

Influence of humidity on aerosol concentrations in a subtropical region

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The climatic characteristics of subtropical southeast Brazil include large-amplitude fluctuations of relative humidity (RH), both diurnally and between seasons. This work investigated the influence of these shifts on ambient aerosol concentrations. Particle numbers were measured in six size fractions using an optical particle counter (Aerotrak, TSI), and the bulk aerosol chemical composition (soluble ions: sodium, ammonium, potassium, calcium, magnesium, formate, acetate, nitrate, sulfate, phosphate, and oxalate) was determined for 85 samples by ion chromatography (Dionex DX120). Meteorological parameters included relative humidity (RH), wind speed, and temperature. The measurements were made in August 2010. The data were treated by agglomerative hierarchical clustering (AHC), and comparison between wet (RH above 70%) and dry periods (RH below 50%) (Zentzsch *et al.*, 2013) enabled elucidation of the influence of relative humidity on aerosol growth and chemical composition.

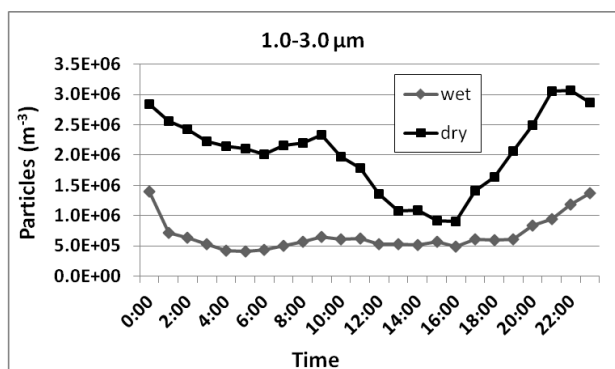


Figure 1. Diurnal number concentrations of aerosols in the size range 1.0-3.0 μm , during dry and wet periods.

Particle number concentrations (in the measured size range) were higher at night (higher RH) than during the daytime (lower RH), and diurnal fluctuations were lower under more humid conditions (Fig. 1). The 1.0-3.0 μm size fraction was most affected by RH, although aerosols of all sizes showed clear humidity-related trends, with number concentrations either increasing or decreasing (Fig. 2). The 1.0-3.0 μm size range appeared to represent a neo-equilibrium in terms of the uptake and loss of water vapor by the particles.

The shifts in RH (the minimum and maximum values were 12% and 95%, respectively) were sufficient to cover the range of deliquescence and efflorescence points (Freney *et al.*, 2009) of many of the salts present in the composition of the aerosols analyzed, including compounds of ammonium and potassium. NH_4^+ and K^+ accounted for 31.5% and 16.7% of the mass of measured cations, respectively, and the hygroscopic behavior of

the corresponding compounds could explain the diurnal fluctuations in the number concentrations of aerosols in the 0.5-5.0 μm size range. Overall, there was an excess of cations, relative to anions (Table 1), which could be explained by the presence of calcium carbonate (carbonate was not determined), since this material is widely used in the region for soil pH correction, and was therefore probably the main source of aerosol basicity.

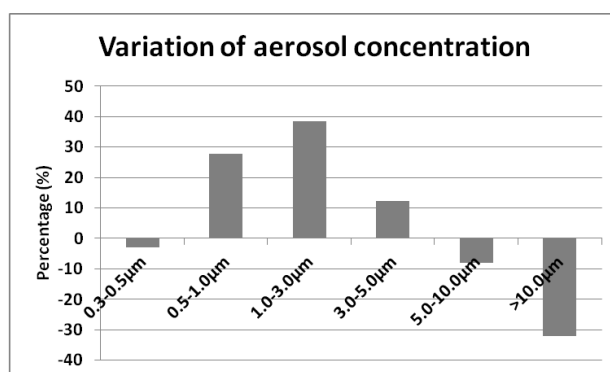


Figure 2. Percentage difference in aerosol concentrations, comparing wet periods (RH >70%) with dry periods (RH <50%).

Table 1. Ion balances for wet and dry periods.

Period	Anions neq/m ³	Cations neq/m ³	Cation/ Anion
Wet	52.7	199.7	3.8
Dry	47.6	226.5	4.8

The results revealed a substantial influence of diurnal changes in relative humidity on the hygroscopic growth of ambient aerosols derived predominantly from biomass burning and soil dust resuspension. Cyclical growth and evaporation of the particles favored both the production of secondary chemical species via aqueous phase reactions and the formation of internal mixtures of chemical components.

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Freney, E. J., Martin, S. T. and Buseck, P. R. (2009) *Aerosol Sci. Technol.* **43**, 799-807.

Zentzsch, P. V., Ciobota, V., Rosch, P. and Popp, J. (2013) *Angew. Chem. Int. Ed.* **52**, 1410-1413.