



Exploring the air/droplet partitioning of volatile organic compounds (VOCs) in the cloudy atmosphere: the puy de Dôme station (France) as a case study

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VOC precursors play a key role in air quality and climate by contributing to ozone production and by modifying the physicochemical properties of aerosols, one of the main agents of the Earth's radiative forcing. Among VOCs, oxygenated VOC (OVOC) and biogenic VOC (BVOC) are of particular interest due to their high reactivity. Meanwhile, the cloud system represents a multiphase medium (gas, aerosol, water) for transformations of VOC and particularly of OVOC, highly soluble.

Indeed, cloud droplets, which are able to trap and dissolve many gaseous and particulate compounds, represent a very reactive media in the atmosphere. Microphysical processes control formation, lifetime and dissipation of the clouds and consequently modify the distribution of the chemical species between the different reservoirs (cloud water, rain, particle phase, gaseous phase, and solid ice phase). Meanwhile, photochemical processes inside the droplets are strongly amplified when compared with the interstitial air. However, speciation and concentrations of organic compounds between gaseous phase (interstitial air) and atmospheric liquid phase (cloud droplets) are still poorly described.

Our objectives are to collect air and cloud water simultaneously by using different samplers and to characterize the gas/liquid partitioning of target organic compounds (OVOC, BVOC) that are considered as efficient SOA precursors both in the aqueous phase and gaseous phase. Several cloud events were sampled at the puy de Dôme station (PUY) in the centre of France (1465 m a.s.l.) belonging to the GAW/ACTRIS network. Air masses reaching the summit present contrasted origins (from the marine influence to the anthropogenic one).

A new analytical approach has been optimized (i.e., linearity, repeatability, sensitivity and relative humidity) to explore VOCs in both gas and liquid phases by taking into account real cloud conditions. First, a newly developed gas sampler (AEROVOCC) collects gaseous VOCs/OVOCs ($-C=O$ and $-OH$ functional groups) simultaneously by deploying three types of Tenax TA sorbent tubes pre-coated with different derivatisation reagents. Simultaneously, cloud sampling is performed with a cloud collector. Then, (O)VOC concentrations in the cloud water samples are evaluated by using direct liquid derivatization and extraction by Stir Bar Sorptive Extraction (SBSE). Finally, collected both gas and aqueous samples are analysed by desorption (TD) coupled with gas chromatography (GC) and mass spectrometry (MS) at the laboratory. The whole set-up has been deployed on the field to study the partitioning of VOCs; this experimental partitioning is evaluated towards the theoretical one described by the Henry's Law constants. Our results show that even observed concentrations of hydrophobic VOCs are significant in the cloud droplet and supersaturated by a factor of 10-10000. Larger and less soluble carbonyl compounds were found to be supersaturated by a factor of 100-1000 in other studies. This result suggests that the pool of reactive organic compounds in the cloud phase is largely underestimated.