



Physico-chemical properties of aerosols in Sao Paulo, Brazil and mechanisms of secondary organic aerosol formation.

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Megacities emissions are increasingly becoming a global issue, where emissions from the transportation sector play an increasingly important role. Sao Paulo is a megacity with a population of about 18 million people, 7 million cars and large-scale industrial emissions. As a result of the vehicular and industrial emissions, the air quality in Sao Paulo is below WMO standards for aerosol particles and ozone. Many uncertainties are found on gas- and particulate matter vehicular emission factors and their following atmospheric processes, e.g. secondary organic aerosol formation. Due to the uniqueness of the vehicular fuel in Brazil, largely based on ethanol use, such characterization currently holds further uncertainties. To improve the understanding of the role of this unique emission characteristics, we are running a source apportionment study in Sao Paulo focused on the mechanisms of organic aerosol formation. One of the goals of this study is a quantitative aerosol source apportionment focused on vehicular emissions, including ethanol and gasohol (both fuels used by light-duty vehicles).

This study comprises four sampling sites with continuous measurements for one year, where trace elements and organic aerosol are being measured for PM_{2.5} and PM₁₀ along with real-time NO_x, O₃, PM₁₀ and CO measurements. Aerosol optical properties and size distribution are being measured on a rotation basis between sampling stations. Furthermore, a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) and an Aerosol Chemical Speciation Monitor (ACSM) are used to measure in real time VOCs and aerosol composition, respectively. Trace elements were measured using XRF and OC/EC analysis was determined with a Sunset OC/EC instrument. A TSI Nephelometer with 3 wavelengths measure light scattering and a MAAP measure black carbon. Results show aerosol number concentrations ranging between 10,000 and 35,000 cm⁻³, mostly concentrated in the nucleation and Aitken modes, with a peak in size at 80-120 nm. Average mass concentrations were measured at 11.5 µg/m³ and 30.7 µg/m³ for fine and coarse mode, respectively. The elemental analysis shows that Fe, Si and Al dominate the coarse mode indicating strong contribution from soil dust resuspension whereas sulfur dominates the fine mode (0.8 micrograms/m³). Scattering coefficients typically range between 20 and 150 Mm⁻¹ at 637 nm, and absorption varied between 10 to 60 Mm⁻¹ at 637 nm, respectively, both of them peaking at 7:00 local time, the morning rush hour. The corresponding single scattering albedo varies between 0.50 and 0.80, indicating a significant contribution of primary soot particles to the aerosol population. Organic aerosol accounts for 70% of the aerosol mass, with nitrates accounting for 11.7%, ammonia 8.4%, sulfate 8.2% and chlorine 1.6% of PM₁ measured by AMS techniques. Most of the organic aerosol were oxygenated. Several new particle formation events were observed, with a clear increase in organic aerosol and VOCs amounts associated with new particle formation. The study allows the characterization of a unique fueled fleet emissions and its impact on atmospheric chemistry, particle formation and other atmospheric dynamic processes.

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