000	6.81	18	0.178	0.140	0.001	0.411
NH_4^+	18	1.08	0.765	0.113	3.56	18	0.768	0.977	0.146	3.71
	SFU									
	Count	AVG	STD	Min	Max	Count	AVG	STD	Min	Max
	µg.m^{-3}					µg.m^{-3}				
	$MP_{2.5}$									
Cl-	43	0.166	0.137	0.0048	0.396	34	0.083	0.076	0.0025	0.271
NO_3^-	43	0.393	0.310	0.003	1.288	34	0.442	0.456	0.0059	1.478
SO_4^{2-}	43	0.621	0.472	0.052	2.283	34	0.762	0.547	0.067	2.263
NH_4^+	43	0.330	0.217	0.094	0.817	34	0.277	0.176	0.0081	0.684
	$MP_{2.5-10}$									
Cl-	38	0.247	0.214	0.0019	0.750	38	0.167	0.268	0.0019	1.544
NO_3^-	38	0.549	0.457	0.00259	1.488	38	0.429	0.393	0.023.3	1.958
SO_4^{2-}	38	0.278	0.214	0.0478	1.035	38	0.192	0.175	0.00	0.892
NH_4^+	38	0.153	0.212	0.0000	0.830	38	0.109	0.136	0.0052	0.511

General comments: The results indicate an effective contribution from industrial sources as well as from combustion of fossil fuel for SJC while in CP although with characteristics of a region with livestock sources seems to have another important sources that must be better investigated to allow its identification. In addition, it is observed that the active substrates are more efficient in collecting PM than that of the neutral ones and that the latter may underestimate the contribution of gaseous phase for the formation of the particulate matter (PM).

[1]Sutton M.A., Tang Y.S., Miners B. e D. Fowler, Water, Air and Soil Pollution. Focus, **2001,** 1(5/6), 1456.

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