

## Formation mechanism and important implications of highly oxidized molecules (HOM) in the gas phase

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It has been found that, on average, more than half of the atmospheric aerosol mass consists of organic compounds (Zhang *et al*, 2007). In most environments, the major part of the organic aerosol (OA) is of secondary origin (Jimenez *et al*, 2009) (SOA), meaning that it has been formed from oxidized organic molecules condensing onto pre-existing aerosol particles. The condensation and evaporation of organics to/from aerosol particles has been modeled with different methods, with varying success. The most generally used method being partitioning theory (Pankow, 1994), although this has also been found to be insufficient in some studies (e.g. Riipinen *et al*, 2011). Riipinen *et al* (2011) found that the growth of newly formed sub-100 nm particles could only be explained using a model where about half of the organic vapors condensed irreversibly, i.e. as though they were completely non-volatile.

Recently, Ehn *et al* (2012) reported on a new group of compounds detected in the gas phase that were much more oxidized than observed before, e.g. C<sub>10</sub>-compounds with atomic O:C ratios up to unity. The compounds were detected both in the laboratory and ambient air, and are expected to have extremely low volatilities. Due to the lack of quantitative measurements, the implications of these highly oxidized molecules (HOM) on aerosol formation could not be determined. With the help of the newly developed instrumentation, we have been able to quantify the HOMs and their contribution to aerosol particle formation and growth.

A novel combination of mass spectrometers (PTRTOF, iodine CIMS, nitrate-CIMS) was deployed to monitor the gas phase oxidation of volatile organic compounds (VOCs) at the Jülich Plant Atmosphere Chamber (Mentel *et al*, 2009). The instruments provided high mass and time resolution data of volatile, semi-volatile, and low-volatility (HOM) compounds, which could be related to aerosol number and mass properties

measured in parallel by an extensive suite of aerosol instrumentation. The main VOC studied was alpha-pinene.

Our results suggest a surprisingly high abundance of the HOMs, consequently suggesting a very important role in aerosol formation. Indeed, the HOMs under many conditions seemed to be the driving force in aerosol formation, both concerning particle number and mass, while semi-volatile species such as pinonic and pinic acid, although more abundant than the detected HOMs, were less important.

We propose that HOMs can explain the major part of the “non-volatile vapors” that Riipinen *et al* (2011) required to explain ambient observations in their model. The role of HOMs in nucleation and initial growth of newly formed particles, as well as their contribution to SOA mass yields will be discussed in more detail.

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Ehn, M. *et al* (2012) *Atmos. Chem. Phys.*, 12, 5113-5127, doi:10.5194/acp-12-5113-2012.

Jimenez, J.L. *et al* (2009) *Science*, 326, 1525-1529.

Mentel, T. F. *et al* (2009) *Atmos. Chem. Phys.*, 9, 4387-4406, doi:10.5194/acp-9-4387-2009.

Pankow, J. F. (1994) *Atmos. Environ.*, 28, 185-188.

Riipinen, I. *et al* (2011), *Atmos. Chem. Phys.*, 11, 3865-3878, DOI 10.5194/acp-11-3865-2011.

Zhang, Q. *et al*. (2007) *Geophys. Res. Lett.*, 34, L13801, doi:10.1029/2007gl029979.