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Fine particle water and pH in the Eastern Mediterranean: Sources, variability and implications for nutrients availability

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Atmospheric particles have the ability to absorb significant amounts of water, which greatly impacts on their physical and chemical properties. Direclty linked to aerosol pH and LWC is the bioavailability of nutrients contained within mineral dust, involving pH-dependent catalyzed redox-reaction pathways. Liquid water content (LWC) and pH, even though are important constituents of the aerosol phase, are rarely monitored. Direct measurements of aerosol pH "in situ" are scarce and require considerations owing to the non-conserved nature of the hydronium ion and partial dissociation of inorganic and organic electrolytes in the aerosol. To overcome these challenges, indirect alternatives such as measuring the semi-volatile partitioning of key species sensitive to pH, combined with comprehensive models are used to provide a reasonably accurate estimate of pH that can be carried out with routine measurements.

Using concurrent measurements of aerosol chemical composition, tandem light scattering coefficients and the thermodynamic model ISORROPIA-II, LWC mass concentrations associated with the aerosol inorganic and organic components are determined for the remote background site of Finokalia, Crete. The predicted water was subsequently compared to the one measured by the ambient versus dry light scattering coefficients. The sum of Winorg and Worg was highly correlated and in close agreement with the measured LWC (on average within 10%), with slope 0.92 (R2=0.8) for the whole measurement period between August and November 2012 (n=5201 points). As expected, the highest fine aerosol water values are observed during night-time, when RH is at its maximum, resulting in important water uptake. The average concentration of total aerosol water was found to be 2.19 ± 1.75 μg m-3, which according to the dry mass measurements, can contribute on average up to 33% to the total aerosol submicron mass. The average Worg was found to be 0.56 ± 0.37 μg m-3, which constitutes about 28% of the total calculated water.

Particle pH is also calculated with the help of ISORROPIA-II, and during the studied period, values varied from 0.5 to 2.8, indicating that the aerosol was highly acidic. pH values were also studied depending on the source/origin of the sampled air masses and biomass burning aerosol was found to exhibit the highest values of PM1 pH and the lowest values in total water mass concentrations. The two natural sources, namely mineral and marine origin, contained the largest amounts of total submicron water and the lowest contribution of organic water, as expected.

The low pH values estimated for the studied period in the submicron mode and independently of the air masses' origin could potentially have important implications for nutrient availability, especially for phosphorus solubility, which is the nutrient limiting sea water productivity of the Eastern Mediterranean.