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Measurements of organic acids in snow samples from two high altitude locations in the Swiss Alps

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Snow samples have been collected at two high-altitude sites in the Swiss Alps in winter 2005/6, 2006/7 and 2007/8 on the Fee Glacier at an altitude from 3000 to 4000 m and at the high altitude research station Jungfraujoch (3580 m) during the measurement campaign CLACE 5 and 6 (CLoud and Aerosol Characterization Experiment). The melted samples have been pre-concentrated by solid phase extraction using a strong anion exchange resin and were then analysed by liquid-chromatography/mass spectrometry using electrospray ionisation. A series of linear dicarboxylic acids with 5 to 13 carbon atoms and phthalic acid were found in all snow samples from the Fee Glacier and during CLACE 6. The identified linear acids were glutaric, adipic, pimelic, suberic, azelaic, sebacic, undecanedioic, dodecanedioic acid and tridecanedioic acid. During CLACE 5 glutaric (C5) and tridecanoic acid could not be observed. In some samples also pinic and pinonic acid (biogenic acids) and 4-nitrocatechol (from wood combustion) were detected. The concentrations of the quantified organic compounds varied strongly between different snow precipitations. The strong variation of the concentrations can be mainly attributed to the history of the air masses arriving at the sampling location by comparison with back trajectories. Low concentrations of the organic acids originate from clean marine air masses arriving directly from the Atlantic, whereas during events with higher concentrations the air masses were mainly of continental origin. Sources of the observed acids are fossil fuel and biomass combustion and the photo-oxidation of volatile precursors. Among the observed acids with the highest concentrations, adipic and phthalic acid have anthropogenic sources, e.g. cyclohexene from car exhaust and aromatic hydrocarbons, respectively. Azelaic acid,

which is also observed in high concentrations is mainly formed by the oxidation of lipid acids, mainly oleic acid, and is of biogenic origin. Using the ratio of adipic to azelaic (C6/C9) or of phthalic to azelaic acid (Ph/C9), the relative contribution of biogenic and anthropogenic emissions can be estimated. Typical ratios (C6/C9 and Ph/C9) were mainly above 1 with maximum values of 7 and 5, respectively, indicating the anthropogenic influence on the air mass history. However, in some samples the ratios were below 1, showing a relatively larger biogenic contribution to the organic compounds in the fresh snow. These were mainly samples with the lowest concentrations at each location and with back trajectories indicating clean marine air masses from the Atlantic.