

# Aqueous phase enrichment of organic carbonyl compounds in orographic clouds during HCCT-2010

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In September/October 2010, the international ground-based cloud experiment “Hill Cap Cloud Thuringia 2010” (HCCT-2010) was performed at Mt. Schmucke in Thuringia, Germany. One of the aims of HCCT-2010 was to study the effects of clouds on the phase partitioning of organic carbonyl compounds. Due to their volatility, these compounds usually exist in the gas phase, but can partition into the aqueous phase upon cloud or fog formation, depending on their Henry constant. Within the aqueous phase, the carbonyls can follow unique reaction pathways which do not exist in the gas phase (e.g. the oxidation of an aldehyde to a carboxylic acid, *Tilgner and Herrmann, 2010*). Their phase partitioning is thus an important process governing the fate of these species in the atmosphere.

During cloud events in HCCT-2010 several organic carbonyl compounds were determined from both the interstitial gas phase as well as the aqueous phase. Interstitial gas phase sampling took place on DNPH-coated cartridges downstream an interstitial inlet (INT), which separated cloud droplets ( $D > 5 \mu\text{m}$ ) from interstitial particles and gas phase. Aqueous phase concentrations were determined by two different methods: i) sampling on DNPH-coated cartridges downstream a counterflow virtual impactor (CVI), which separated cloud droplets from the interstitial phases and subsequently evaporated the droplets to release volatile constituents back to the gas phase, and ii) bulk sampling of cloud water using the Caltech Active Strand Cloud Water Collector (CASCC2, *Demoz et al., 1996*). For analysis, the DNPH-derivatized carbonyls were eluted from the cartridges and determined by LC-MS, while the carbonyls from the cloud water samples were derivatized by PFBHA and analyzed by GC-MS. All samples were stored at  $-20^\circ\text{C}$  until analysis.

In general, cloud concentrations determined from the CVI cartridges tended to be higher than the ones obtained from bulk cloud water. A reason for this could be artifacts from the counterflow air in the CVI, which might still have carried traces of carbonyls. Therefore, for the calculation of phase partitioning, bulk cloud water concentrations were used.

Measured aqueous phase fractions were obtained by dividing the cloud water loading (CWL) by the total in-cloud budget (CWL + interstitial concentration)

and compared to theoretically expected aqueous phase fractions derived from the respective Henry constant of a given compound and the cloud conditions during sampling (LWC and temperature). The mean ratio for all analyzed samples of measured vs. calculated aqueous phase fraction is shown in Figure 1 as a function of the Henry constant.

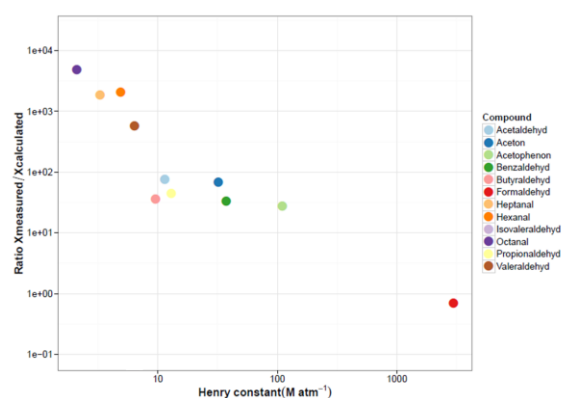


Figure 1: Average ratio of measured vs. calculated aqueous phase fractions as a function of the respective compounds' Henry constant.

High aqueous phase enrichment as compared to thermodynamic equilibrium conditions (Henry) were obtained especially for longer-chain carbonyls with lower Henry constants. Similar observations have been made before (*van Pinxteren et al., 2005; Li et al., 2008*).

Although the reasons for these observations remain unknown at present, several possibilities will be discussed and evaluated within this contribution.

## References

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