

## Wall losses of vapours distort yield calculations in SOA chamber experiments

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Organic compounds can amount to 50% or more of atmospheric aerosol mass (Jimenez et al., 2009) and therefore have an important role in determining the climate and air quality effects of particulate matter. However, currently the contribution of secondary organic aerosol (SOA) formation both to aerosol total mass and particle growth from nucleation size to climatically relevant sizes is poorly understood (Riipinen et al., 2012). In this work, we shed some light on the formation of atmospheric SOA as we use well-constrained new particle formation experiments in a Teflon chamber together with aerosol microphysics modelling to demonstrate that low-volatile organic compounds formed in chamber studies may have gone undetected in previous experiments due to their very rapid partitioning onto chamber walls.

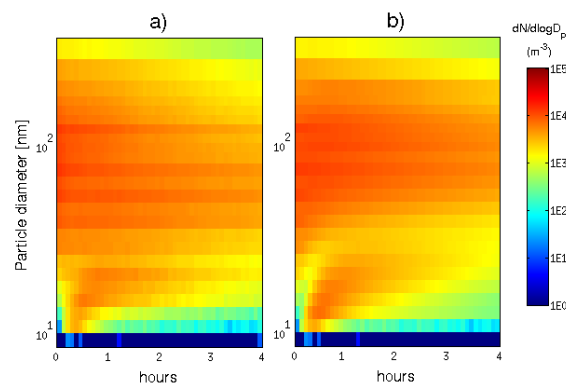
Our measurements were performed in a 4 m<sup>3</sup> Teflon chamber, in which three semi-volatile organic gases of distinctly different volatilities were injected. In the experiment, 20 ppb of these organic gases was repeatedly injected at 30 min intervals. Between the injections, a high-resolution proton transfer reaction mass spectrometer (PTR-TOF-MS) measured the gas-phase concentration of the compound and revealed that the equilibrium between the gas-phase and the chamber walls was reached within a few minutes of each injection. Such rapid equilibrium suggests that detection of very low-volatility compounds, which partition almost exclusively to chamber walls, is extremely difficult in chamber experiments and may therefore have gone unnoticed in several previous studies.

We tested this hypothesis further in a chamber experiment of  $\alpha$ -pinene ozonolysis in the presence of an ammonium sulphate seed aerosol. In this experiment, new particle formation and subsequent growth of the nucleation mode was observed shortly after the injection of  $\alpha$ -pinene and ozone. The formation of new particles indicates presence of gas phase compounds of very low volatility.

We attempted to simulate the observed growth with the aerosol microphysics model SALSA (Kokkola et al., 2009) by using the frequently used volatility bins and stoichiometric coefficients (Pathak et al., 2007) in the volatility basis set (VBS) framework, which have been derived from previous chamber studies. Using this set-up, the model was clearly unable to simulate the observed growth of the nucleation mode. To reproduce the growth of these small particles we optimized the values of stoichiometric coefficients for different

volatility classes by minimizing the difference between the observed and modelled total number concentration in different particle size classes. The optimization resulted in approximately two orders of magnitude higher coefficient for the lowest volatility bins. When these optimized stoichiometric coefficients were applied in SALSA, the observed new particle growth event was reproduced with good fidelity as can be seen in Figure 1.

Our results indicate that very low-volatile organic compounds capable of contributing to nucleation mode growth form in the first-generation reactions of  $\alpha$ -pinene oxidation. In previous chamber experiments these compounds have gone undetected because they are depleted to the chamber walls before being detected by measurement devices. Our findings call for new experimental approaches that can constrain the SOA formation yields in chambers in a more reliable way.



**Figure 1.** Measured (a) and modelled (b) growth of new particles in the presence of ammonium sulphate seed aerosol

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