Preliminary Fog Chemistry Analysis at two different sites: Castello Branco and Raposo Tavares Roads in São Paulo St., Brazil

(1) Dept. of Atmospheric Sciences (IAG)-University of São Paulo, Brazil, (2) Institute for Chemical Technologies and Analytics, Univ. of Technology-Austria, (3) Institute of Chemistry-University of São Paulo, Brazil

Abstract
The aim of this study is characterize the fog composition at two sites nearby the important roads, at surrounding São Paulo City, in the São Paulo State, Brazil. Both sites (CB and RT) present high number of fog events and they cause traffic problems, mainly due to radiative fogs. Castello Branco (CB) site also presents a great number of chemical industries, opposite of Raposo Tavares (RT) site. Those industries may produce CCN (sulfates, nitrates and ammonia, mainly) and due to these fog events are observed. Five events were collected from May to August 2009 at both sites. The overall results show elevated values of ammonium particularly (96 mg.L-1) at CB site as expected due to the fertilizer industries in surroundings. Additionally, it presents a high standard deviation (131 mg.L-1), perhaps due to the industry exhaustion time schedule. High values of chlorine were evaluated as well (860 mg.L-1), suggesting industrial sources, and landfill waste burning often observed in Brazilian cities. Sodium concentrations were the highest at CB site (av. 352 mg.L-1) on June 22nd event, which may be it is from Atlantic Ocean source, despite that it is more than 100 km far. CB site also presents high values of sulfate, potassium and nitrates. Compared to RT site, all these chemical species present higher values at CB site, except nitrates, with similar concentrations. Oxalate (between 0.5 mg.L-1 at RT and 0.3 mg.L-1 at CB) and levoglucosan (0.3 mg.L-1 at RT and 0.2 mg.L-1 at CB) were found in fog water which indicates biomass burning (sugar cane) which are common during that period (May to November) of the year. It must be notified as well that the weather conditions during last winter were atypical, particularly from July to August. They were influenced by El Niño phenomena, which increased rain amount and higher temperatures at Southeastern Brazil where São Paulo site is located. The increase of rain events affected the number of radiative fogs. Advection fog events were formed, in which were difficult to collect due to its density. Additionally, at advection events, the industry impact is decreased to the air dispersion and wind. These are preliminary results which demands air mass trajectories.

1. Introduction
Fog events are characterized by visibility impacts on traffic around the whole planet. Besides, fog droplets are known to be efficient scavengers of air pollutants close to the surface as well as they are formed by them through CCN nucleation processes. Due these facts, there are many studies taking in account fog chemistry. For example, during 1980s, it was demonstrated the high acidity of fog water in southern California (Munger et al., 1983), while another study in this area showed that fogs were frequently 100 times more acidic than rain (Hileman, 1983). Since this time, a large number of studies showed very high concentrations of inorganic and organic compounds in fog water such as Munger et al, 1990; Millet et al., 1995; Richartz et al., 1990; Millet et al., 1997; and Herckes et al. (2002).

On the other hand, although night traffic represents only 10% of the total traffic, one third of accidents take place during night time. Fog events take place usually at night time, where the accidents may occur. Consequently, the traffic road managers pay a lot of attention during night time which is more propitious for fog formation. Therefore, the aim of this study is characterize the fog composition at two sites nearby the important roads, at surrounding São Paulo City, in the São Paulo State, Brazil. Both sites (Castello Branco and Raposo Tavares roads) present high number of fog
2. Methodology

Techniques for collection of fog and cloud water have received considerable attention over the past two decades in response to a desire to better understand bow clouds and fog process atmospheric CCN. Several instruments have been developed and utilized for collecting fog and cloud water samples for chemical analysis which have shifted somewhat to the design of instruments that can segregate collected drops by size (Collett et al., 1993, Collett et al.,1995). The primary use of most cloud water samplers is to collect cloud water samples for the analysis of chemical concentrations. Therefore the herein used sampler was developed by Dr. Collett and placed at two sites described above during the winter of 2009. Five events were collected and analyzed. The chemical methodology is divided in 2 parts: Brazilian analysis evaluated by Dr. Vasconcellos of IQ-USP, and 2- analysis made in Austria evaluated by Dr. Heidi Bauer of Institute for Chemical Technologies and Analytics, Vienna University of Technology.

3. Preliminary Results and conclusion

The overall results show elevated values of many air pollutants which may cause fog nucleation such as \( \text{NH}_4^+ \), NaCl, \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \) (see Table 1). Ammonium particularly at CB site was found with high concentration (96 mg.L\(^{-1}\)) as expected due to the fertilizer industries in surroundings. Additionally, ammonium also presents a high standard deviation (131 mg.L\(^{-1}\)), perhaps due to the industry exhaustion time schedule in the area. It must be notified that the ammonium smell in the area is much punctuated. High values of chlorine were evaluated as well (860 mg.L\(^{-1}\)) in this site, suggesting industrial sources, and landfill waste burning often observed in Brazilian cities. Sodium concentrations were the highest at CB site (av. 352 mg.L\(^{-1}\)) on June 22\(^{nd}\) event, which may be it is from Atlantic Ocean source, despite that it is more than 100 km far. Atmospheric transportation must be evaluated in order to clarify it. CB site also presents high values of sulfate, potassium and nitrates when compared to RT site. All these chemical species present higher values at CB site, except nitrates, with present similar concentrations. In Table 2, oxalate (0.5 mg.L\(^{-1}\) at RT and 0.3 mg.L\(^{-1}\) at CB) and levoglucosan (0.3 mg.L\(^{-1}\) at RT and 0.2 mg.L\(^{-1}\) at CB) were found in fog water which indicates biomass burning (sugar cane, probably) which are common during that period of the year (May to November). Other sugars (see Table 2) could also emphasize it.

It must be notified as well that the weather conditions during last winter were atypical, particularly from July to August. They were influenced by El Niño phenomena, which increased rain amount and higher temperatures at Southeastern Brazil where São Paulo site is located. The increase of rain events affected the number of radiative fogs. Some advective fog events were formed, in which were difficult to collect due to its density, usually quite soft. Additionally, at advection events, the industry impact is decreased to the air dispersion and wind. These are preliminary results which demand air mass trajectories and more events to be sampled and analyzed in which will be done in the 2010 winter time.

Table 1. Average of cations and anions in each site (mg.L\(^{-1}\)) and their standard deviations (sd). CB means Castello Branco and RT, Raposo Tavares.
Table 2. Analyses made in Austria (in µg.mL$^{-1}$ or mg.L$^{-1}$) for the event of June 15 at RT and for the event of June 22 at CB.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>RT 15/6</th>
<th>CB 22/6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan</td>
<td>0.597</td>
<td>0.328</td>
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<tr>
<td>Arabitol</td>
<td>0.025</td>
<td>0.075</td>
</tr>
<tr>
<td>Mannitol</td>
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<td>0.321</td>
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<tr>
<td>Mannosan</td>
<td>0.113</td>
<td>0.030</td>
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<td>Glucose</td>
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<td>0.257</td>
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<td>Oxalate</td>
<td>0.491</td>
<td>0.260</td>
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</tbody>
</table>

4. References


