

Título: Reactive nitrogen, hydrochloric acid, sulfur dioxide and major ions data, in the atmosphere of diverse regions of South America

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## **1. Introduction**

The data set presented here comes out from an active denuder sampling system developed to quantify the content of reactive nitrogen species (Nr), hydrochloric acid (HCl), sulfur dioxide (SO<sub>2</sub>) as well as the major cations, in the gas and particle phases, present in the atmosphere of different regions of South America, mostly located in Brazil. The data presented here were obtained using a low cost sampling system, named DELTA (Long Term Atmospheric Sampling) and was developed at the Center for Ecology and Hydrology in Edinburgh in 1995 (Sutton, et al., 2001; Tang et al., 2009). This system was based on the method described by Ferm (1979) and initially was used to sample reactive nitrogen species being subsequently extended to the other species for the gas and particle phases. These data set may aid and complement studies about the understanding of different ecosystems functioning in regard to the increase of reactive nitrogen deposition as well as to a better understanding of the interaction and coupling of the N cycle with the one from other species such as C, S and P. This is important because the concentration of reactive nitrogen species variation within different terrestrial environments is closely linked to environmental changes, the contamination of aquatic and terrestrial ecosystems and the loss of biodiversity.

The analytical results were produced in the Laboratory of Biogeochemical Cycles Research (LPBio in Portuguese) of the Earth System Science Center of the National Institute for Space Research (CCST/INPE). The laboratory participates of the International Intercalibration Program (<http://www.qasac-americas.org/>), in which the chemical analysis results were validated using the samples and results of the program. The objective of the International Intercalibration Program is to ensure the analytical quality of the laboratories participating in the monitoring networks linked to the World Meteorological Organization - WMO (Meneghetti, 2017). The statistical analyzes for the qualification of the data set were done with the Statgraphics® software.

This work aims to disseminate a data set obtained in the project supported by FAPESP 2012 / 06416-1 (1<sup>st</sup> phase) and IAI Grant number: CRN3005 (2<sup>nd</sup> phase), entitled "Nitrogen Cycle in Latin America: Impacts and Vulnerabilities " (<http://nitrogen.ccst.inpe.br/>).

## **2. Sampling sites**

In this study, samplers were installed in sites located in diverse research institutions. To carry out the sampling program, we counted with collaborators from each institution that hosted the sampler. In addition, two samplers were deployed in sites out of Brazil, one in Venezuela and one in Argentina, and they were under the responsibility of the collaborators of those countries. Chemical analyzes of samples from Argentina were performed in our laboratory, and Venezuela was responsible for sample collection and analysis. Table 1 presents the number of each site (according with its indication in the map of Figure 1), the name of the person in charge of each site, the sampling date and number of samples collected.

Table 1 – Sampling sites number, name, collaborators, start and end date of sampling and total number of samples.

| Nº | Site Name  | Collaborators   | Start Date | End Date   | Number of samples |
|----|--|---|------------|------------|-------------------|
| 1  | Instituto Nacional de Pesquisas Espaciais (INPE) (sede), São José dos Campos/SP (SJ)         | Maria Cristina Forti; presently Felipe Siqueira Pacheco | 23/05/2013 | 30/11/2018 | 108               |
| 2  | Instituto Nacional de Pesquisas Espaciais (INPE), Cachoeira Paulista/SP (CP)                 | José Carlos dos Santos                                  | 28/08/2013 | 30/11/2018 | 90                |
| 3  | *Universidade Federal de São Carlos (UFSCar), São Carlos/SP (SC)                             | Ademir Barbassa   | 25/09/2013 | 01/08/2015 | 33                |
| 4  | *Instituto de Botânica, São Paulo/SP (SP)  | Sílvia Ribeiro de Souza                                 | 05/02/2014 | 21/11/2016 | 43                |
| 5  | Núcleo Cunha-Indaiá, Reserva da Serra do Mar, Cunha/SP (CN)                                  | Maurício Ranzini  | 18/02/2014 | 30/11/2018 | 96                |
| 6  | Reserva Ecológica, IF, Assis/SP (AS)   | Eliane Honda  | 25/02/2014 | 30/11/2018 | 80                |
| 7  | *Parque Estadual do Morro do Diabo, Teodoro Sampaio/SP (TS)                                  | Alex Francisco de Souza                                 | 26/02/2014 | 24/07/2015 | 27                |
| 8  | Universidade de São Paulo (USP) em Ribeirão Preto/SP (RP)                                    | Maria Lúcia A. M. Campos                                | 09/09/2015 | 30/11/2018 | 56                |
| 9  | Universidade Federal de Mato Grosso do Sul no Pantanal, Rio Miranda, Passo do Lontra/MS (PT) | Hamilton Germano Pavão                                  | 07/11/2015 | 29/08/2016 | 11                |
| 10 | UnB - Reserva Ecológica do IBGE em Brasília/DF (BR)  | Leandro Garcia  | 11/05/2016 | 30/11/2018 | 47                |
| 11 | Universidade Anhanguera/UNIDERP Campus III em Campo Grande/MS (CG)                           | Widinei Alves Fernandes                                 | 21/08/2017 | 30/11/2018 | 17                |
| 12 | Parque Estadual, Campos do Jordão/SP (CJ)  | László Károly Nagy                                      | 04/12/2017 | 30/11/2018 | 23                |
| 13 | Instituto Venezolano de Investigaciones Cientificas Venezuela (VE)                           | Tibisay Perez   | n.i.       | n.i.       | n.i.              |
| 14 | Faculdade de Agronomia, Universidade de Buenos Aires, Argentina (AR)                         | Gervasio Piñeiro  | 01/09/2017 | 16/07/2018 | 19                |

n.i. = not informed. \* Discontinued.

The larger number of sites located in Brazil is due to its bigger extension in relation to South America and also due to logistic difficulties such as customs bureaucracy and mail system delays across borders. Within the Brazilian territory, the logistic system was based on the post-office services as well as on the support given by the researchers from the collaborating institutions. In addition, the larger number of sites in the state of São Paulo is due to the fact that the project was started there. The sampler case was sent forward and back to São José dos Campos via the post service and was replaced, in the field, by the collaborator of each institution.

The project consisted of a first phase, where samplers were installed in 7 sites in the São Paulo state (between 2013 and 2015, sites numbered from 1 to 7 in Table 1), and a second phase when some sites of the first phase were deactivated and others were installed (indicated in Table 1).

The first DELTA sampler was installed in August 2013 on the INPE's campus in São José dos Campos (N° 1) which has a green area with high vegetation (average height of the canopies is about 20 m). The sampler was installed above the canopy level (~30 m high). This site is classified as an urban area, since São José dos Campos has approximately 713,000 inhabitants (IBGE, 2018) and INPE is inserted in the urban area.

In August of 2013, a DELTA sampler was installed in Cachoeira Paulista (INPE's campus, N° 2), classified as a rural region, with livestock and agriculture being the main activities in the region. The sampling site is located on the top of a hill at a distance of 2.5 km from the urban border, and the municipality has 33,000 inhabitants (IBGE 2018).

São Carlos site (N°3) is located in the Midwest region of São Paulo state and the sampler was deployed inside a meteorological station located in a peri-urban area, about 5 km distant from the central part of the city center. This system was active from September 2013 until August 2015 and was closed down due to the lack of operator. The DELTA system of this site was transferred to the city of Ribeirão Preto (N° 8) with 695,000 inhabitants (IBGE, 2018), and installed within the University of São Paulo campus that is located in the sugar cane belt of the state of São Paulo. Its operation began in September of 2015. The campus is located in the outskirts of the city and about one kilometer apart from extensive sugarcane plantations. In the Ribeirão Preto region the main economic activity is sugarcane production and processing.

The DELTA sampler located in the municipality of São Paulo (N°4), with 12,176,866 inhabitants, was installed in February 2014 at the Institute of Botany, within an urban forest of 550 ha named State Park of Fontes do Ipiranga. Due to the vegetation height, the sampler was installed atop of a platform 15 meters from the ground. This system was deactivated in November 2016 due to the lack of operator.

The DELTA sampler installed in the State Park of Serra do Mar (N° 5), a reserve of Atlantic Forest with 10,000 ha, in the municipality of Cunha with 21,000 inhabitants (IBGE, 2018), was deployed in February 2014; the site is 12 km off the coast and 250 km away from the city of São Paulo, and the nearest urban areas are the municipalities of Cunha and Paraty, 15 and 20 km away, respectively. This site is considered as an atmospheric reference because there is no significant rural activity and it is far from urban areas and therefore with low or no influence of vehicular or industrial sources.

The Assis municipality site (N° 6) is located within the Ecological Station of Assis (IF-SEMA) and has been in operation since February 2014. It is considered a rural area, surrounded by pastures and its sampling point is 9.7 km from the city center, which has 103,000 inhabitants according IBGE, 2018.

Morro do Diabo State Park site (N° 7) is in the far western region of the State of São Paulo, and the sampling site is 7.8 km distant from the city center of Teodoro Sampaio (23,000 inhabitants, IBGE 2018). The Morro do Diabo State Park region is dominantly a rural area whose main activity is livestock. The sampling program lasted from February 2014 until July 2015 and the sampler was deactivated due to lack of operator.

A DELTA sampler was installed in November 2015, in the region of Passo do Lontra (N° 9), near the Miranda River, 80 km from Corumbá/MS, at the Pantanal Study Base (SBP), which belongs to the Federal University of Mato Grosso do Sul (UFMS). However, due to logistical difficulties this site was deactivated in August 2016 and the sampler moved to Campo Grande/MS (N° 11). This region is periodically flooded by the Miranda River and its tributaries. The Campo Grande/MS region is characterized by a mixture of “cerrado” vegetation (Brazilian savana), forest and grassland. It is located about 1000 km from the coastline located at the outskirts of the Campo Grande city (885,711 inhabitants, IBGE 2018).

A sampler was also installed in May 2016 in the Ecological Reserve of Brasília (N° 10), in the Institute of Geography and Statistics (IBGE), located 35 km south of Brasilia, with 2,974,700 inhabitants (IBGE, 2018), representing the central region of Brazil within the Biome “cerrado”.

In December 2017 a sampler was installed in Campos do Jordão (51,763 inhabitants, IBGE 2018) located in the Serra da Mantiqueira at an altitude of 1,642 m and. The sampling site is located at the State Park of Campos do Jordão, which is highly vegetated, without industries nearby and with no considerable traffic of heavy duties vehicles. Therefore its atmosphere can be considered of background levels in relation to Brazilian air quality standards.

Outside Brazil, two DELTA sampler were deployed, one in Venezuela (N° 13) and another one in Argentina (N° 14). In Venezuela, the DELTA system was operational since September 2015 and was installed at the Venezuelan Institute of Scientific Research (IVIC) (Altos de Pipe, Miranda state, Venezuela), at the Altos Canales Air Quality Station (ECAAP). The ecosystem is cloud forests within the interior part of the Coastal Range. The forest area is about 832 hectares with an altitude range of 1000-1750 m above sea level.

In Argentina, the DELTA sampler is installed inside the Campus of the University of Buenos Aires, in the municipality of Buenos Aires, Argentina. The city is entirely within the Pampas domain and has approximately 2,890,151 inhabitants.

each site is indicated in Figure 2, containing the map by and the sampling site number (according with Tables 1 and 2). Table 2 presents the sampling sites coordinates and their main characteristic such as, main land cover, altitude, annual average temperature between 2010 and 2018, and the average annual precipitation between 2013 and 2018.

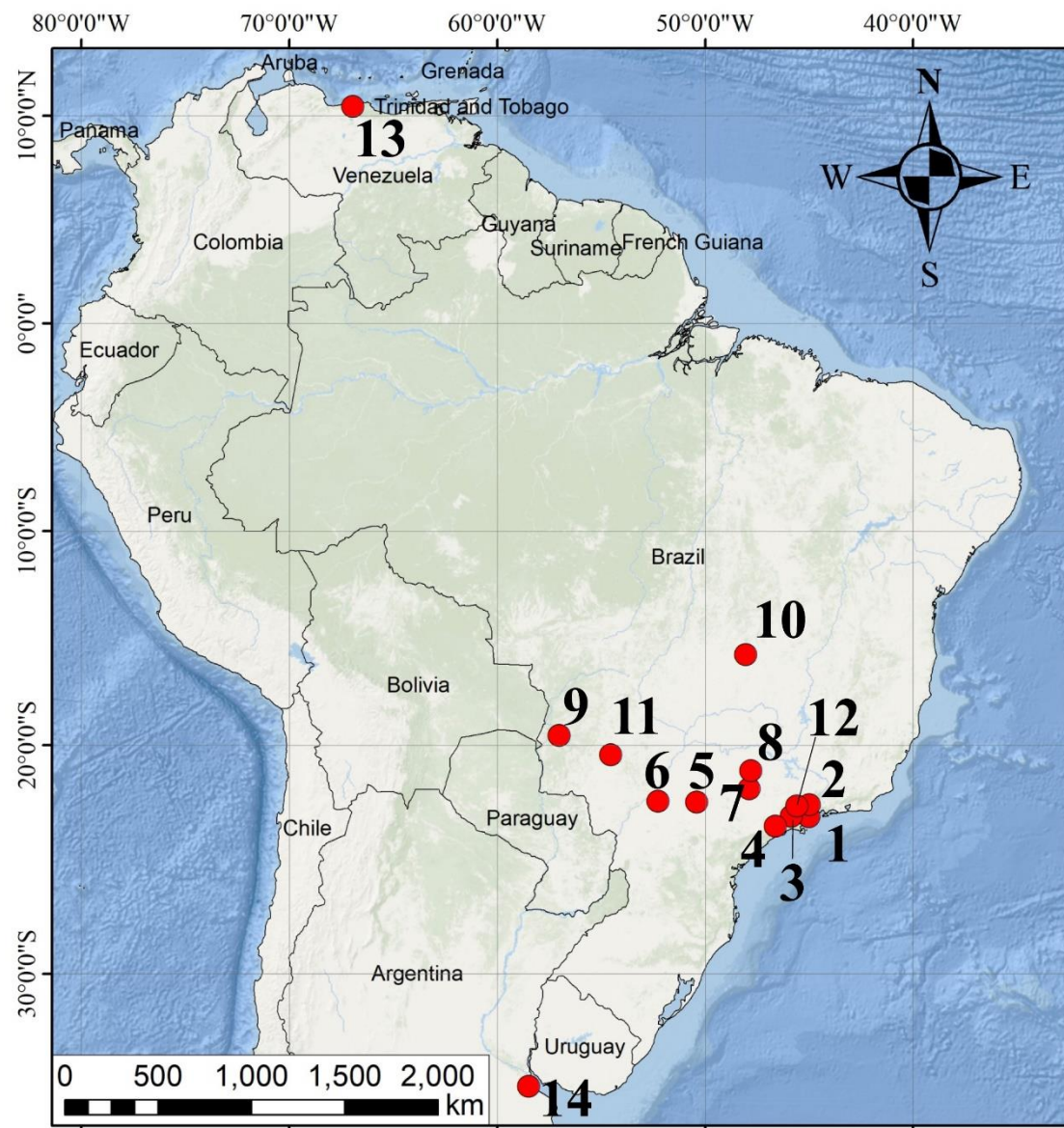


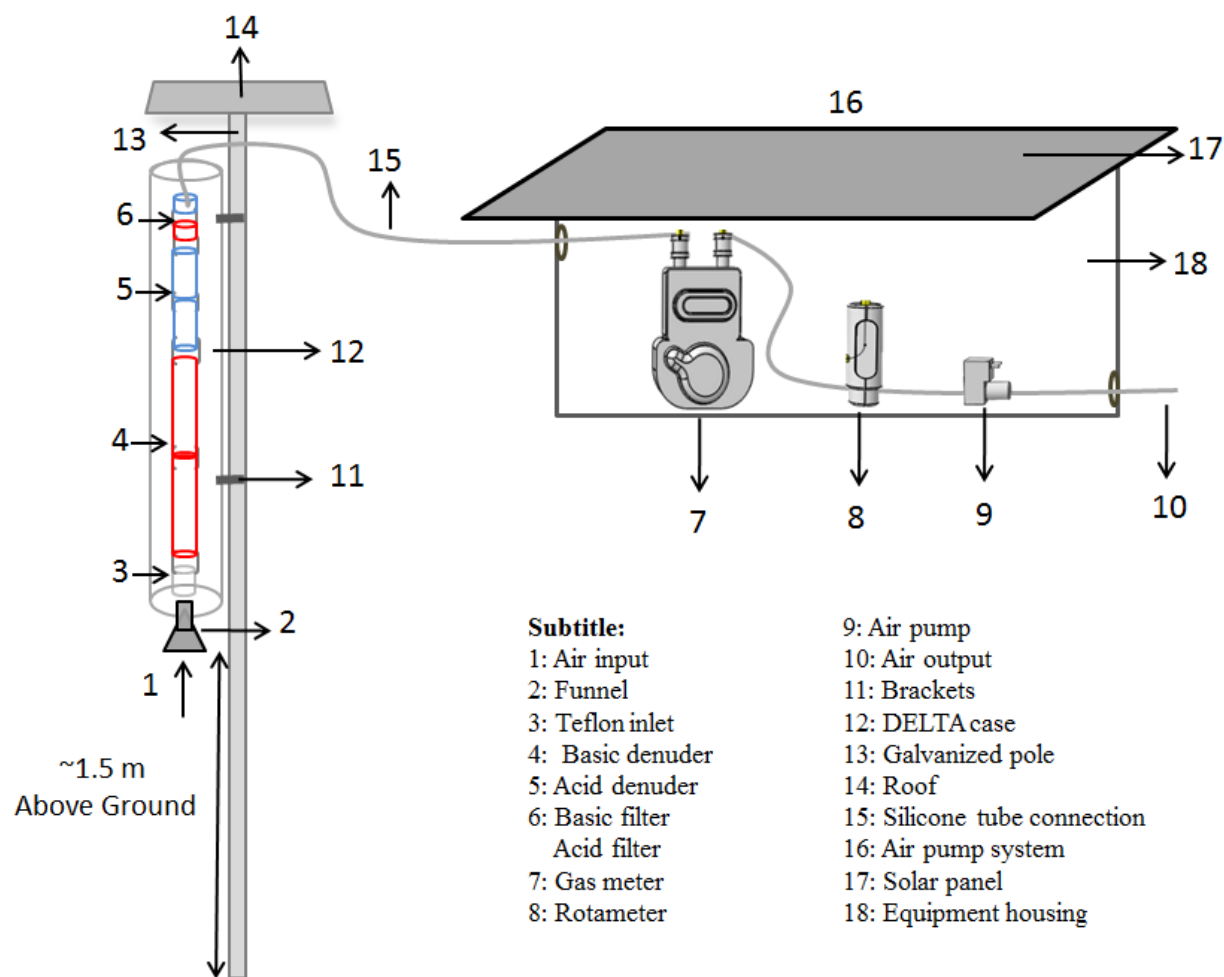
Figure 1 – Map showing the sampling site locations numbered according to tables 1 and 2.

Table 2 – General characteristic of each sampling site

| Nº | Site   | Coordinates                     | Annual rainfall average (mm) | Annual temperature average (°C) | Altitude (m) | Ecosystem   |
|----|--|---------------------------------|------------------------------|---------------------------------|--------------|---|
| 1  | Serra do Mar State Park, Cunha/SP                            | 23°13'57.62"S;<br>45°01'12.1"W  | 2200                         | 16.8                            | 1081         | Secondary Atlantic Forest   |
| 2  | INPE, Cachoeira Paulista/SP                                  | 22°41'12.2"S;<br>44°59'05"W     | 1500                         | 23                              | 580          | Degraded Atlantic Forest  |
| 3  | INPE, São José dos Campos/SP                                 | 23°12'26.37"S;<br>45°51'42.57"W | 1300                         | 22                              | 612          | Urban   |
| 4  | Institute Botany, USP – São Paulo/SP                         | 23°38'30.41"S;<br>46°37'22.92"W | 1380                         | 21                              | 804          | Urban   |
| 5  | Forest Institute, Assis/SP                                   | 22°34'16.39"S;<br>50°24'40.41"W | 1450                         | 21.8                            | 544          | Rural, “savannah” and Seasonal Semideciduous Forest                     |
| 6  | Morro do Diabo State Park, Teodoro Sampaio/SP                | 22°32'42.54"S;<br>52°15'39.57 W | 1370                         | 21.9                            | 415          | Rural, “savannah” (Brazilian Savanna) and Seasonal Semideciduous Forest |
| 7  | UFSCar, São Carlos/SP.                                       | 21°58'51.56"S;<br>47°52'56.48"W | 1515                         | 20.6                            | 863          | Urban   |
| 8  | USP, Ribeirão Preto/SP                                       | 21°09'39.5"S;<br>47°48'24"W     | 1500                         | 23.2                            | 530          | Atlantic Forest   |
| 9  | Passo do Lontra, Miranda River, Corumbá/MS                   | 19° 34' 31" S,<br>57° 01' 01" W | 1074                         | 25.4                            | 118          | Wetland   |
| 10 | Ecological Reserve IBGE, (UnB) Brasília/DF                   | 15°51'S;<br>47°63'W             | 1480                         | 21.4                            | 1100         | “savannah”  |
| 11 | UNIDERP/ ANHANGUERA Campo Grande/MS                          | 20° 26' 18" S<br>54° 32' 18" W  | 1534                         | 23.3                            | 532          | “savannah” forest and grassland.  |
| 12 | Campos do Jordão State Park                                  | 22° 44' 20" S<br>45° 35' 27"W   | 1850                         | 14.5                            | 1642         | Atlantic Forest and Brazilian Pine Forests                              |
| 13 | Venezuelan Institute of Scientific Research (IVIC) Venezuela | 10°25'N<br>66°56' W             | 1010                         | 16,1                            | 1000-1750    | Montane, Cloud Tropical Forest  |
| 14 | Buenos Aires University - Argentina                          | 34°35'28.6"S<br>58°28'46.5"W    | 1147                         | 17,6                            | 1147         | Urban   |

### 3. Data acquisition

The construction, assembly and sampling procedures of the DELTA system are described in detail in Forti et al., 2016 and Palandi et al., 2017. Briefly, the pumping system is fixed at the sampling site. The system is exposed for 15 consecutive days, with the expectation of being sampled from 12 to 17 m<sup>3</sup> of air per month. Figure 2 shows the assembly diagram of denuders and filters. The system consists of a sequence of four glass tubes (denuders) and a unit with stacked filters (two filters).



Fonte: Souza et al, 2019.

Figure 2 - Denuders and stacked filters assemblage schema.

A sequence of two denuders and two filters (DELTA cartridge), and a pumping schema constitutes the DELTA system. The first two denuders are glass cylinders with 15 cm long and internal diameter of 0.7 cm coated with sodium hydroxide solution (NaOH 1% w/v) and 1% glycerol m/v in methanol forming a fine hydroxide film that reacts with acid gases such as HNO<sub>3</sub>, SO<sub>2</sub> and HCl. In the sequence, there are other two 10 cm long denuders with internal diameter of 0.7 cm coated with 5% w/v citric acid in methanol to react with NH<sub>3</sub>. The denuders train is followed by the staked cellulose filters (Whatman, diameters of 25 mm and pore diameter of 11 microns) to capture the particulate matter. The first filter is impregnated with an alkaline solution (NaOH 5% w/v) and 10% glycerol m/v in methanol to retain particulate matter as well as to react with NH<sub>4</sub><sup>+</sup> salts to form NH<sub>3</sub> that percolates and is captured by the second filter which is impregnated with 13% w/w citric acid in methanol to react with NH<sub>3</sub>.

The DELTA sampler is based on the principle that gases in an air flow have a faster diffusion rate than the particles, therefore it is possible to separate the gaseous phases from the particulate allowing for the gaseous species to react with the coating of the tube while the particles are transported to impact on the filters (Fern, 1979). The air inlet consists of a 2.8 cm Teflon tube to stabilize the flow, a pumping system,

built to keep the airflow between 0.3-0.4 L min<sup>-1</sup> and a volume meter. The DELTA system assembly scheme is shown in the diagram of Figure 2.

After the sampling period, the DELTA cartridges were sent to the laboratory where denudes and filters were subjected to extraction in aqueous medium. The species extraction from the basic coated denuders and filter is made with a solution of deionized water type II and 0.05% hydrogen peroxide. The species of interest are extracted from the two denudes and filter coated with acidic solution using deionized water type II. In these extracts, the following species are analyzed: for the gaseous forms NH<sub>3</sub>, HNO<sub>3</sub>, SO<sub>2</sub> and HCl, the equivalent aqueous ionic species are measured (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, and Cl<sup>-</sup>); and from the filters, the same species are extracted as in the gaseous, however associated to the particles forms (Souza et al, 2019).

Concentration values of the measured species are expressed in µg m<sup>-3</sup>, and they were determined using liquid ion chromatography (Metrohm, model 850) using the protocol described in Forti et al, 2016.

#### 4. Data Availability.

The data presented here were validated through statistics, comparisons between laboratories and discussions between collaborators. The metadata and data set are available at the link shown below.

Tabela 3 –Metadata and data links.

| Identification | FAPESP 2012 / 06416-1<br>(1 <sup>st</sup> phase)  | Metadata CRN3005<br>(2 <sup>nd</sup> phase)   |
|----------------|---|---|
| data           | <a href="http://urlib.net/rep/8JMKD3MGP3W34P/3TSLHUP">http://urlib.net/rep/8JMKD3MGP3W34P/3TSLHUP</a> | <a href="http://urlib.net/rep/8JMKD3MGP3W34P/3TSLK85">http://urlib.net/rep/8JMKD3MGP3W34P/3TSLK85</a> |

The species collected in the filters with the DELTA system are derived from the emission of particulate material from natural and anthropic sources, adsorption of gases into the particulate phase, as well as gas-particle conversion. In the gas phase, ammonium is the result of the reaction of ammonia with the denuder acid coating. The same refers to sulfate which is the oxidation of sulfur oxides to sulfate in the denuder. The nitrate is the result of the adsorption of HNO<sub>2</sub> and HNO<sub>3</sub> in the denuder coated surface. It is known that nitrate, sulfate and ammonium may have a natural component source derived from seawater, vegetation (exudate) and soils. Nevertheless, in most of the studied sites, anthropogenic sources of these species are also an important fraction of the atmospheric composition, however, its magnitude depends on their geographical location, with contribution from sources such as vehicular emissions and industry due to the burning of fossil fuels, petrochemical industry, biomass burning, agriculture, animal husbandry, etc.

Tables from 5.1 to 5.12 show the statistics for each species of interest and for each site, considering the sampling period from March 2013 to November 2018.



Table 5.1 – DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for São José dos Campos-SP (INPE).

| <b>São José dos Campos</b>    |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 108   | 0.18029 | 0.03695 | 0.24382 | 2.00x10 <sup>-4</sup> | 1.22238 |
| HNO <sub>x</sub>              | 108   | 1.31934 | 0.87698 | 1.21466 | 5.30x10 <sup>-4</sup> | 8.39802 |
| SO <sub>2</sub>               | 108   | 1.75937 | 0.98369 | 1.52127 | 5.40x10 <sup>-4</sup> | 7.48112 |
| NH <sub>3</sub>               | 108   | 1.76155 | 1.01958 | 1.75973 | 1.70x10 <sup>-4</sup> | 9.50935 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 91    | 0.42328 | 0.14382 | 0.39391 | 0.50x10 <sup>-4</sup> | 1.99951 |
| NO <sub>3</sub> <sup>-</sup>  | 91    | 1.04757 | 0.71311 | 0.87723 | 2.45x10 <sup>-3</sup> | 4.24218 |
| SO <sub>4</sub> <sup>2-</sup> | 91    | 0.76841 | 0.36457 | 0.88857 | 9.90x10 <sup>-4</sup> | 5.64042 |
| NH <sub>4</sub> <sup>+</sup>  | 106   | 0.73275 | 0.22671 | 0.78330 | 1.30x10 <sup>-4</sup> | 4.20732 |

Table 5.2 – DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for Cachoeira Paulista (INPE)-SP.

| <b>Cachoeira Paulista</b>     |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 90    | 0.17304 | 0,02391 | 0,29556 | 1.50x10 <sup>-4</sup> | 1,82004 |
| HNO <sub>x</sub>              | 90    | 0.61528 | 0,20286 | 0,67008 | 4.00x10 <sup>-4</sup> | 2,84432 |
| SO <sub>2</sub>               | 90    | 0.34805 | 0,11803 | 0,36337 | 3.80x10 <sup>-4</sup> | 1,72658 |
| NH <sub>3</sub>               | 90    | 0.92042 | 0,41191 | 0,88241 | 1.00x10 <sup>-4</sup> | 3,83236 |
| Cl <sup>-</sup>               | 70    | 0.21161 | 0.09635 | 0.18969 | 1.90x10 <sup>-4</sup> | 0.65363 |
| NO <sub>3</sub> <sup>-</sup>  | 73    | 0.60294 | 0.21622 | 0.79084 | 6.50x10 <sup>-4</sup> | 3.23333 |
| SO <sub>4</sub> <sup>2-</sup> | 74    | 0.52092 | 0.14333 | 0.84087 | 7.30x10 <sup>-4</sup> | 4.91078 |
| NH <sub>4</sub> <sup>+</sup>  | 86    | 0.60168 | 0.22790 | 0.71626 | 1.20x10 <sup>-4</sup> | 3.86358 |

Tabela 5.3 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for São Carlos-SP.

| <b>São Carlos</b>             |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 33    | 0.27836 | 0.02685 | 0.51447 | 1.80x10 <sup>-4</sup> | 2.17314 |
| HNO <sub>x</sub>              | 33    | 0.54430 | 0.27058 | 0.55731 | 4.60x10 <sup>-4</sup> | 1.89919 |
| SO <sub>2</sub>               | 33    | 0.38101 | 0.15029 | 0.41119 | 3.70x10 <sup>-4</sup> | 1.61637 |
| NH <sub>3</sub>               | 33    | 1.41504 | 0.88735 | 1.26930 | 4.73x10 <sup>-2</sup> | 4.86124 |
| Cl <sup>-</sup>               | 33    | 0.15812 | 0.03222 | 0.16880 | 2.20x10 <sup>-4</sup> | 0.55281 |
| NO <sub>3</sub> <sup>-</sup>  | 33    | 0.58934 | 0.31429 | 0.64504 | 9.56x10 <sup>-3</sup> | 2.58455 |
| SO <sub>4</sub> <sup>2-</sup> | 33    | 0.24180 | 0.05827 | 0.48947 | 4.70x10 <sup>-4</sup> | 2.68667 |
| NH <sub>4</sub> <sup>+</sup>  | 33    | 0.58342 | 0.25836 | 0.74263 | 2.37x10 <sup>-3</sup> | 3.53154 |

Tabela 5.4 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for São Paulo-SP.

| <b>São Paulo</b>              |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 43    | 0.22503 | 0.06557 | 0.25127 | 2.50x10 <sup>-4</sup> | 1,34165 |
| HNO <sub>x</sub>              | 43    | 1.82111 | 1.01849 | 1.34447 | 9.00x10 <sup>-4</sup> | 5,88987 |
| SO <sub>2</sub>               | 43    | 1.59826 | 0.58783 | 1.11066 | 5.40x10 <sup>-4</sup> | 3,91345 |
| NH <sub>3</sub>               | 43    | 2.32128 | 1.34746 | 1.57922 | 2.00x10 <sup>-4</sup> | 8,01564 |
| Cl <sup>-</sup>               | 27    | 0.73881 | 0.37281 | 0.70967 | 3.21x10 <sup>-3</sup> | 2.57174 |
| NO <sub>3</sub> <sup>-</sup>  | 27    | 2.05826 | 1.47927 | 1.50678 | 1.97x10 <sup>-2</sup> | 6.30614 |
| SO <sub>4</sub> <sup>2-</sup> | 27    | 0.87337 | 0.50736 | 0.67749 | 4.87x10 <sup>-4</sup> | 2.57829 |
| NH <sub>4</sub> <sup>+</sup>  | 43    | 0.99175 | 0.54736 | 0.65984 | 1.90x10 <sup>-3</sup> | 3.10085 |

Tabela 5.5 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for Cunha-SP.

| <b>Cunha</b>                  |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 96    | 0.16464 | 0.01797 | 0.49686 | 1.20x10 <sup>-4</sup> | 4.37261 |
| HNO <sub>x</sub>              | 96    | 0.19700 | 0.05595 | 0.31436 | 3.10x10 <sup>-4</sup> | 1.75678 |
| SO <sub>2</sub>               | 96    | 0.06649 | 0.01603 | 0.11782 | 3.10x10 <sup>-4</sup> | 0.78183 |
| NH <sub>3</sub>               | 96    | 0.57523 | 0.20069 | 0.99731 | 1.70x10 <sup>-4</sup> | 6.88582 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 84    | 0.26994 | 0.04569 | 0.52918 | 2.20x10 <sup>-4</sup> | 3.51739 |
| NO <sub>3</sub> <sup>-</sup>  | 84    | 0.26653 | 0.06055 | 0.46087 | 4.40x10 <sup>-4</sup> | 3.03832 |
| SO <sub>4</sub> <sup>2-</sup> | 84    | 0.27557 | 0.08097 | 0.40160 | 9.40x10 <sup>-4</sup> | 2.25182 |
| NH <sub>4</sub> <sup>+</sup>  | 100   | 0.47538 | 0.18073 | 0.54052 | 1.60x10 <sup>-4</sup> | 2.89783 |

Tabela 5.6 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for DELTA sampler Statistics results for Assis-SP.

| <b>Assis</b>                  |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 80    | 0.09274 | 0.02721 | 0.11829 | 1.10x10 <sup>-4</sup> | 0.50790 |
| HNO <sub>x</sub>              | 80    | 0.46099 | 0.29357 | 0.31631 | 1.30x10 <sup>-4</sup> | 1.38173 |
| SO <sub>2</sub>               | 80    | 0.12341 | 0.05977 | 0.11025 | 1.30x10 <sup>-4</sup> | 0.50824 |
| NH <sub>3</sub>               | 80    | 1.13796 | 0.66127 | 0.83787 | 2.40x10 <sup>-4</sup> | 4.34799 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 80    | 0.22060 | 0.08727 | 0.29078 | 3.70x10 <sup>-4</sup> | 1.74824 |
| NO <sub>3</sub> <sup>-</sup>  | 80    | 0.50733 | 0.21169 | 0.68133 | 6.00x10 <sup>-4</sup> | 4.06333 |
| SO <sub>4</sub> <sup>2-</sup> | 80    | 0.26616 | 0.13894 | 0.28975 | 3.80x10 <sup>-4</sup> | 1.66869 |
| NH <sub>4</sub> <sup>+</sup>  | 80    | 0.56158 | 0.17341 | 1.04166 | 9.00x10 <sup>-5</sup> | 8.18772 |

Tabela 5.7 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for DELTA sampler Statistics results for Teodoro Sampaio-SP.

| <b>Teodoro Sampaio</b>        |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 27    | 0.10280 | 0.01376 | 0,29907 | 1.90x10 <sup>-4</sup> | 1.57633 |
| HNO <sub>x</sub>              | 27    | 0.17871 | 0.11768 | 0,13141 | 1.06x10 <sup>-3</sup> | 0,50660 |
| SO <sub>2</sub>               | 27    | 0.06252 | 0.02489 | 0,05875 | 2.30x10 <sup>-4</sup> | 0,18388 |
| NH <sub>3</sub>               | 27    | 0.81629 | 0.52215 | 0,43194 | 3.50x10 <sup>-4</sup> | 1,90676 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 27    | 0.11243 | 0.03903 | 0.12302 | 1.20x10 <sup>-4</sup> | 0.56565 |
| NO <sub>3</sub> <sup>-</sup>  | 27    | 0.26590 | 0.15571 | 0.20930 | 7.10x10 <sup>-4</sup> | 0.81998 |
| SO <sub>4</sub> <sup>2-</sup> | 27    | 0.08355 | 0.04805 | 0.07580 | 4.10x10 <sup>-4</sup> | 0.33448 |
| NH <sub>4</sub> <sup>+</sup>  | 27    | 0.61697 | 0.22453 | 1.43574 | 2.26x10 <sup>-2</sup> | 7.32172 |

Tabela 5.8 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for DELTA sampler Statistics results for Ribeirão Preto-SP.

| <b>Ribeirão Preto</b>         |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 56    | 0.14900 | 0.04113 | 0.30773 | 3.70x10 <sup>-4</sup> | 2.22678 |
| HNO <sub>x</sub>              | 56    | 0.74002 | 0.44078 | 0.59087 | 8.40x10 <sup>-4</sup> | 2.25873 |
| SO <sub>2</sub>               | 56    | 0.19904 | 0.07449 | 0.27920 | 8.40x10 <sup>-4</sup> | 1.73372 |
| NH <sub>3</sub>               | 56    | 1.52696 | 0.57374 | 1.57382 | 1.60x10 <sup>-4</sup> | 9.26326 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 43    | 0.21208 | 0.06856 | 0.24419 | 5.90x10 <sup>-4</sup> | 0.91914 |
| NO <sub>3</sub> <sup>-</sup>  | 43    | 0.74284 | 0.29915 | 0.77816 | 8.20x10 <sup>-4</sup> | 4.29914 |
| SO <sub>4</sub> <sup>2-</sup> | 43    | 0.46799 | 0.20251 | 0.73156 | 7.40x10 <sup>-4</sup> | 4.68098 |
| NH <sub>4</sub> <sup>+</sup>  | 56    | 0.63345 | 0.25042 | 0.70454 | 2.40x10 <sup>-4</sup> | 3.78657 |

Tabela 5.9 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for Pantanal-MS.

| <b>Pantanal</b>               |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 11    | 0.23165 | 0.02819 | 0.50361 | 2.20x10 <sup>-4</sup> | 1.73651 |
| HNO <sub>x</sub>              | 11    | 0.26357 | 0.18279 | 0.26842 | 6.42x10 <sup>-2</sup> | 0.94872 |
| SO <sub>2</sub>               | 11    | 0.06049 | 0.04084 | 0.04167 | 4.60x10 <sup>-3</sup> | 0.13713 |
| NH <sub>3</sub>               | 11    | 0.48458 | 0.16120 | 0.59261 | 3.05x10 <sup>-3</sup> | 1.95485 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 3     | 0.00068 | 0.00066 | 0.00022 | 4.30x10 <sup>-4</sup> | 0.00084 |
| NO <sub>3</sub> <sup>-</sup>  | 3     | 0.79226 | 0.57654 | 0.77248 | 2.61x10 <sup>-1</sup> | 1.67844 |
| SO <sub>4</sub> <sup>2-</sup> | 3     | 0.00884 | 0.00393 | 0.00753 | 3.60x10 <sup>-4</sup> | 0.01476 |
| NH <sub>4</sub> <sup>+</sup>  | 11    | 0.18248 | 0.08294 | 0.13019 | 2.0x10 <sup>-4</sup>  | 0.39494 |

Tabela 5.10 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for Brasília-DF.

| <b>Brasília</b>               |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 47    | 0.07058 | 0.01608 | 0.10150 | 3.50x10 <sup>-4</sup> | 0,36247 |
| HNO <sub>x</sub>              | 47    | 0.40370 | 0.27158 | 0.26894 | 8.70x10 <sup>-4</sup> | 1,23409 |
| SO <sub>2</sub>               | 47    | 0.11187 | 0.03584 | 0.19619 | 8.60x10 <sup>-4</sup> | 1,25616 |
| NH <sub>3</sub>               | 47    | 1.03175 | 0.45514 | 1.09957 | 1.50x10 <sup>-4</sup> | 5,38314 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 47    | 0.19556 | 0.05647 | 0.23621 | 9.70x10 <sup>-4</sup> | 0.91960 |
| NO <sub>3</sub> <sup>-</sup>  | 47    | 0.42561 | 0.12025 | 0.62413 | 7.10x10 <sup>-4</sup> | 2.46755 |
| SO <sub>4</sub> <sup>2-</sup> | 47    | 0.27627 | 0.09557 | 0.28469 | 9.20x10 <sup>-4</sup> | 1.23443 |
| NH <sub>4</sub> <sup>+</sup>  | 47    | 0.51316 | 0.07408 | 0.77378 | 1.40x10 <sup>-4</sup> | 3.41893 |

Tabela 5.11 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for Campo Grande-SP.

| <b>Campo Grande</b>           |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 17    | 0.06060 | 0.01872 | 0.06716 | 3.00x10 <sup>-4</sup> | 0.18943 |
| HNO <sub>x</sub>              | 17    | 0.36153 | 0.20447 | 0.22481 | 3.40x10 <sup>-4</sup> | 0.69520 |
| SO <sub>2</sub>               | 17    | 0.10610 | 0.04803 | 0.15038 | 3.40x10 <sup>-4</sup> | 0.55321 |
| NH <sub>3</sub>               | 17    | 1.47094 | 0.89020 | 0.91735 | 2.96x10 <sup>-3</sup> | 3.06717 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 17    | 0.26529 | 0.07685 | 0.31094 | 2.70x10 <sup>-4</sup> | 1.19729 |
| NO <sub>3</sub> <sup>-</sup>  | 17    | 0.62108 | 0.18525 | 0.76345 | 4.50x10 <sup>-4</sup> | 3.08625 |
| SO <sub>4</sub> <sup>2-</sup> | 17    | 0.31787 | 0.16569 | 0.24548 | 2.18x10 <sup>-4</sup> | 0.74642 |
| NH <sub>4</sub> <sup>+</sup>  | 17    | 0.69814 | 0.30103 | 0.76945 | 1.40x10 <sup>-4</sup> | 3.04013 |

Tabela 5.12 – DELTA sampler Statistics results for DELTA sampler Statistics (Count, Arithmetic Mean: Mean; Geometric Mean: GMean; Standard Deviation: STD, Minimum: Min and Maximum: Max) for Campos do Jordão-SP.

| <b>Campos do Jordão</b>       |       |         |         |         |                       |         |
|-------------------------------|-------|---------|---------|---------|-----------------------|---------|
| Species                       | Count | Mean    | Gmean   | STD     | Min                   | Max     |
| ug/m <sup>3</sup>             |       |         |         |         |                       |         |
| Gaseous form                  |       |         |         |         |                       |         |
| HCl                           | 23    | 0.11481 | 0,01633 | 0,13145 | 3.30x10 <sup>-4</sup> | 0,33211 |
| HNO <sub>x</sub>              | 23    | 0.14185 | 0,02946 | 0,22149 | 5.70x10 <sup>-4</sup> | 0,80269 |
| SO <sub>2</sub>               | 23    | 0.04848 | 0,00998 | 0,08610 | 8.60x10 <sup>-4</sup> | 0,32036 |
| NH <sub>3</sub>               | 23    | 0.48800 | 0,06005 | 0,83032 | 3.20x10 <sup>-4</sup> | 3,60554 |
| particulate form              |       |         |         |         |                       |         |
| Cl <sup>-</sup>               | 23    | 0.23510 | 0.05890 | 0.36500 | 6.80x10 <sup>-4</sup> | 1.66884 |
| NO <sub>3</sub> <sup>-</sup>  | 23    | 0.57653 | 0.08114 | 1.36339 | 1.11x10 <sup>-4</sup> | 5.61233 |
| SO <sub>4</sub> <sup>2-</sup> | 23    | 0.31877 | 0.03326 | 1.02278 | 1.51x10 <sup>-4</sup> | 4.91400 |
| NH <sub>4</sub> <sup>+</sup>  | 23    | 0.32066 | 0.07113 | 0.32013 | 2.00x10 <sup>-4</sup> | 1.04819 |

## 5. Comments

The concentration values obtained at each site, when compared to each other, are coherent according to the location and its atmospheric characteristic. The lower sulfur dioxide and sulfate concentration values can be observed in the sites where the urban activities are minor because the vehicular emissions as well as industries are not significant sources.

This broader spatialization allows a better evaluation of the processes and changes in the atmospheric composition since the data set can be used in deposition models. The use of models with real data allows the encompassing of large geographic areas through a spatialization permitting the development of different scenarios associated with different soil uses.

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## **7. Thanks**

Prof. Dr. A. Barbassa and Sr. J.B. Rosa (UFSCAR / CCET), J.B.A. dos Santos and Sr. V.C. Pereira (Serra do Mar State Park, Cunha/SP), Dra. Silvia Souza and Giselle Pedrosa (Institute Botany, USP – São Paulo/SP), Mercedes Bustamante and Gabriela Nardoto (Ecological Reserve IBGE, UnBBrasília/DF), Thanks for sampling and help during sampling in respective sites.