



Wind tunnel investigations on the retention of carboxylic acids during riming

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In mid-latitudes, precipitation is mainly initiated via the ice phase in mixed phase clouds. In such clouds the ice particles grow to precipitation sizes at the expense of liquid drops through riming which means that supercooled droplets collide with ice particles and subsequently freeze. Water-soluble trace substances present in the liquid phase might remain only fractionally in the ice phase after freezing. This fractionation is called retention and is an important ratio which quantifies the partitioning of atmospheric trace substances between the phases.

Laboratory experiments were carried out at the Mainz vertical wind tunnel to determine the retention of lower mono- and di-carboxylic acids during riming. Due to their low molecular weight and their polarity these acids are water-soluble. In the atmosphere formic acid and acetic acid are the most abundant mono-carboxylic acids in the gas and aqueous phase, thus, they represent the major fraction of carboxylic acids in cloud water. Oxalic and malonic acid are common coatings on aerosol particles because of their relatively low saturation vapor pressure. These di-carboxylic acids might therefore promote the aerosol particles to act as cloud condensation nuclei and additionally contribute to the aqueous phase chemistry in cloud droplets. The conditions during the riming experiments in the wind tunnel were similar to those in atmospheric mixed phase clouds, i.e. temperatures from -18°C to -6°C , liquid water contents between 0.5 and 1.5 g/m^3 , and liquid drop radii between 10 and $20\text{ }\mu\text{m}$. The liquid phase concentrations ranged from 3 to 5 mg/l ($4.1 < \text{pH} < 4.5$). As rime collectors captively floating ice particles and quasi-floating snowflakes with diameters between 0.6 and 1.5 cm were used. The wind speed in the vertical wind tunnel was very close to the terminal velocities of the rime collectors, thus, the ventilation during riming was in the same order of magnitude as under atmospheric riming conditions. After riming the collectors were removed from the wind tunnel, their melt water was analyzed by ion chromatography and the retention coefficients, i.e. the fractions of the species which remained in the ice phase were determined. Average retention coefficients of formic acid and acetic acid were 0.73 ± 0.07 and 0.62 ± 0.12 , respectively; both oxalic and malonic acids had average retention coefficients of 0.98 ± 0.04 . These variations can be explained by the fact that retention depends on the one hand on the dissociation state of the substance together with its solubility (described by the effective Henry's law constant) and on the other hand on the latent heat removal from the collector to the environment. This is affected by ventilation, shape of the rime collector, liquid water content, and droplet size.