

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

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## INTRODUCTION

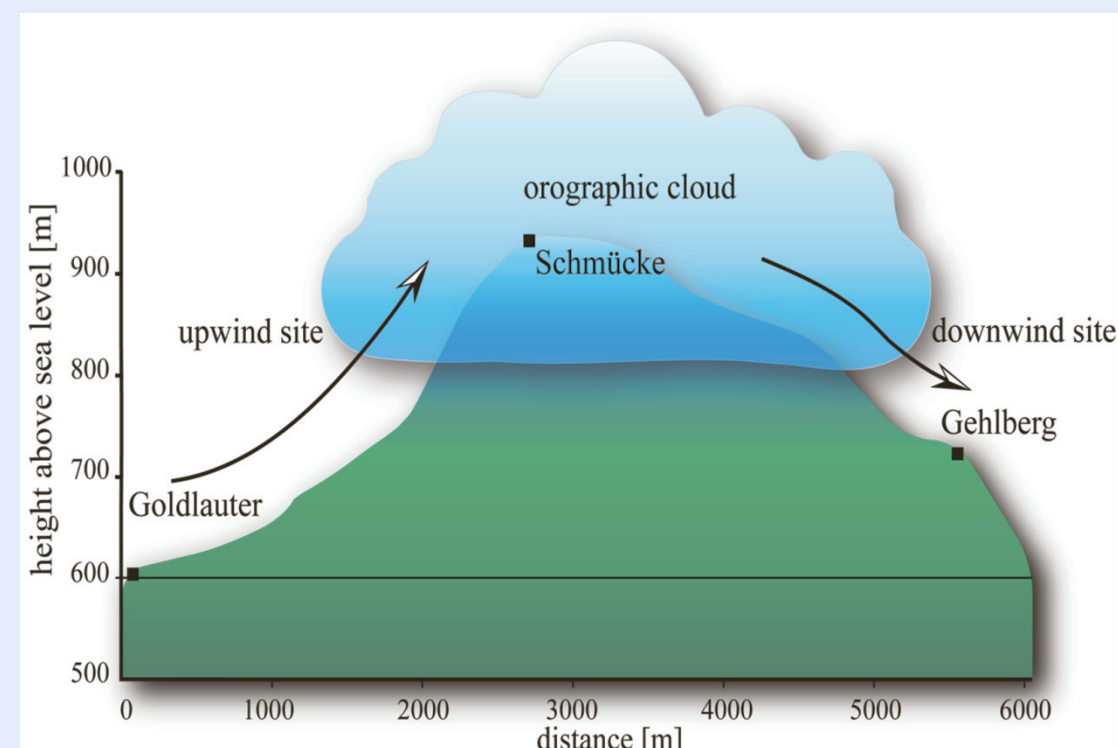


Figure 1: Scheme of the campaign area.



Figure 2: Measurement tower

### HCCT-2010

- Hill Cap Cloud Thuringia 2010 (HCCT-2010): Ground-based cloud chemistry and aerosol-cloud interaction
- Conducted in September and October 2010 at the Schmücke mountain, Thuringia, Germany
- Similar campaign setup as during FEBUKO 2001 and 2002 experiments (Herrmann, 2005)
- Lagrangian-type approach with three sampling sites (Fig. 1):
- Joint project with partners from Germany (Leipzig, Mainz, Frankfurt), France (Lille, Lyon), Great Britain (Leeds), and the US (Fort Collins, CO)

### Organic carbonyl compounds

- volatile gas-phase species
- can partition into aqueous phase upon cloud or fog formation
- can follow unique reaction pathways in aqueous phase (e.g. oxidation to carboxylic acid)
- severe deviations from Henry equilibrium observed in field studies (van Pinxteren et al., 2005; Li et al., 2008)

## EXPERIMENTAL

- Bulk cloud water sampling by Caltech Active Strand Cloud Water Collectors (CASCC2, Demoz et al., 1996) on a tower 20 m above ground
- Interstitial Inlet (INT) for sampling of interstitial particles and gas phase (Mertes et al., 2005)
- INT carbonyl compounds trapped on DNPH-coated cartridges
- Analysis of DNPH-derivatives by LC-MS after elution from sampling cartridges
- Analysis of carbonyls from bulk cloud water samples by PFBHA-derivatization and GC-MS
- Calculation of theoretical aqueous phase fraction  $X_{\text{calculated}}$  of carbonyls assuming Henry equilibrium by:

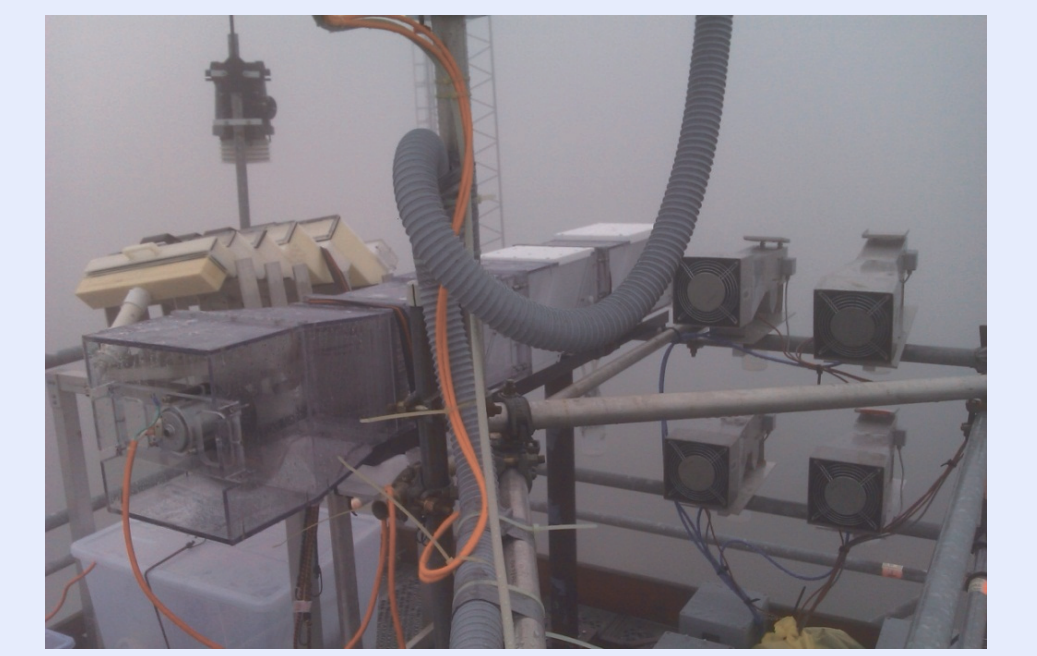


Figure 3: Cloud water samplers

$$X_{\text{calculated}} = \frac{HRTLWC \times 10^{-6}}{1 + HRTLWC \times 10^{-6}}$$

where H: effective Henry constant, R: universal gas constant, T: Temperature during sampling, LWC: liquid water content during sampling

- Calculation of experimental aqueous phase fraction  $X_{\text{measured}}$  by:

$$X_{\text{measured}} = \frac{CWL}{CWL + c_{\text{int}}}$$

- where CWL: cloud water loading (or equivalent air concentration) in  $\text{ng m}^{-3}$ ,  $c_{\text{int}}$ : interstitial gas phase concentration in  $\text{ng m}^{-3}$

## RESULTS

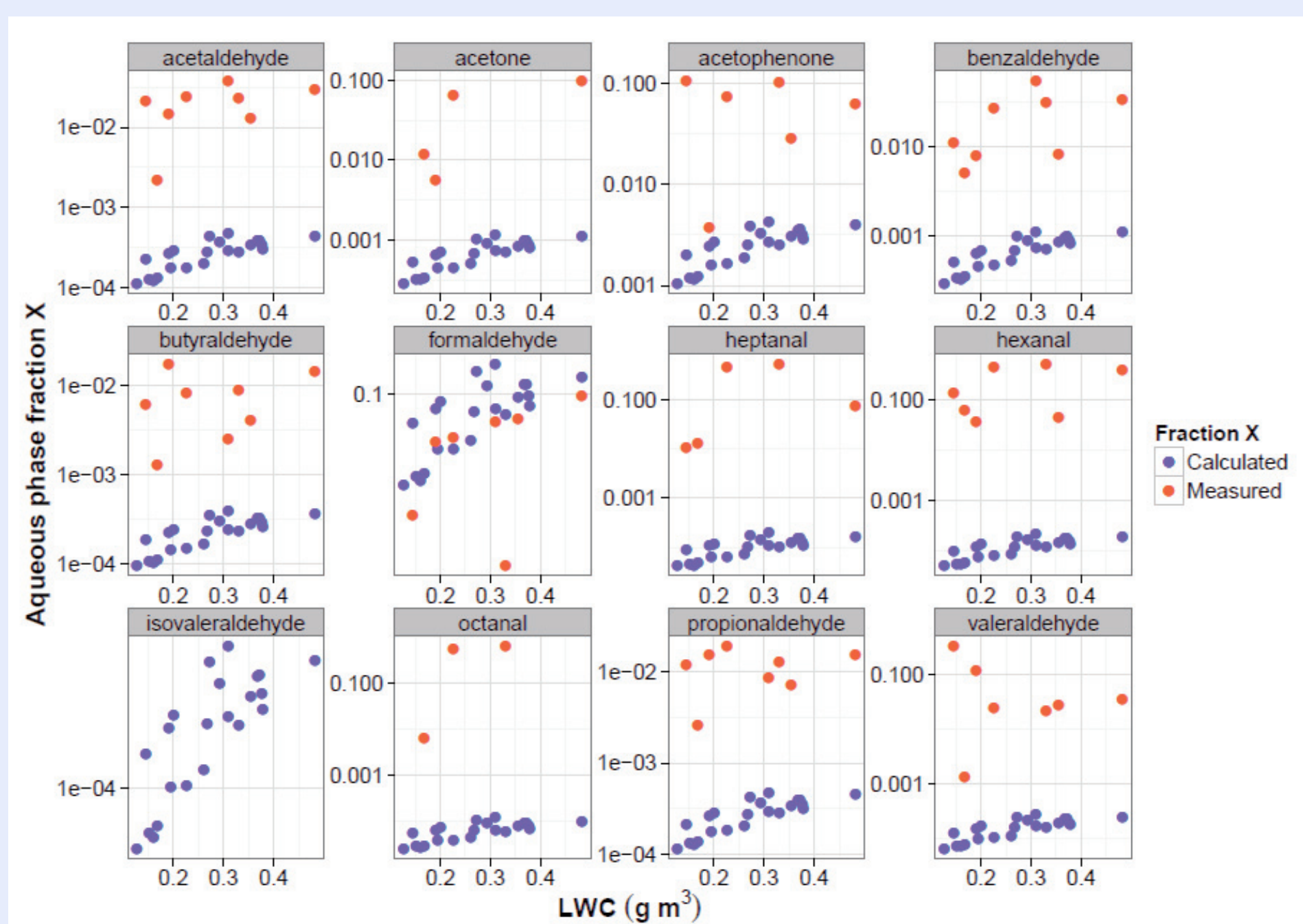


Figure 4: Calculated versus measured aqueous phase fraction  $X$  for all samples above detection limit

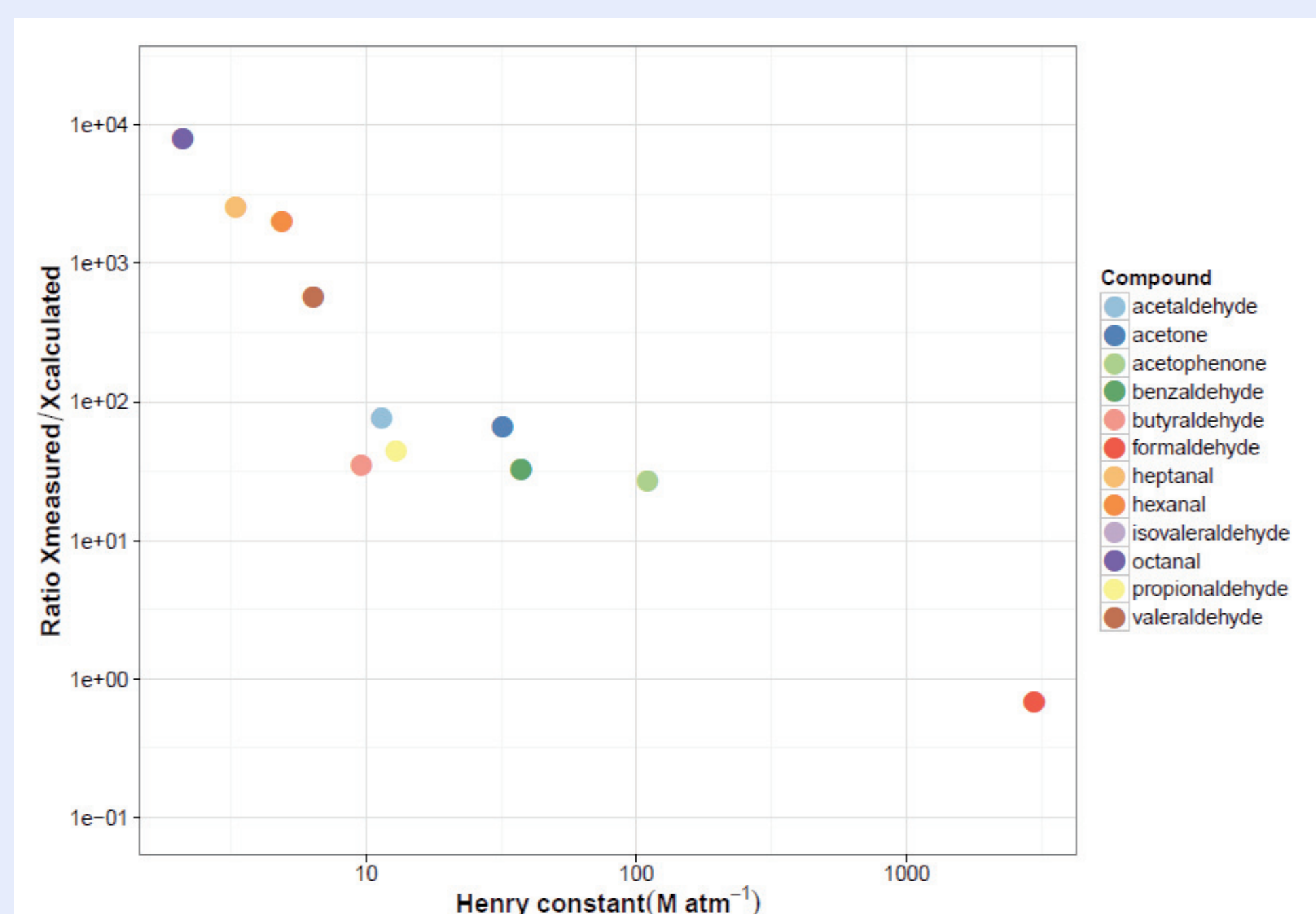


Figure 5: Average aqueous phase enrichment factor versus Henry constant of respective carbonyl

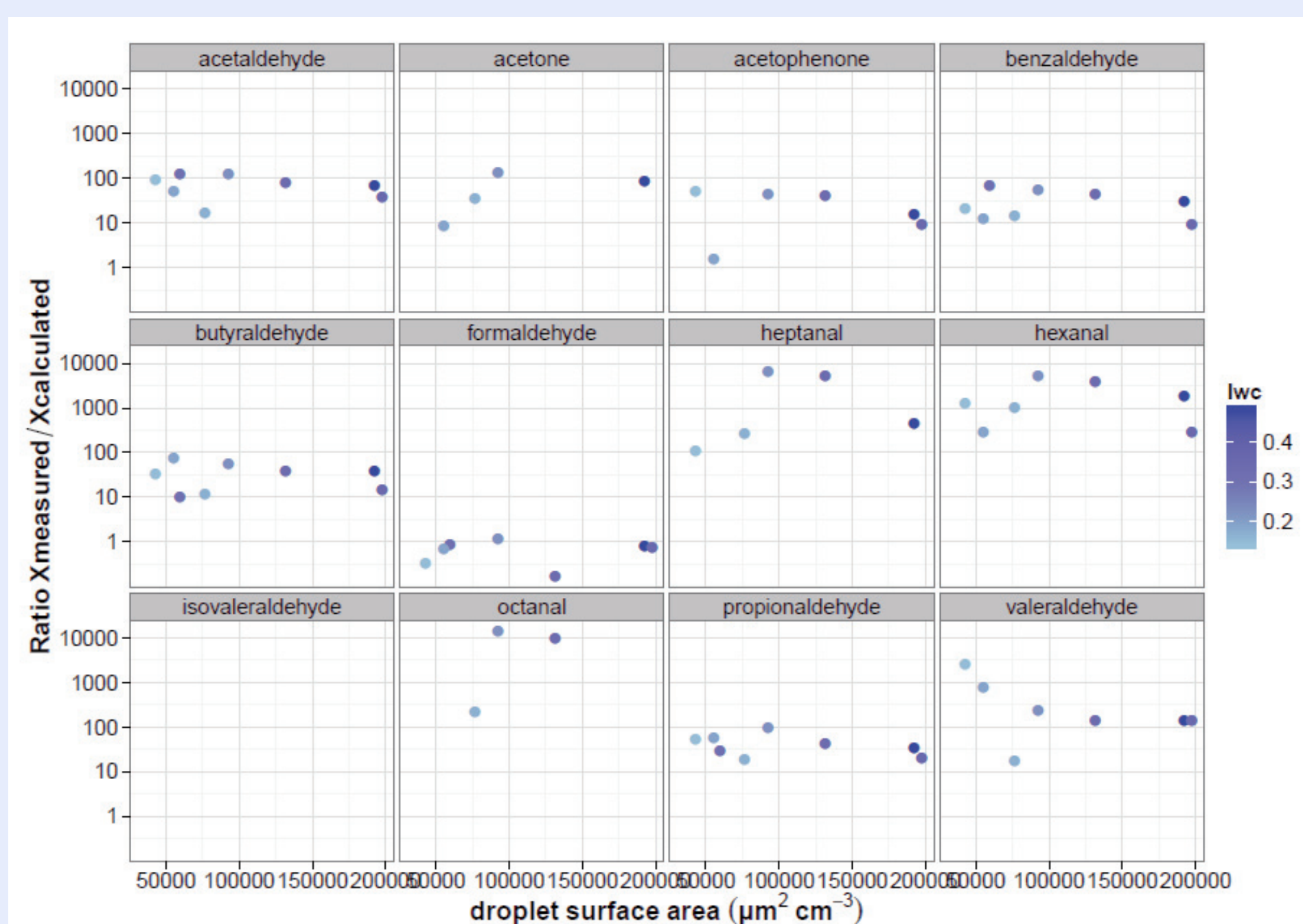


Figure 6: Enrichment factor as a function of droplet surface area (and LWC)

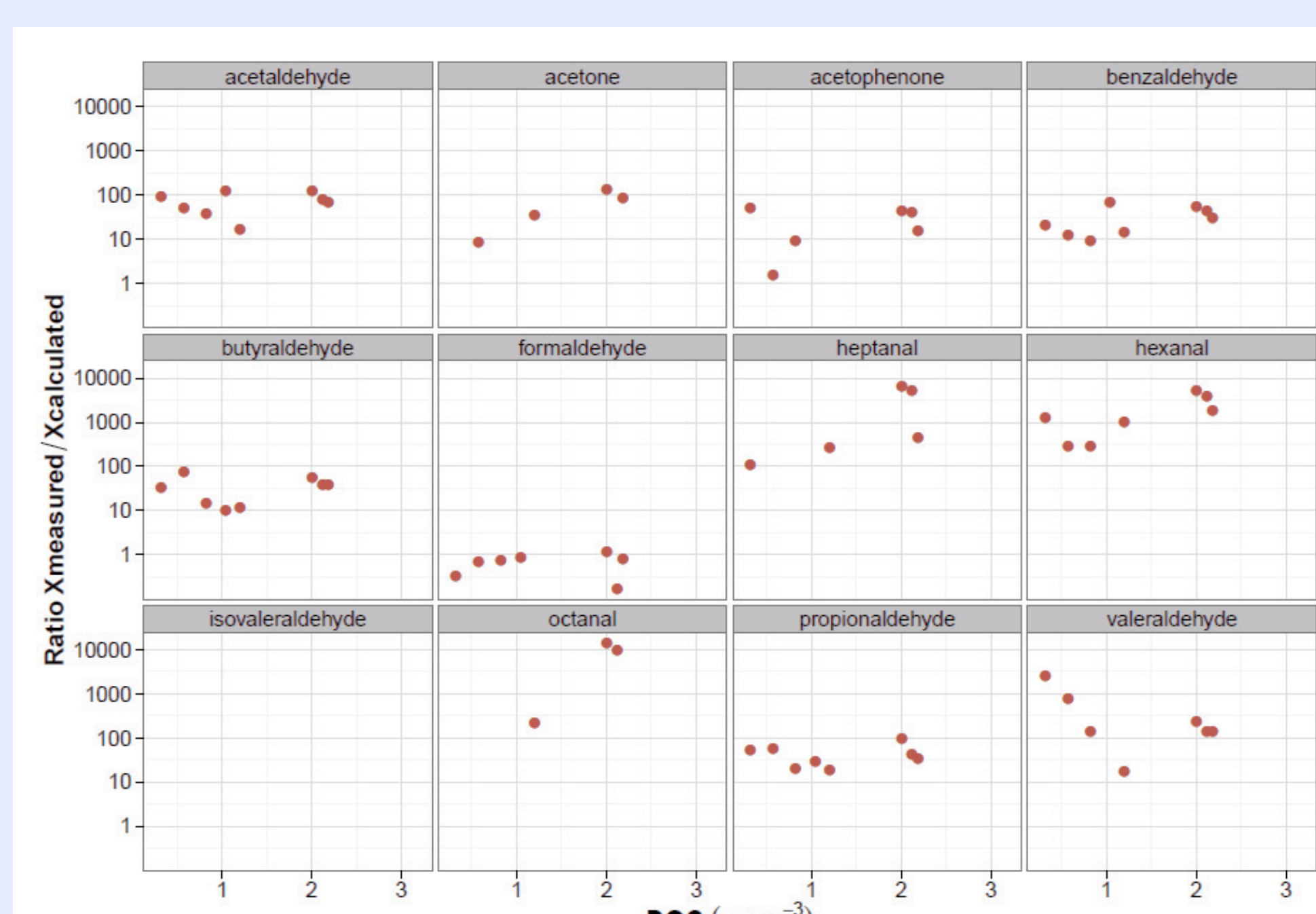


Figure 7: Enrichment factor as a function of cloud water DOC

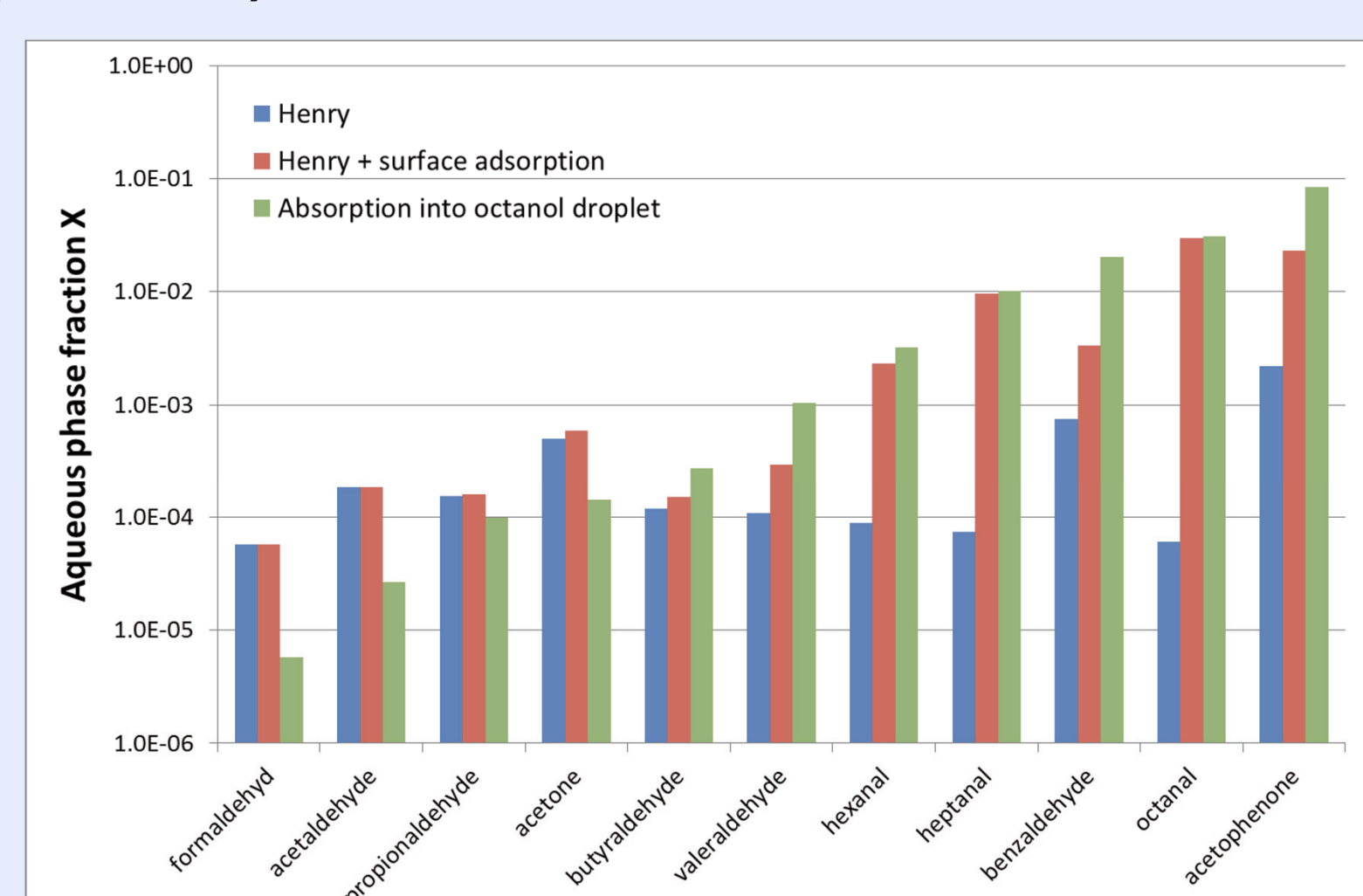


Figure 8: Calculated aqueous phase fraction for Henry only, Henry + surface adsorption, and absorption into organic material

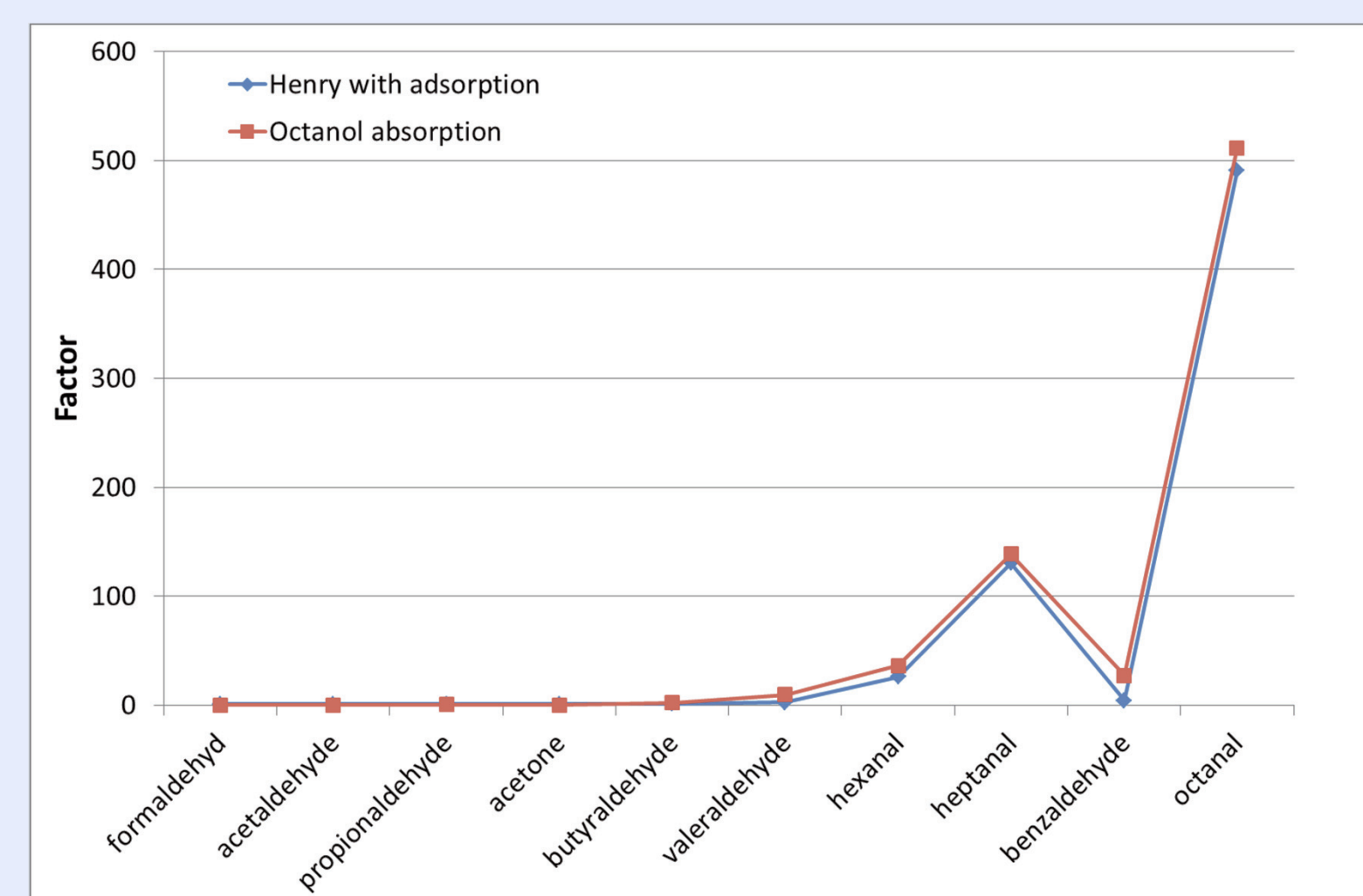


Figure 9: Increase in aqueous phase fraction when considering surface adsorption and absorption into organic material

### Experimental findings

- Observed aqueous phase fractions are much higher than calculated ones based on Henry equilibrium (Fig. 4), however, many samples were below detection limit after blank correction
- Apparent supersaturation of aqueous cloud phase for some of the samples, unknown partitioning for BDL samples
- Aqueous phase enrichment up to 4 orders of magnitude for compounds with very low Henry constants ( $< 10 \text{ M atm}^{-1}$ ), approx. 1-2 orders of magnitude for compounds with Henry constants between 10 - 100, and close to equilibrium for formaldehyde (high Henry constant, highly soluble)
- For most carbonyls, enrichment factor shows no trend with average droplet surface area obtained from FSSP measurements (Fig. 6). For most hydrophobic compounds (octanal, heptanal, hexanal), there might be some trend
- Adsorption of hydrophobic carbonyls might be important
- Similarly, a trend of increasing enrichment with increasing dissolved organic carbon (DOC) as a proxy for absorbing organic material, might be present for the same three hydrophobic compounds (Fig. 7)
- Absorption into organic cloud phase might be important

### COSMOtherm calculations

- The quantum-mechanical software COSMOtherm v2.1 (COSMOlogic, Germany) was used to predict air-water adsorption constants (Goss 2009) and air-octanol absorption constants for the measured carbonyls
- Data was used to calculate theoretical aqueous phase fraction for i) Henry equilibrium including adsorption to droplet surface, and ii) absorption of carbonyls into pure octanol droplets (as extreme case scenario) under typical cloud conditions during HCCT (10  $\mu\text{m}$  droplet, 5 °C, 0.2  $\text{g m}^{-3}$  LWC) (Fig. 8)
- Significant effects of both processes on the in-cloud aqueous phase fraction can only be expected for most hydrophobic compounds (hexanal, heptanal, octanal) (Fig. 9)
- Consistent with experimental findings

### Conclusions

- Adsorption and absorption important for more hydrophobic carbonyls
- Possible mechanisms for aqueous phase enrichment of less hydrophobic compounds remain speculative:
  - aqueous phase production with kinetic limitation of outgassing (organic films?)
  - reservoir species (e.g. oligomers) releasing monomers during analytical preparation of sample

## REFERENCES AND FUNDING