Particle water and pH in the city of Athens during wintertime and the role of biomass burning

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Atmospheric particles can absorb large amounts of water, which can modulate their physical and chemical properties (Khlystov et al. 2005) and impact atmospheric processes. Apart from LWC, the pH of aqueous aerosols is another critically important, but poorly constrained aerosol property that influences many processes related to the aerosol chemical composition and gas-aerosol partitioning (Surratt et al. 2010). This study uses aerosol chemical composition measurements in conjunction with the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007) to predict the aerosol pH for air masses that influenced air quality downtown Athens. The real-time, quantitative measurements of the main ions concentrations of the $PM_{2.5}$ aerosol were provided by a Particle-Into-Liquid Sampler with a 30-min resolution (PILS) together with T and RH measured at the site.

Particle water (LWC) and pH are calculated for the fine fraction of aerosols sampled at the Thissio station at downtown Athens, during wintertime 2013-2014. Using concurrent measurements of aerosol chemical composition and the thermodynamic model ISORROPIA-II, LWC mass concentrations associated with the aerosol inorganic and organic components are determined. As during wintertime the low temperatures favour the use of biomass burning (BB) for domestic heating, a discrimination is made between days with intense and no BB influence. The average value for total aerosol water was 15.1±7.5 μg m^{-3} and 8.5±3.1 μg m^{-3} for BB and non-BB days, respectively. The large difference in LWC is associated with the intense biomass burning activities, contributing significant amounts of organics, especially during nighttime. Aerosol at Athens was found to be acidic with pH varying from -0.69 to 4.9. Days with high BB influence exhibited the highest pH (2.83±0.47) while days with no BB influence exhibited lower pH values (2.08±0.23). A significant diurnal variability is found for both organic/inorganic water as well as pH during BB days.

W_{org} exhibits a significant diurnal variability (shaded area) with morning and afternoon average mass concentrations being 10-15 times lower than nighttime ones. During daytime W_{inorg} (line with circle markers) appears to be the main component of particle water but during nighttime, the two components appear to have almost the same contribution, especially during no BB influence, which could be attributed to the higher concentration of organics during strong BB influence This can be translated as an almost 10-fold increase of the H^{+}_{air}/LWC ratio from early morning to mid-day. This significant variation in pH can be partially explained by the diurnal variation of H^{+} and by the reduction of aerosol water (LWC) during daytime compared to the higher LWC during nighttime. This implies the diurnal variability of pH is mostly driven by the reduction of aerosol water during daytime. On the other hand, pH variability was less pronounced during days with limited BB activities, which is also consistent with the lower LWC and variability during those days.

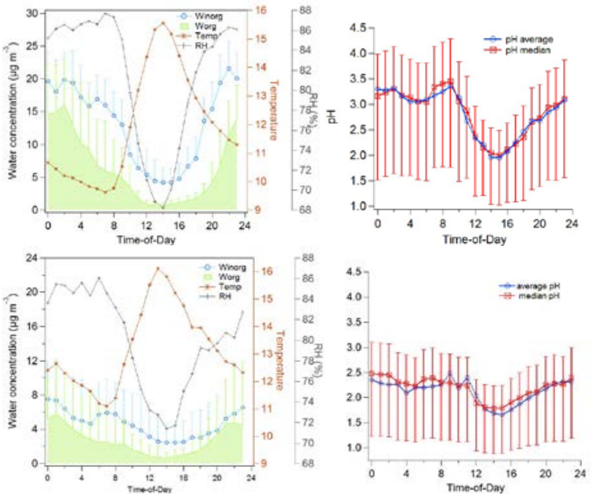

Figure 1. Diurnal profiles as hourly averages of predicted water components (left) and pH (right), along with measured RH and T for BB (up) and non-BB (down) days.

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