

# Water soluble ionic species of particulate matter in an urban road tunnel

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The megacity of São Paulo is facing recurring problems regarding the degradation of air quality, with intense vehicular emissions accounting for a substantial part of this situation. The São Paulo vehicle fleet is quite diverse, containing old and new vehicles powered with gasol (gasoline with 20 - 25% ethanol), hydrated ethanol, CNG (compressed natural gas) and diesel. This fact, coupled with the changing fleet profile (addition of flex-fuel engines), increases the complexity of emissions and physical and chemical processes that involves aerosols.

In order to understand the limiting factors for the formation of aerosol in the atmosphere of São Paulo, in particular the participation of the major inorganic ionic species (sulfate, nitrate, ammonium and chloride), measurements campaigns were carried inside an urban road tunnel (Jânio Quadros) and in the surrounding region (Parque do Povo).

The campaign used two particle samplers (Tupiniquim - AFG model, and Partisol - automatic dichotomous model - Thermo Fischer). The samples were collected in May, 2011 with distinct sampling intervals, for the inner region the sampling period was divided into: (i) 8:00 to 14:00, (ii) 14:00 to 20:00, and (iii) 20:00 to 08:00 of the next day; and for the external region: (i) 08:00 to 20:00 and (ii) 20:00 to 08:00. Besides the particle samplers, two impinger systems for ammonia measurements were employed.

The soluble ions analysis of the fine and coarse particulate matter were performed by chromatographic system Methron 850, and ammonia measurements (in acid medium like ammonium ion) were performed using a flow injection system with gas diffusion and contactless conductivity detection (FIA-GD-C4D).

The results indicated that the median concentration of NH<sub>3</sub> inside the road tunnel (TJQ) was approximately four times higher than in the external region (PP). The mean concentration for the PM<sub>2.5</sub> major ions (SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>) were 2.42±1.45, 1.14±0.71, 0.80±0.52 µg m<sup>-3</sup>, respectively, for the outside region and 3.27±1.76, 1.27±0.69, 0.76±0.53 µg m<sup>-3</sup> for the road tunnel. The total mass concentration for fine particulate matter in the inner region was 41.2±10.8 µg m<sup>-3</sup> and 29.2±17.9 µg m<sup>-3</sup> for the PP region.

Regarding the representativeness of inorganic species, a simulation from the equilibrium model Isorropia II (Figure 1) attributes 20%, at least, of the total PM<sub>2.5</sub> mass for the samples collected in the surrounding region. Nonetheless, a maximum of 25% was attributed for the inner region. To verify the relation between the ionic species, a multiple regression analysis was calculated considering the NH<sub>4</sub><sup>+</sup> ion as a dependent variable and the major ionic species, temperature and relative humidity as independent variables. The

regression indicated an increase of the adjusted determination coefficient by adding the chloride ion for the external region. However this increase is not observed for the road tunnel which indicates that ammonium ion has no association with this species in an environment with high sulfur oxides concentrations. A greater dependence of thermodynamic variables was observed in the road tunnel, whose slope coefficient for temperature was,  $\beta_T = -0.11$ , with significance level of 5% ( $p < 0.05$ ).

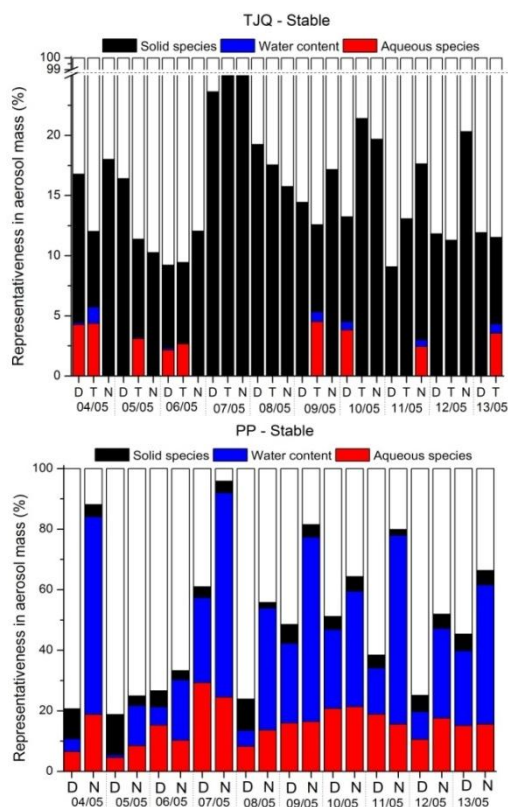


Figure 1. Distribution of solid and aqueous species and water content in the fine particulate matter. This simulation was performed using the ISORROPIA II equilibrium model for PM<sub>2.5</sub> sampled inside the Jânio Quadros road tunnel (upper graph - TJQ) and surrounding region (lower graph - PP).

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