

Chemical composition of newly formed and growing particles in the atmosphere

A.L. Vogel^{1,2}, J. Schneider³, C. Müller-Tautges², J. Nowak⁴, D.R. Worsnop⁴, J. Kirkby¹, T. Hoffmann² and the CLOUD collaboration

¹CERN, European Centre for Nuclear Research, Geneva, 1211, Switzerland

²Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, 55128, Germany

³Particle Chemistry Department, Max Planck Institute for Chemistry, Mainz, 55128, Germany

⁴Aerodyne Research Inc., Billerica, USA

Keywords: SOA, Online-CIMS, NPF, Growth.

Presenting author email: alex.vogel@cern.ch

Predicting the number of particles in the atmosphere which can serve as cloud condensation nuclei (CCN) is a major uncertainty in global climate models (IPCC, 2013). New particle formation (NPF) is one of the dominant sources of particles, however, it needs condensing vapours to let them grow into sizes where they become climatically relevant.

It has been (and still is) a challenge to measure the involved compounds that contribute to the condensing mass. In recent years it has been recognized that oxidized organic compounds are the major contributors to particle growth (Riipinen *et al.*, 2012), since the condensation of inorganic compounds, such as sulphuric acid vapours, cannot explain observed growth rates alone. However, the determination of the precursor gases that become oxidized and subsequently condense, as well as the quantitation of their mass yields, is a prerequisite for global climate models to more accurately predict particle numbers from natural and anthropogenic emissions.

In this study we used complementary mass spectrometric techniques to resolve the organic species that contribute to particle growth in (A) a summertime field study at the Taunus Observatory (Germany), during which several NPF events occurred, and (B) a controlled nucleation experiment at CERN's CLOUD chamber.

The particular instrumentation used in (A) was field deployed online atmospheric pressure chemical ionization mass spectrometry (APCI-MS) (Vogel *et al.*, 2013), aerosol mass spectrometry (AMS), and filter sampling for laboratory based analysis using ultrahigh performance liquid chromatography coupled to electrospray ionization ultrahigh resolution (OrbitrapTM) mass spectrometry (UHPLC/ESI-UHRMS). A non-target analysis approach of filters that were exclusively sampled during NPF events was conducted to obtain a comprehensive picture on the exact molecular composition, additional to the online-MS spectra which provide unit mass resolution at one minute measurement frequency.

The key instrument used in (B) was the Filter Inlet for Gases and Aerosols (FIGAERO) (Lopez-Hilfiker *et al.*, 2014) coupled to a chemical ionization time of flight mass spectrometer. The sampling strategy was to resolve the chemical composition during the early particle formation, requiring the instruments operation close to the detection limit.

The AMS analysis of a NPF case study at the Taunus Observatory revealed that sulphate was the most abundant component during the first hours of the event, and subsequently condensing oxidized organics strongly contributed to the total aerosol mass. During the first hour of one particular NPF the average total sulphate mass was 0.25 $\mu\text{g}/\text{m}^3$ and total organic mass contributed with 0.30 $\mu\text{g}/\text{m}^3$. Significant signals of organic species in the 250 to 350 Da range were detected by the online-APCI-MS. The analysis of a filter sample of the first six hours of the NPF proved the existence of several compounds that appeared in the online-APCI-MS spectrum. Due to the chromatographic separation, isobaric organic compounds were resolved and the detection by UHR-MS ($R=70.000$) allowed the unambiguous determination of the exact masses.

At the CLOUD chamber, oxidation products of α -pinene ozonolysis that reside in the condensed phase were for the first time determined using the FIGAERO-CIMS. The precisely controlled conditions and low contaminations at the CLOUD chamber allowed exclusive sampling of newly formed particles, which could not be achieved in the field measurement.

Acknowledgements

This work was supported by the Max Planck Graduate Center together with the Johannes Gutenberg University Mainz and the EC Seventh Framework Programme (Marie Curie Initial Training Network MC-ITN "CLOUD-TRAIN" no. 316662).

References

- IPCC: Climate Change (2013) *The Physical Science Basis*, Cambridge University Press.
- Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., and Donahue, N. M. (2012) *Nature geosci.* **5**, 453-458.
- Vogel, A.L., Äijälä, M., Brüggemann, M., Ehn, M., Junninen, H., Petäjä, T., Worsnop, D.R., Kulmala, M., Williams, J. and Hoffmann, T. (2013) *Atmos. Meas. Tech.* **6**, 431-443.
- Lopez-Hilfiker, F.D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T.F., Lutz, A., Hallquist, M., Worsnop, D.R. and Thornton, J.A. (2014) *Atmos. Meas. Tech.* **7**, 983-1001.