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Two hours interval gas and particle-phase measurements of low-molecular weight organic acids with an on-line MARGA extension at the TROPOS research site Melpitz, Germany

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For one year, low-molecular weight organic acids (formic, acetic, propionic, butyric, pyruvic, glycolic, oxalic, malonic, succinic, malic, glutaric and methanesulfonic acid) were quantified on-line in the tropospheric gas and particle-phase. Therefore, a Monitor for AeRosols and Gases in ambient Air (MARGA, Metrohm-Applikon, The Netherlands) system were combined with an additional ion chromatography instrument (Compact-IC, Metrohm, Switzerland) equipped with a pre-concentration column leading to an enrichment factor of 400. The MARGA allows the separation of the gas and particle-phase by the Wet Rotating Denuder (WRD) and the Steam-Jet Aerosol Collector (SJAC). Every second hourly integrated MARGA gas and particle sample were collected and analyzed by the Compact-IC resulting in a time resolution of two hours. Several laboratory tests were required to detect each organic acid without coelutions and interferences with the higher concentrated inorganic ions (chloride, nitrite, nitrate and sulphate). Best results were achieved using a gradient system with two coupled anion-exchange separation columns.
The precision of the Compact-IC were below 1% except for glycolate (2.9%) and succinate (1.0%). The limits of detection ranged between 0.5 ng m-3 for malonate and 17.4 ng m-3 for glutarate. Calculated annular denuder efficiencies were above 99.15% for each organic acid. In periods with high particulate concentrations, no gas-phase concentrations were detected leading to the conclusion that particle losses within the WRD can be neglected.
In agreement with the vapor pressures of each organic acid, the monocarboxylic acids (MCAs) were predominantly found in the gas-phase. However, formate, acetate and glycolate were also frequently quantified within the particle-phase. Higher data coverages for the dicarboxylic acids (DCAs) were observed in the particle-phase. The high time resolution allowed the analysis of the diurnal cycles and find distinct courses with maximum concentrations during the afternoon and evening for the MCAs. The lowest concentration were found in the early morning. A parallel course were observed for the temperature that have an influence of the stability of the boundary layer and the vertical mixing. Photochemical processes of precursor compounds explain the high concentrations during daytime. Another advantage of the described setup are the phase partitioning investigations of the organic acids that are of huge interest in the tropospheric multiphase chemistry. As example, glycolate show a seasonal dependency with a favored occurrence within the gas-phase in summer, whereas higher particulate concentrations were detected in winter.