Molecular characterization of organic matter in aerosol particles and in cloud water – a high-resolution mass spectrometry study

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A Summary

- Ambient **aerosol particles** and **cloud water droplets** were **sampled in parallel** at a mountain site in Central Germany (Schmücke, August 2016)
- Samples were analyzed by **liquid chromatography** coupled to **high-resolution Orbitrap mass spectrometry** (full scan at R = 280k & ddMS^2 at R = 70k)
- A **versatile non-target analysis workflow** was developed **for samples of atmospheric organic matter** and applied to both sample types
- A large fraction of **organic compounds** was observed **in cloud water samples only**, suggesting **aqueous-phase chemistry** and **gas-phase uptake** to determine largely the chemical composition of organic matter in cloud droplets

B Methods

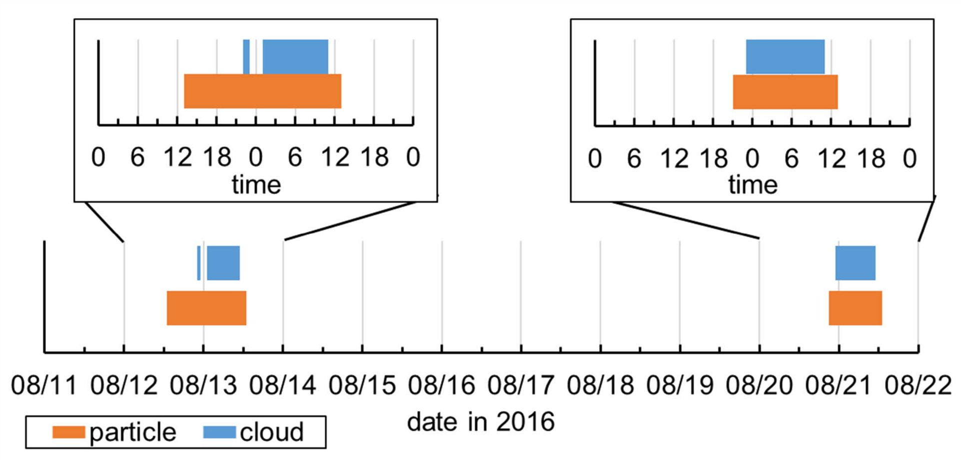

Fig. 1: Sampling times of aerosol particles and cloud water.

sample analysis

- Cloud water samples were only filtrated prior to analysis
- Aerosol filter samples were extracted in ACN/H_2O
- Each sample was measured in triplicate by LC-ESI/HRMS in negative mode (fullMS at R=280k / ddMS2T5 at R=70k)
- Randomized measurement sequence

- Structural information obtained from automated fragmentation by data-dependent MS^2 (ddMS2T5)
- Quality control samples were added to account for shifts in instrumental performance and to assess the peak picking

data processing

- Automated peak picking using MZmine2 (ADAP and CAMERA algorithms)[1][2][3]
- Customized formula assignment procedure to identify CHONSPX compounds, e.g.,
  - H/C = 0.3…3; O/C = 0…3; S/C < 1; N/C < 1; P/C < 0.3; X/C < 1 (X = Cl, Br, I);
  - OS_C = –4…4 [4]
  - minimum isotope score = 66%
- For ddMS^2 spectra, *in silico* fragmentation predictions and formula assignments from SIRIUS software package[5][6]

C Composition and Molecular Properties

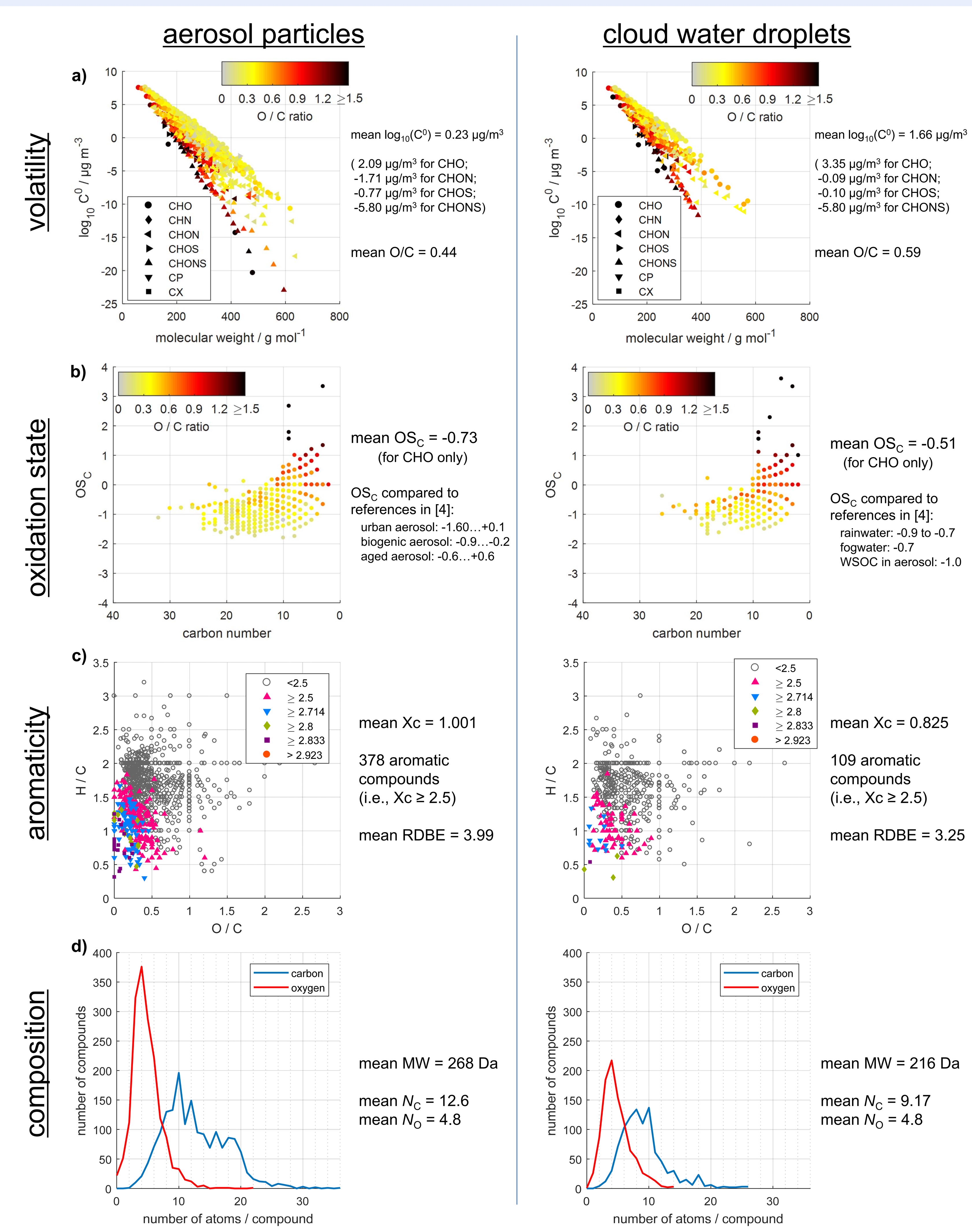

Fig. 2: Molecular properties and composition of organic compounds. a) Saturation mass concentrations C^0 for each compound, according to Li *et al.*[7] b) Average carbon oxidation state OS_C of CHO compounds.[4] c) Van Krevelen plot and aromaticity equivalents Xc [8] for all assigned molecular formulas. Potential aromatic compounds are highlighted by the color-code. d) Distributions of carbon and oxygen for the assigned molecular formulas.

D Comparison and Overview

Table 1: Overview and comparison of the composition of cloud water and droplets and aerosol particles. Despite longer sampling times for aerosol particles, a large number of compounds was observed only in cloud water samples, indicating that <u>aqueous-phase chemistry altered the chemical composition after nucleation scavenging of organic particles, or that a major fraction of organic compounds is taken up from the gas phase.</u>

	filter samples	cloud water	common compounds	only in cloud water samples
number of compounds	1492	971	186	785
…CHO	714	557	123	434
…CHN	29	5	0	5
…CHON	439	272	47	225
…CHOS	15	9	1	8
…CHONS	9	8	1	7
P-containing (of which P- & X-containing)	269 (7)	111 (3)	14 (0)	97 (3)
X-containing (X = Cl, Br, I)	15	8	0	8
average MW / Da	267	216	194	221
average OS_C	-0.70	-0.50	-0.40	-0.53
average Xc	1.298	1.083	0.979	1.107
organonitrates (CHON with O/N ≥ 3)	227	140	28	112
organosulfates (CHOS with O/S ≥ 4)	12	6	1	5
nitrooxy-OS (CHONS with O/S ≥ 7)	0	8	1	7

E Organic Compounds in Cloud Water Droplets Only

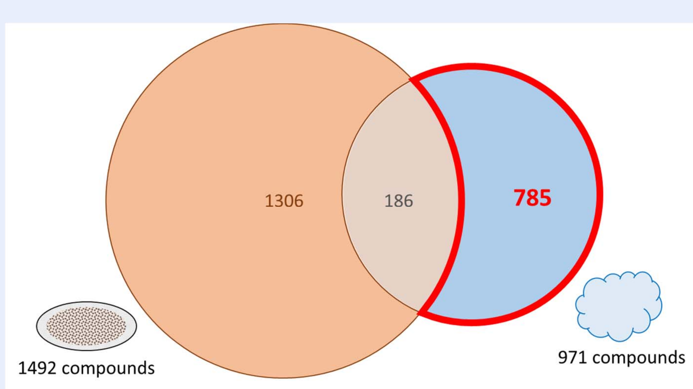

Fig. 3: Number of total, common, and unique compounds in aerosol particle and cloud water droplets.

- Compared to the aerosol particle phase, organic compounds detected only in cloud water samples are:
  - more volatile (average $\log_{10}(C^0)$ = 1.58)
  - higher oxidized (average OS_C = –0.53; average O/C = 0.57)
  - less aromatic (average Xc = 1.107; 88 aromatic compounds)
  - smaller / more lightweight (average molecular weight = 221)

➡ **a large fraction of organic compounds was likely taken up from the gas phase**

- Remarkably, compounds detected in both sample types are even more volatile / oxidized / less aromatic / lightweight (see Table 1), indicating that less oxidized and larger compounds are rapidly reacting upon water condensation and activation of particles into cloud condensation nuclei

➡ **aqueous-phase chemistry was significantly changing the composition of organic particle phase components upon water condensation**

In contrast to numerous studies applying direct infusion ESI/HRMS for the analysis of atmospheric organic matter,[9][10][11] the combination of LC and high-resolution Orbitrap MS allows the detection of single compounds in the two-dimensional RT – *m/z* space (i.e., isomeric and isobaric compounds are separated by LC).

After an automated untargeted peak picking, customized algorithms were used to assign molecular formulas to the detected features. To find accurate molecular formulas, we slightly modified the element heuristics suggested by Kind and Fiehn,[12] reflecting elemental ratios and abundances, as well as chemical processes, in the atmosphere.

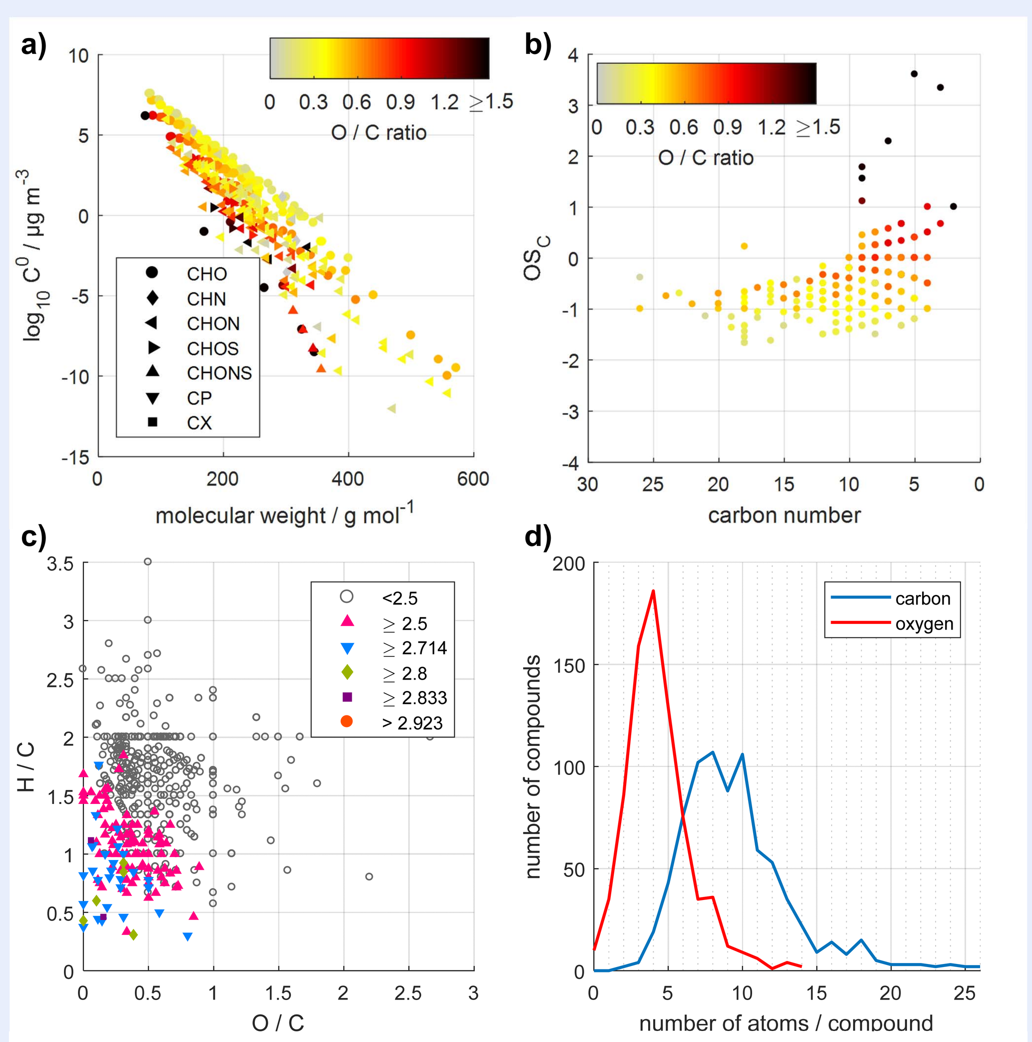

Fig. 4: Molecular composition and properties of compounds observed in cloud water samples only. a) Saturation mass concentrations C^0 [5] versus molecular weight. b) OS_C for CHO compounds.[4] c) Aromaticity equivalents Xc.[6] d) Carbon and oxygen distributions for the assigned molecular formulas.

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