Fine particulate emission sources identification in the atmosphere of São Paulo

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Abstract
The contribution of this work was related to the evaluation of the emission sources profile for the fine particles concentration, mainly the role of vehicular emission in São Paulo atmosphere. During a year, starting in August 2007, daily 24 hours samples were collected. The particles were characterized for its mass concentration, elemental speciation by means of X-Ray fluorescence analysis, ionic composition and Black Carbon mass concentration. Receptor modeling was applied as the methodology for the identification of fine particles pollutants sources.

Introduction
The Metropolitan Region of São Paulo (MRSP) holds a lot of polluter industries and a 7 million car’s fleet. These features are responsible for strong air quality degradation and a complex mixture of aerosols and gases in the atmosphere. The aerosol consists in solid and liquid particles suspended in the atmosphere. The chemical composition (origin and
source) and size distribution (nanometers to micrometers) may vary according to emission and secondary process in the atmosphere.

The aerosol can be split in two different size modes: course particulates (diameter between 2.5 and 10 μm) and fine ones (diameter below 2.5 μm). The last one, although harmful to the health, is not regulated in Brazil by the national government environmental agency (Seinfeld e Pandis, 1998, CETESB, 2008).

Methodology

The samples were collected at the Medical School building, located at Dr. Arnaldo Avenue, using the fine particulate sampler, during 24 hours, between August 2007 and August 2008, totaling one year data. The filters were submitted to a gravimetric analysis, (weighing) before and after the sampling period. The weighing’s objective is to quantify the PM$_{2.5}$. The samples were submitted to analysis for the determination of: black-carbon, by means of reflectance analysis, elementary constitution with X-ray fluorescence analysis and cation-anion concentration, with chromatography analysis.

The sources identification was accomplished using multivariate models: principal component analysis (PCA) and absolute PCA. The objective is to reduce a dataset, with a large variables number (elements identified in the elementary analysis), to a small one, only with independent variables (sources indicated by this analysis).

Results

The figure 1 shows the dataset obtained by the gravimetric and reflectance analysis. The BC concentrations follow the MP$_{2.5}$ variability. The higher concentrations ($75 μg m^{-3}$ PM$_{2.5}$ and $25 μg m^{-3}$ BC) occurs during the winter (less precipitation period and with more stable atmosphere). In these months a wet removal process reduction are observed. The lower concentration occurs (in both cases) during the summer, a rainy and airy period. The Figure 2 presents the elementary concentrations obtained by the X-ray fluorescence analysis. The lower concentrations were identified in V, Cr and Ni, below than 1.6 ng m$^{-3}$ and the higher concentrations were observed in S, K and Fe (important urban center markers). The higher Al, Si and Fe concentrations indicates soil dust re-suspension. The S concentrations were due to the gas-particle conversion, (mainly the SO$_2$ gas).
The sources quantification was accomplished by PM$_{2.5}$ normalized regression calculation, applied to the FA absolute scores. These results can be visualized in the table 1. The identified sources were: light and heavy vehicles, industry and soil resuspension, a factor related to industries present mixture sources. The regression explained about 93.5% of the PM$_{2.5}$ possible sources. The heavy vehicles (diesel fuel) and industries distinguish of this total.
Table 1. Sources identification and participation.

<table>
<thead>
<tr>
<th>Identified source</th>
<th>Participation (%)</th>
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<tbody>
<tr>
<td>Heavy vehicle</td>
<td>38,5</td>
</tr>
<tr>
<td>Light vehicle</td>
<td>13,7</td>
</tr>
<tr>
<td>Industry (and vehicles)</td>
<td>24,7</td>
</tr>
<tr>
<td>Soil</td>
<td>16,7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>93,5</strong></td>
</tr>
</tbody>
</table>

Conclusions
The most significative PM$_{2.5}$ and BC concentrations occur during the winter with less precipitation and more stable atmosphere. The lower concentrations were observed during the summer. Four main sources were identified by the PCA technique (some uncertainty still remains because more than one source can contribute to same element emission). The most important emission was the vehicular one, contributing with more than 50%, mainly heavy vehicles (39%), due to the diesel burning.

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*Bibliography*