Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 8, 2243-2254, 2008
www.atmos-chem-phys.net/8/2243/2008/

Properties of atmospheric humic-like substances – water system

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Abstract. Urban-type $PM_{2.5}$-fraction aerosol samples were collected and samples of pure atmospheric humic-like substances (HULIS) were isolated from them. Atmospheric concentrations of organic carbon (OC), water soluble organic carbon (WSOC) and HULIS were determined, and UV/Vis spectroscopic properties, solubility and conductivity of HULIS in aqueous samples were investigated. Atmospheric concentrations of OC and WSOC were 8.5 and 4.6 μg m^{-3}, respectively. Hydrophilic WSOC accounted for 39% of WSOC, carbon in HULIS made up 47% of WSOC, and 14% of WSOC was retained on the separation column by irreversible adsorption. Overall average molecular mass and aromatic carbon abundance of HULIS were estimated from molar absorptivity to be 556 Da and 12%, respectively. Both results are substantially smaller than for standard reference fulvic acids, which imply different mechanisms for the formation processes of atmospheric HULIS and aquatic or terrestrial humic matter. HULIS were found to be water soluble as ionic unimers with a saturation concentration of 2–3 g l^{-1}. Their solubility increased again with total HULIS concentration being above approximately 4 g l^{-1}, which was most likely explained by the formation of HULIS aggregates. Solubility increased linearly from approximately 5 up to 20 g l^{-1} of dissolved HULIS concentration. The ionic dissolution was confirmed by electrochemical conductivity in the investigated concentration interval. Limiting molar conductivity was extrapolated and this was utilized to determine the apparent dissociation degree of HULIS for different concentrations. The dissociation degree was further applied to derive the concentration dependence of the van't Hoff factor of HULIS. The van't Hoff factor decreased monotonically with HULIS concentration; the decrease was substantial for dilute solutions and the relationship became weak for rather concentrated solutions.

Final Revised Paper (PDF, 1767 KB) Discussion Paper (ACPD)

Citation: Salma, I., Ocskay, R., and Láng, G. G.: Properties of atmospheric humic-like substances – water system, Atmos. Chem. Phys., 8, 2243-2254, 2008. Bibtex EndNote Reference Manager